CENTRE FOR ADVANCED MATERIALS
(MODULE 1)

Second Workshop on Size-Dependent Effects in Materials for Environmental Protection and Energy Application

September 19 – 21, 2010, Nessebar, Bulgaria

Organized by the

Institute of General and Inorganic Chemistry,
Bulgarian Academy of Sciences

and

Faculty of Chemistry,
University of Sofia “St. Kliment Ohridski”

http://sizemat2.igic.bas.bg

Supporting Organizations

Institute of General and Inorganic Chemistry at the Bulgarian Academy of Sciences (IGIC-BAS)
Acad. G. Bontchev Str., bldg. 11, 1113 Sofia, Bulgaria, http://www.igic.bas.bg

The Institute of General and Inorganic Chemistry is one of the principal and oldest chemical institutes of the Bulgarian Academy of Sciences. The activities include fundamental and applied studies in the field of inorganic materials science: systematic investigations of the basic relationships "composition-structure-properties" with a view to the design of advanced materials with tailored properties.

Priorities:

- Synthesis, analysis and characterization of advanced high-tech materials with industrial application;
- Studies of materials related to environmental protection;
- Utilization of natural chemical resources;
- Innovation activities and transfer of knowledge and technologies towards industry.

University of Sofia "St. Kliment Ohridski", Faculty of Chemistry (FC-SU)
1 James Bourchier Ave., 1164 Sofia, Bulgaria
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The Faculty of Chemistry is the oldest and one of the most respected institutions in the field of chemistry in Bulgaria. It is a unique institution for the country, covering, to a high extent, all branches of modern chemistry, from physical, computational, colloid and analytical chemistry to organic synthesis and materials science. About 650 students are trained (simultaneously) at the bachelor, master and PhD level.

Materials Related Research Priorities:

- Synthesis of bulk nanomaterials and study of the structure-property relations of various functional materials;
- Synthesis of metastable and amorphous materials and study of their relaxation and crystallization;
- Hybrid materials with special properties;
- Quantum chemical methods for modeling, and design of materials at the molecular level;
- Radical thermo- and sonopolymerization; polymeric microheterogeneous nanophase and nanostructural materials;
- Electrodeposition of nanometals, nanooxides and polymers;
- Self-organization of colloid particles under the effect of capillary forces

SECOND WORKSHOP ON
SIZE-DEPENDENT EFFECTS IN MATERIALS FOR ENVIRONMENTAL PROTECTION AND ENERGY APPLICATION

SEPTEMBER 19 - 21, 2010, NESSEBAR, BULGARIA

Dear Colleagues,

On behalf of the Organizing Committee, it is our pleasure and honor to welcome you all to the SizeMat-2 Workshop.

The first edition of the SizeMat Workshop was held in 2006 with prime objective to promote debates on the size-dependent phenomena as a promising way to control the materials properties. The success of the meeting was beyond our expectations, confirming the interest of the scientific community towards the topics covered by the Workshop.

The present SizeMat-2 Workshop will cover a broader range of advanced materials: traditional materials associated with energy production, energy storage and environmental protection and new classes of materials such as materials for optics and molecular electronics and biology-related materials. The focus will be on the materials characteristics at the molecular and cluster level and their relation to the properties of the bulk phase. The Workshop will also address the spectroscopic and computational methods for characterization of materials.

During the three days of the Workshop there will be a copious programme, which includes 3 plenary lectures, 6 keynote talks and 13 oral presentations. In addition, three parallel sessions with 36 flash oral presentations and two poster sessions with 90 posters will be organized. We hope that the diversity of topics will provide a basis for an exciting meeting with resourceful and fruitful discussions.

We would like to thank the National Science Fund (Bulgaria) for supporting the SizeMat-2 Workshop.

We look forward to welcoming you in Nessebar – a city-museum featuring more than three millennia of dynamic history.

Konstantin Hadjiivanov (Coordinator, IGIC-BAS)
Tony Spassov (Coordinator, FCSU)
Alia Tadjer (Scientific Secretary, FCSU)
Radostina Stoyanova (Scientific Secretary, IGIC-BAS)

Workshop Topics

Topic A. Materials for Energy Storage and Conversion

- Synthesis of Nanocomposites and Nanostructured Alloys
- Spectroscopic Properties and Structure Characterization
- Hydrogen and Lithium in Nanostructured Materials
- Phase Transformations in Nanostructured Materials
- Electrochemical Hydriding/Dehydriding, Lithiation and Corrosion Nanocomposites
- Design of Novel Energy-Related Materials

Topic B. Materials for Environmental Protection

- Size-Controlled Synthesis
- Spectroscopic Analysis of Surfaces
- Cluster Modeling and Simulation
- Size-Dependent Catalytic and Sensor Properties
- Impact of Nanomaterials on Environment, Human Health and Sustainability

Topic C. Materials for Optics and Molecular Electronics

- Nanostructured Transparent Ceramics
- Molecular Modeling and Simulation
- Development of Novel Sol-Gel Optical Materials

Topic D. Biology-Related Materials

- QSAR Analysis of Nanomaterials
- Biomaterials for Bone Implants
- New Bioactive Heterocyclic Compounds
- Molecular Simulations

Workshop Organizers

Scientific Organizing Committee

Konstantin Hadjiivanov (Coordinator, IGIC-BAS)
Tony Spassov (Coordinator, FC-SU)
Radostina Stoyanova (Scientific Secretary, IGIC-BAS)
Alia Tadjer (Scientific Secretary, FC-SU)
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Milen Bogdanov (FC-SU)
Nina Petkova (FC-SU)

Invited Speakers

Topic A

Prof. Dr. Uwe Köster – Technical University of Dortmund, Dortmund, Germany
Nanostructures (and MetallicGglasses) for Hydrogen Technology

Dr. Antoine Maignan – Laboratoire CRISMAT, UMR 6508 CNRS/ENSICAEN, Caen, France
Thermoelectric Oxides: Important Role of the Electronic Correlations

Dr. Daniel P. Abraham – Argonne National Laboratory, Chicago, USA
Long Range and Local Structure in Layered Oxides for Lithium Batteries

Topic B

Prof. Şefik Süzer – Department of Chemistry, Bilkent University, Ankara, Turkey
Doping of TiO_2 *for Improving its Photochemical Activity*

Dr. Aleksander Astel – Environmental Chemistry Research Unit, Biology and Environmental Protection Institute, Pomeranian Academy, Poland
Receptor Modeling of Nanofine Air-Borne Particulate Matter

Topic C

Prof. Mirosław Mączka – Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, Poland
Nanostructured Optical and Ferroelectric Materials: Size-Dependent Changes of Physical and Chemical Properties

Prof. Dirk Walter – Faculty of Medicine, Justus Liebig University, Giessen, Germany
"The Thermal Transformation from Lanthanum Hydroxide to Lanthanum Oxide"

Topic D

Prof. Rui Fausto – Department of Chemistry, University of Coimbra, Coimbra, Portugal
Light Induced Reactions in Cryogenic Matrices

Prof. Ahmet Cuneyt Tas – Department of Biomedical Engineering, Yeditepe University, Istanbul, Turkey
Calcium Phosphate Biomaterials in Orthopaedic and Dental Applications

Schedule

Sunday 19 September	**Monday 20 September**	**Tuesday 21 September**
8:50 – 9:00 Opening		
9:00 – 10:30 Session 1 – Topic A: PL1, KN1, OP1	9:00 – 10:40 Session 5 – Topic C: KN4, KN5, OP7, OP8	9:00 – 10:30 Session 6 – Topic D: PL3, OP9, OP10
10:30 – 10:50 Coffee Break	10:40 – 11:00 Coffee Break	10:30 – 10:50 Coffee Break
10:50 – 12:05 Session 2 – Topic A: OP2, KN2, OP3	11:00 – 11:45 Flash Oral Presentations - Topics C and D	10:50 – 11:40 Session 7 – Topic D: KN6, OP11
		11:40 – 11:55 Intermission
12:15 – 13:00 Flash Oral Presentations - Topics A and B	11:45 – 12:45 Poster Session 2	11:55 – 12:45 Session 8 – Topic A: OP12, OP13
		12:45 – 13:00 Closing
13:00 – 16:00 Recess	12:45 – 14:30 Recess	
16:00 – 17:30 Session 3 – Topic B: PL2, OP4, OP5	14:30 – 19:30 Excursion	16:00 Departure
17:30 – 17:50 *Coffee Break*		
17:50 – 18:40 Session 4 – Topic B: KN3, OP6		
18:45 – 19:30 Flash Oral Presentations - Topics A and B		
19:30 – 20:30 Poster Session 1	20:30 – 22:30 Banquet Dinner	

SizeMat2 Preliminary Program

Saturday 18 September

16:00 – 20:00	Registration
20:00 – 22:00	Welcome Party

Sunday 19 September

8:50 – 9:00	**Opening – Radostina Stoyanova**
Session 1	***Materials for Energy Storage and Conversion (1)*** **Chairing: Tony Spassov**
9:00 – 9:40 PL1	**Uwe Köster**, Technical University of Dortmund, Germany *Nanostructures (and metallic glasses) for Hydrogen Technology*
9:40 – 10:05 KN1	**Antoine Maignan**, Laboratoire CRISMAT, UMR 6508 CNRS/ENSICAEN, Caen, France *Thermoelectric Oxides: Important Role of the Electronic Correlations*
10:05 – 10:30 OP1	**Harald Morgner** , Wilhelm-Ostwald Institute for Physical and Theoretical Chemistry, University of Leipzig, Germany *Fluids in Mesopores. A New Theory and its Applications*
10:30 – 10:50	Coffee Break
Session 2	***Materials for Energy Storage and Conversion (2)*** **Chairing: Ekaterina Zhecheva**
10:50 – 11:15 OP2	**Tony Spassov**, Faculty of Chemistry, University of Sofia, Sofia, Bulgaria *Nanostructured Mg and Ti Based Alloys for Hydrogen Storage*
11:15 – 11:40 KN2	**Daniel Abraham**, Argonne National Laboratory, Chicago, USA *Long Range and Local Structure in Layered Oxides for Lithium Batteries*
11:40 – 12:05 OP3	**Octavian Buiu -** Honeywell Romania, Romania *New Design Approach to Quantum Dot Solar Cell*

12:15 – 13:00	**Flash oral presentations A/B sessions**
	Chairing: Anton Naydenov
12:50 – 16:00	Recess
Session 3	***Materials for Environmental Protection (1)***
	Chairing: Vasil Simeonov
16:00 – 16:40 PL2	**Şefik Süzer**, Department of Chemistry, Bilkent University, Turkey *Doping of* TiO_2 *for Improving its Photochemical Activity*
16:40 – 17:05 OP4	**Margarita Kantcheva** , Department of Chemistry, Bilkent University, Turkey *Gold Catalysts Supported on Ceria Doped by Al(III) and Sm(III) for Water Gas Shift Reaction*
17:05 – 17:30 OP5	**Pedro González**, Complutense Universitry of Madrid, Spain *Microporous Carbon Nanostructures Derived from* $Cr(C_5H_5)_2$ *and* $Cr(C_6H_6)_2$
17:30 – 17:50	Coffee Break
Session 4	***Materials for Environmental Protection (2)***
	Chairing: Elisaveta Ivanova
17:50 – 18:15 KN3	**Aleksander Astel**, Environmental Chemistry Research Unit, Biology and Environmental Protection Institute, Pomeranian Academy, Poland *Receptor Modeling of Nanofine Air-Borne Particulate Matter*
18:15 – 18:40 OP6	**Vasil Simeonov**, Faculty of Chemistry, University of Sofia, Bulgaria *Environmetric Interpretation of Different Size Fractioned Aerosol Monitoring Data*
18:45 – 19:30	**Flash oral presentations A/B sessions**
	Chairing: Borjana Donkova
19:30 – 20:30	Poster Session 1 (A/B) and Refreshments

Monday 20 September

Session 5	***Materials for Optics and Molecular Electronics*** **Chairing: Stoyan Gutzov**
9:00 – 9:25 KN4	**Mirosław Mączka**, Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, Poland *Nanostructured optical and ferroelectric materials: size-dependent changes of physical and chemical properties*
9:25 – 9:50 KN5	**Dirk Walter**, Faculty of Medicine, Justus Liebig University, Giessen, Germany *The thermal transformation from lanthanum hydroxide to lanthanum oxide*
9:50 – 10:15 OP7	**Sabina Cherneva**, Institute of Mechanics, Bulgarian Academy of Sciences, Bulgaria *Determination of Hard Alumina-Film Material Characteristics by Means of Nano-Indentation Measurements*
10:15 – 10:40 OP8	**Michail Michailov**, Institute of Physical Chemistry, Bulgarian Academy of Sciences, Bulgaria *Classification Order of Surface-Confined Intermixing. Nanoscale Pattern Formation on Stepped Crystal Surfaces*
10:40 – 11:00	Coffee Break
11:00 – 11:45	**Flash oral presentations C/D sessions** **Chairing: Stefka Tepavitcharova**
11:45 – 12:45	Poster Session 2 (C/D) and Refreshments
12:45 – 14:30	Recess
14:30 – 19:30	Excursion
20:30 – 22:30	Banquet dinner

Tuesday 21 September

Session 6	***Biology-Related Materials (1)***
	Chairing: Sonia Ilieva
9:00 – 9:40 PL3	**Rui Fausto**, Department of Chemistry, University of Coimbra, Coimbra, Portugal *Light Induced Reactions in Cryogenic Matrices*
9:40 – 10:05 OP9	**Maria Velinova**, Faculty of Chemistry, University of Sofia, Sofia, Bulgaria *Molecular design of micelles for drug delivery purposes*
10:05 – 10:30 OP10	**Georgi Yordanov**, Faculty of Chemistry, University of Sofia, Sofia, Bulgaria *Development of Poly(n-butyl cyanoacrylate) Colloidal Nanospheres Loaded with Lipophilic Anticancer Drugs Intended for Targeted Drug Delivery*
10:30 – 10:50	Coffee Break
Session 7	***Biology-Related Materials (2)***
	Chairing: Galina Gencheva
10:50 – 11:15 KN6	**Ahmet Cuneyt Tas**, Department of Biomedical Engineering, Yeditepe University, Istanbul, Turkey *Calcium phosphate biomaterials in orthopaedic and dental applications*
11:15 – 11:40 OP11	**Diana Rabadjieva,** Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Bulgaria *Biomimetic Transformations of Calcium Phosphates - Thermodynamic and Kinetic Studies*
11:40 – 11:55	Intermission
	Materials for Energy Storage and Conversion (3)
	Chairing: Konstantin Hadjiivanov
11:55 – 12:20 OP12	**M. Graczyk-Zajac**, TU Darmstadt, Institut of Material Science, Darmstadt, Germany *Nanostructured TiO_2 obtained by MOCVD: promising anode material for Li-ion batteries*

12:20 – 12:45 OP13	**Violeta Koleva**, Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Bulgaria *Morphology-Controlled Synthesis of Phospho-Olivines as Cathodes in Lithium-Ion Batteries*
12:45 – 13:00	**Closing – Alia Tadjer**
16:00	Departure

Topic A.

Materials for Energy Storage and Conversion

Nanostructures (and Metallic Glasses) for Hydrogen Storage

Uwe Köster

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Hydrogen is an energy carrier which holds tremendous promise as a renewable and clean energy option. For automotive applications the onboard hydrogen storage is inevitable and an integral part of the system. Hydrogen can be stored using different methods and phenomena, for example in (1) high-pressure gas cylinders, as (2) liquid hydrogen in cryogenic tanks, or as (3) adsorbed hydrogen in materials (the safest storage method). Critical properties of hydrogen storage materials are (a) high volumetric and gravimetric density of hydrogen, (b) cost and availability, (c) fast kinetics and (d) low temperature of dissociation or decomposition, (e) high degree of reversibility, and (f) long-term cycling stability. Any success for a hydrogen technology for future application will depend on materials development.

The present paper will review advantages as well as disadvantages for the three principle forms of hydrogen storage, in particular for hydrogen storage in rechargeable metal hydrides. Such nanostructured materials have potential promise in hydrogen storage because of their unique features such as faster diffusion and adsorption on the surface, inter- and intragrain boundaries, and bulk absorption. In addition, amorphous or quasicrystalline Mg- as well as Ti- and Zr-based materials will be evaluated.

It seems that currently no hydrogen storage material can reach the required storage densities for a hydrogen-powered vehicle and new strategies for storage systems are necessary. Therefore, finally a number of new storage methods/systems will be mentioned and prospects for improvement are given.

Thermoelectric Oxides: Important Role of the Electronic Correlations

Antoine Maignan

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As compared to the physics of the degenerated semiconductors which is used to describe the classical thermoelectric materials such as Bi_2Te_3, thermoelectric oxides are characterized by their strongly correlated electrons. This leads to very different behaviors which depend on the transition metal, its electronic configuration and the crystallographic structure.

For the Chemists, oxides form an ideal playground to tailor new thermoelectric oxides by spin/orbital engineering or nanostructuration or co-doping. Several examples will be used to give a general review of the best thermoelectric oxides in the perspective of their use as p and n-legs of thermoelectric generators to recover waste-heat.

Long Range and Local Structure in Layered Oxides for Lithium Batteries

J. Bareño [1,2], C.H. Lei [2], J.G. Wen [2], S.-H. Kang [1], I. Petrov [2] and D.P. Abraham[1]

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Li-ion batteries are promising candidates for electrical energy storage in applications ranging from portable electronics to hybrid and electric vehicles. In this context, layered compounds in the $Li_{1+\delta}(TM_xMn_{1-x})_{1-\delta}O_2$ family (TM=transition metal) have received much attention due to their high capacity and stability. In this Research News article we describe recent advances on structural characterization of Li-ion electrode materials using state-of-the-art electron microscopy. Direct evidence of the monoclinic nature of Li_2MnO_3 has been provided. It has been demonstrated that differences in Z-contrast imaging between Li_2MnO_3 and $LiTMO_2$ may be used to screen samples for phase separation in the 10–100 nm scale.

Fluids in Mesopores. A New Theory and its Applications

Harald Morgner

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Over the last few years, we have worked out a new theory for "Thermodynamics of Confined Systems". A first version of this theory has been shown to explain the key experiments in this field [1]. A short outline of the fully developed new theory will be presented at the workshop as basis for discussing a few applications. Further, it will be shown, that the theory allows simulating diffusional and convectional transport (nanofluidics) at the same time without the need to introduce capillary forces (surface or interface tensions) by phenomenological parameters.

The second part of the talk is devoted to the potential for practical use. It turns out that the new theory does not only remove conceptual problems, but at the same time opens the route to a number of new states found in porous systems which may lead to improved applications. In particular we will focus on the possibility to drive a fluid in a pore into exotic states under static and under dynamic conditions. E.g. it turns out that states with negative pressure can be reproducibly controlled, provided one has full control over the phenomenon of adsorption hysteresis. Negative pressure states are in principal known since the time of Torricelli and they have been discussed in the literature [2, 3] as experimentally accessible situations. Still, they have not been turned into practical usefulness which is likely to be caused by the notion of their metastability in macroscopic systems.

Possible applications refer to controlling chemical reactions as well as new routes to energy efficient separation processes.

References

1. H. Morgner, *J.Phys.Chem.*, C 114 (2010) 8877.
2. A. R. Imre, *Phys. Stat. Sol.*, (b) 244 (2007) 893.
3. A. R. Imre et al., NATO Science Series II, Mathematics, *Physics and Chemistry* (2007) 242 (Soft Matter under Exogenic Impacts) 389.

Nanostructured Mg and Ti Based Alloys for Hydrogen Storage

Tony Spassov

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Amorphous and nanocrystalline alloys on the base of Mg and Ti, produced by rapid solidification and ball milling, were studied as hydrogen storage materials. Through alloying and variation of the preparation conditions materials with different microstructure were synthesized.

The hydriding and dehydriding properties of the nanostructured alloys were investigated in a hydrogen gas atmosphere as well as electrochemically. It was proved that the microstructure of the nanocrystalline materials has a strong influence on their hydrogen capacity and hydriding thermodynamics and kinetics. Smaller nanocrystallites size generally results in noticeable enhancement of the hydriding kinetics and reduction of the temperature of hydrogen sorption as well as in an increase of the electrochemical capacity. The presence of amorphous phase between the nanocrystallites leads to additional raise of the electrochemical capacity of the alloys. The influence of different alloying elements on the hydriding and dehydriding of Mg and Ti based alloys has been studied and optimization of the alloys composition with respect to the hydrogen capacity has been carried out.

The comprehensive set of methods (volumetric Sievert’s type technique, high pressure DSC and electrochemical methods), applied for studying the hydrogen sorption processes, allowed new results concerning the thermodynamics and kinetics of the low temperature hydrogen sorption in nanostructured and amorphous materials to be obtained. Additionally, the dependence of the corrosion stability on the chemical composition and microstructure of the alloys was elucidated. All these issues are directly related to the potential application of amorphous and nanocrystalline Mg and Ti based materials for hydrogen storage.

New Design Approach for Quantum Dot Solar Cell

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Increased energy demand requires new technologies for manufacturing cheap solar cell devices. Different approaches have been attempted in order to fabricate effective and low-cost solar cell structures. One of this approaches is to use quantum dots (QDs) as light absorber, titanium dioxide (TiO_2) as n-type semiconductor and p-type semiconducting polymers as electrode for hole conduction. The interface between the n-type semiconductor and the quantum dot (light absorber) is ensured by polyfunctional ligands (linkers), able to interact with both the TiO_2 layer and the quantum dots.

In this paper, we propose the selection of quantum dots, linkers, and p-type semiconducting polymers according to the Hard Soft Acids Bases Lewis rule (HSAB) [1], according to which hard bases prefer to bond to hard acids, while soft bases prefer soft acids. The selected quantum dots are CdS, CdSe, CdTe. The proposed ligands are three aminoacids: cysteine, homocysteine and isocysteine. These ligands have mercapto groups, which ensure the interface with the QDs, and carboxylic acid groups, that ensure the interface with TiO_2. According to the HSAB rule, Cd^{2+} cations present at the surface of the QDs are soft acids and prefer to bond with the mercapto groups, which are soft Lewis bases. The interaction between TiO_2 and the polyfunctional linker can be either ionic or covalent. This could be beneficial for the solar cell structure design and performance. The nature of the TiO_2 - polyfunctional ligand interaction can be controlled by varying the pH of the solution. Cysteine, homocysteine and isocysteine are amphoteric molecules (having both basic and acidic properties). In acidic medium ($pH<1$), these aminoacids are mostly in cationic form (the deprotonation of the carboxylic group is prevented). Thus, a covalent bond can be generated by the esterification of the carboxylic group and of the hydroxil group of TiO_2. In basic medium ($pH>12$), these aminoacids are presented mostly in anionic form. The carboxylic groups are deprotonated, generating carboxylate groups (COO^-), which have ionic interaction with Ti^{4+}. Ti^{4+} is a surface defect in TiO_2 that introduces specific energy levels in the TiO_2 electronic density of states. According to the HSAB theory, COO^- are hard bases and Ti^{4+} are hard acids, thus having a strong interaction.

For the p-type semiconducting polymers, we suggest the use of poly 3-6mercaptohexyl thiophene, poly 3-11mercaptoundecyl thiophene and poly 3-12 mercaptododecyl thiophene, all of them containing mercapto groups as anchors that ensure the link with the QDs.

References

1. R. G. Pearson, Hard and soft acids and bases, *J. Am. Chem. Soc.*, 85 (22), 3533.

Nanostructured TiO_2 Obtained by MOCVD: Promising Anode Material for Li-Ion Batteries

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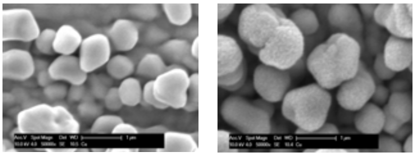
Nanostructured TiO_2 has a slightly lower density compared with the other TiO_2 polymorphs and thus it is an excellent intercalation host for lithium [1,2].

We have produced nanostructured TiO_2 by metalorganic chemical vapour deposition (MOCVD). TiO_2 was deposited at pre-treated (porous) copper foil which is standard current collector for anodes in lithium ion batteries. The material exhibits the mixed structure of rutile and anatase. The compact layers covering porous copper structure are well visible in Figure 1 where copper foil before (a) and after (b) TiO_2 deposition is presented. The excellent distribution of deposit, in a form of small, well adhering grains assuring good electronic contact can be observed.

Figure 2 presents galvanostatic cycling of TiO_2 deposited at copper foil. Note that the charge and discharge capacity increases with cycling; moreover there is no influence of higher current of charge/discharge. After 20 cycles the reversible capacity is higher than 400 mAh/g. This phenomenon might be explained by the formation of the new pathways for lithium during each insertion/extraction. Additionally, in consequence of new paths formation

Some structural rearrangements could take place and it might increase the electronic conductivity of TiO_2. CV curves registered in various potential intervals show that lithium insertion/extraction takes place at the potential about 1.75V/2V what is usual for anatase [1,2]. However, lithium reacts also at 0.75 /1V, respectively. We believe that due to the second electroactivity interval, TiO_2 synthesized by MOCVD demonstrates properties superior with respect to other forms [1].



a) b)

Fig. 1 SEM micrographs of copper foil (a, 50000x magnification) and foil after TiO_2 deposition (b, 50000x)

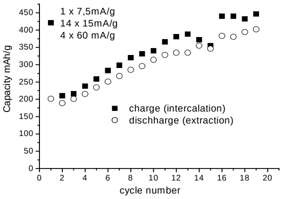


Fig. 2. Extended cycling of TiO_2 deposited at copper foil with various rates.

Acknowledgements: This study was performed within the collaborative research center SFB 595/A4 funded by the Deutsche Forschungsgemeinschaft (DFG), Bonn, Germany.

References

1. P.G. Bruce, *Solid State Science* 7 (2005) 1456.
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Morphology-Controlled Synthesis of Phospho-Olivines as Cathodes in Lithium-Ion Batteries

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Lithium-transition metal orthophosphates with olivine-type structure ($LiMPO_4$, M = Fe, Mn, Co and Ni) are the most intensive studied compounds as cathode materials for lithium-ion batteries in the last years. The best electrochemical performance is achieved with the iron analogue, $LiFePO_4$. By simple replacement of iron by manganese, cobalt and nickel, a higher operating voltage and energy density of the phospho-olivines can be achieved, which is beneficial for their electric vehicle applications. The state-of-the-art research is focused on the elaboration of the specific methods that allow controlling the morphology and nano-crystallinity of the phospho-olivines. In this contribution the synthesis of phospho-olivines with controlled morphology is reported. The morphology of phospho-olivines is modified by using of two new methods: phosphate-formate precursor method and ion-exchange reactions. The specific features of both methods are compared and discussed.

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Mechanochemical Synthesis and Thermal Stability of Cu-Ag Solid Solutions

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The objective of this work was the study the microstructure, morphology, and thermal stability of different supersaturated solid solutions that would be attractive for fabrication of nanoporous structures. Nanocrystalline $Cu_{50}Ag_{40}Al_{10}$ and $Cu_{50}Ag_{40}Sn_{10}$ solid solutions are synthesized by high energy ball milling. For both compositions milling for 8 h leads to formation of amorphous phase. After 10 h of milling only fcc solid solutions with different lattice parameters are obtained. Increasing the milling time no diffraction peaks of pure Ag and Cu elements can be observed, indicating almost completed alloying process.

Broad overlapped exothermic effects for all samples are detected by DTA. These can be explained with solid solution decomposition and a grain growth process. An exothermic effect at about 340°C can also be detected on the DTA curve of the ball-milled $Cu_{50}Ag_{40}Sn_{10}$ alloy, associated with crystallization of the amorphous phase formed during milling.

Electrocatalytic Behavior of Ni-(Nb,Ta,Mo)-B Amorphous Alloys for Hydrogen Evolution

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Ni-(Nb,Ta,Mo)-B amorphous alloys were synthesized by rapid quenching from the melt, using a planar flow technique. Their thermal stability and crystallization behavior were studied by differential scanning calorimetry and x-ray diffraction. The electrocatalytic activity of the as-quenched amorphous alloys with respect to the hydrogen evolution reaction (HER) in alkaline water electrolysis was studied in relation to the alloy composition. The kinetic parameters of the HER were evaluated by cyclic voltammetry and impedance spectroscopy techniques in 6M KOH at room temperature. The as-quenched alloys revealed good stability relative to that of crystalline Ni. The electrocatalytic activity of the amorphous alloys was found to depend on the alloy composition. It was obtained that molybdenum and niobium containing amorphous alloys showed an increased electrocatalytic activity in the HER compared to pure Ni. This is due to an improved intrinsic activity of the material, explained with the change of the electron density in the d-shell upon alloying Ni with Mo and Nb.

Influence of Activated Carbons Derived from Agricultural By-Products on Hydrogen Storage Characteristics of Magnesium

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The mechanical activation method, along with an appropriate additive could resolve the drawbacks as sluggish hydriding/ dehydriding kinetics and high temperatures of hydrogen absorption and desorption of Mg. The addition of carbonaceous compounds to magnesium based composites prepared by ball milling enhances the hydrogen sorption kinetics. In consequence of these facts the present work discusses the hydrogen sorption properties of magnesium ball milled with activated carbon (AC) derived from agricultural by-products.

The absorption- desorption characteristics towards hydrogen of the composites 95wt.% Mg- 5wt.% activated carbon derived from bean pods and apricot stones obtained by ball milling under argon were investigated. Hydriding measurements were performed at temperatures 573 K and 473 K and $P = 1$ MPa and dehydriding at $T = 623$ K and $P = 0.15$ MPa. The absorption capacity values for the composites containing 5wt.% activated carbon derived from apricot stones and from bean pods at $T = 573$ K and $P = 1$ MPa are 5.5 wt.% and 3.2 wt.% after 1h of hydriding, respectively. The composite 95 wt% Mg -5 wt % AC derived from apricot stones were subjected to 80 cycles of hydriding/ dehydriding in order to investigate the change of hydrogen sorption properties and morphology during long cycling. This composite reached 6.25 wt% hydrogen absorption capacity at 40 cycles at 573 K and 1 MPa.

All investigated composites are characterized by X- ray diffraction analyses and scanning electron microscopy.

More pronounced positive effect on the hydrogen sorption properties showed the activated carbon derived from apricot stones. When the activated carbon additive has higher specific surface area, thus reflect favorably the hydrogen sorption kinetics. It appears that, some other characteristics of activated carbons, such as surface chemistry and porosity, also affect these processes. According to our results we can make the conclusion that the activated carbons object of this study can be used as suitable additives for magnesium based hydrogen storage materials.

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Hydriding and Dehydriding of Mg_2Ni-AB Nanocomposites Synthesized by Ball Milling

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The present work deals with the hydriding and dehydriding of Mg_2Ni-AB (AB=TiFe and TiNi) nanocomposites, prepared by mechanical milling. The as-produced composites are characterized using x-ray diffraction and electron microscopy. The morphology, microstructure, thermal behavior and the possibility for hydriding and dehydriding of these materials are systematically studied. Different synthetic conditions are applied with the aim to optimize the hydrogen storage properties of the composites.

The hydriding ability of the materials is determined using two methods – electrochemical hydrogen charge/discharge and differential scanning calorimetry under hydrogen pressure. A number of experimental conditions are varied, incl. temperature, pressure, charge/discharge current density etc. The parameters, which have the most significant influence on the hydriding process are defined and confirmed. The gas phase analysis reveals very low temperatures of the composites hydrogenation. The results obtained allow us to make some essential conclusions for the hydriding processes of this type of composites.

Nanomodified NiFe-Carbon Felt as Anode in Mediatorless Yeast-Biofuel Cell

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Biofuel cells represent an innovative technology for simultaneous electricity generation and organic waste purification [1,2]. The principle is based on the direct conversion of the biochemical energy of living cells into electrical energy. The utilization of entire microorganisms oxidizing the biodegradable organic matter, the operation at ambient temperatures, and the use of neutral electrolytes and inexpensive carbon-type electrodes are the biggest advantages of the biofuel cells over the chemical fuel cells. The low electrical output, however, is the major drawback for their wide application. The improvement of the electron transfer from the microorganisms to the anode is considered to be one of the most important factors for increasing the biofuel cell efficiency.

In our recent study [3], a significant improvement of yeast-biofuel cell output was achieved by application of Ni-modified carbon felt anodes. In the present study, the electrocatalytic properties of new nanomodified carbon materials were investigated. Nickel-iron nanostructures were electrodeposited on carbon felt by means of pulse plating technique. The newly produced materials were tested for cytotoxicity and applied as anodes in a double-chamber mediatorless yeast-biofuel cell. The obtained by means of polarization measurements results show that the maximum power density of 110 mW/m^2 achieved with galvanostatically electrodeposited NiFe-carbon felt anode exceeds three times those obtained with potentiostatically modified anodes and four times comparing with the nonmodified ones.

A hypothesis for expression of adaptive mechanisms as a response to Ni and Fe presence, resulting in facilitated electron transfer across the cell membrane, is proposed.

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Potential Application of Novel CoNiMoW Nanocomposites in a Hybrid Direct Borohydride Fuel Cell – Hydrogen-on-Demand System

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Direct borohydride fuel cell (DBFC) is a promising alternative of hydrogen fuel cells for portable applications [1]. DBFCs possess some attractive features such as high open circuit voltage, low operational temperature and high power density [1,2].

In this study, newly synthesized CoNiMoW nanocomposites, electrodeposited under different galvanostatic conditions, were investigated as anode materials in DBFC. As a tendency, higher generated power was obtained with nanocomposite anodes, produced at lower currents. A maximal power of 94 mW was achieved with DBFC using CoNiMoW-anode, electrodeposited at 1 A, and one air gas-diffusion cathode. Proportional increase of the power was obtained with stacks of two or more DBFCs, connected in series. Significant improvement of generated current and power was attained by applying two gas-diffusion electrodes, which indicates that the oxygen reduction reaction on the cathode is the rate-limiting step of the overall process.

In addition, the catalytic properties of applied CoNiMoW nanocomposites towards the “non-productive” borohydride hydrolysis reaction were also examined. Activation energy of 36.5 ± 2.5 kJ/mol was obtained for all materials studied, but the highest hydrogen generation rate of 15 ml/min (at 315 K) was achieved with CoNiMoW electrodeposit, produced at the lowest current.

Summarizing results from both fuel cell and catalytic tests, it can be concluded that electrodeposited CoNiMoW nanocomposites are potential candidates for application in a hybrid DBFC – Hydrogen-on-demand system.

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IT-SOFC Electrolytes Investigated by Impedance Spectroscopy

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Solid Oxide Fuel Cells (SOFCs) have attracted worldwide interest for their high energy conversion efficiency (50 % – 70 %), structure integrity, easy operation, and less impact to environment as well as the high tolerance to fuels [1, 2]. Due to the high operating temperatures (900^0 C – 1000^0 C) the requirements imposed to the materials that constitute the cells with solid oxide electrolyte, to produce them, at the present moment, is very restrictive. In response to these challenges, intermediate temperature solid oxide fuel cells (IT-SOFCs) are being developed to reduce high-temperature material requirements, which will extend useful lifetime, improve durability and reduce cost, while maintaining good fuel flexibility[3, 4]. A major challenge in reducing the operating temperature (600^0 C – 800^0 C) of SOFCs is the development of solid electrolyte materials with sufficient conductivity to maintain acceptably low ohmic losses during operation. Impedance spectroscopy is a powerful technique for unraveling the complexities of such materials, which functions by utilizing the different frequency dependences of the constituent components for their separation [5-7]. Thus, electrical inhomogeneities in ceramic electrolytes and electrode/electrolyte interfaces can all be probed, successfully, using this technique. In the present work we have studied by impedance spectroscopy the bulk and grain boundary effects on electrical conduction of $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{3-\delta}$ / GCO electrolyte, and the temperature dependence of their ionic conduction. Our investigations show that these $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{3-\delta}$ / GCO systems are promising materials as electrolytes for reduced-temperature solid oxide fuel cells.

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Preparation and Characterization of Doped Lanthanum Gallate (LSGM) Solid Electrolyte Obtained by Non-Conventional Sintering Method

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Doped $LaGaO_3$ is an excellent ions conductor oxide, with potential application in oxide solid fuel cells. Sr^{2+} and Mg^{2+} simultaneous doped lanthanum gallate (LSGM) powders, prepared by a modified Pechini route, were dandified using an activated microwave technique at 2.45 GHz to develop a dense stable electrolyte layer for application in intermediate temperature - solid oxide fuel cells (IT-SOFC).

The evolution of secondary phases, such as $LaSrGa_3O_7$ has been identified to be a problem in the preparation of LSGM. Actually, no mater what technical preparation route was adopted (wet-based or solid state-based method) the presence of the secondary phases is related accompanying the main phase.

The present paper deals with investigations regarding the preparation and characterization of doped $La(Sr)Ga(Mg)O_3$ powders and sintered bodies. Thermal analysis (DTA/TG) on the stoichiometric raw mixture was realized. Morphological and structural aspects were investigated by mean of X-ray diffractometry, FT-IR spectrometry, scanning electron microscopy and dilatometry measurements. The electrical behaviour of the obtained ceramic were characterized by impedance spectroscopy.

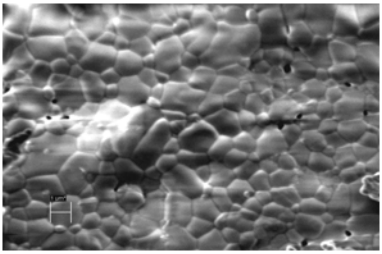

Fig 1. SEM micrographs of sintered pellets at activated microwave field 1400^0C/10min

Good densities (90-93%) and constant TEC (α ~ 9.5x10-6 K-1) were obtained. The LSGM electrolyte prepared through these techniques has higher quality than the solid-state route and is suitable for thick films preparation.

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Thermal Analysis of Doped Lanthanum Gallate Electrolyte (LSGM)

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Sr and Mg substituted $LaGaO_3$ (LSGM) is a promising solid electrolyte for intermediate temperature solid oxide fuel cells (IT-SOFC). Phase purity of this material and bulk high densities were a subject of investigation for a long time [1 - 3]. Thermal behavior of intermediate phases and final LSGM phase were investigated by means of differential scanning calorimetry (DSC), DTA/TG analysis combined with FTIR spectrometry and dilatometry analysis. The thermodynamic parameters of intermediary phases were evaluated.

The powders and sintered bodies were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD). On the basis of thermal analysis combined with FTIR spectrometry a detailed reaction mechanism was proposed.

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Nanostructure Carbon Formation in Sol-Gel Polymerization of Resorcinol and Formaldehyde

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Organic gels based on formaldehyde and resorcinol (RF) were first synthesised in a sol-gel process in 1980s and since then they have become increasingly important. Being electrically conductive and having very large surface areas, RF aerogels are ideal novel materials for electrodes in electrochemical double-layer supercapacitors, making their research of great importance in terms of energy storage and management. They are also used to produce electrodes for batteries and for capacitive deionization units, as well as materials for hydrogen fuel storage due to their porosity and highly developed surface areas. Among their other applications, one can mention filters and absorbing media, as well as catalyst supporting materials.

Previous research proved that RF gels properties can be tailored to match specific requirements by changing the conditions of synthesis, allowing them to cover a wide range of applications. The sol-gel process is a convenient and environmental friendly synthesis method in which numerous factors can be changed independently, influencing the structural properties of the final product. The key to successful synthesis design targeted at certain final properties of the RF gel is to understand its mechanism. The objective of this research is to investigate the reactions which lead to formation of RF gels and thus to enable to control the structure of final product - both its pore size and surface area – in a predictable manner. The investigated factors are ratios of resorcinol to formaldehyde and to catalyst (sodium carbonate), dilution of the reactants and temperature of synthesis. Dynamic Light Scattering was employed to examine the particle growth in the early stages of the sol-gel process. The results proved that regardless of the temperature and resorcinol to catalyst ratio, the hydrodynamic radii of particles before gelation were 3-6 nm. This finding proves that previous assumptions towards the role of the catalyst call for revision, as the amount of catalyst appears not to affect these values. ^{13}C and ^{1}H Nuclear Magnetic Resonance was used to analyse the composition of formaldehyde aqueous solutions at a variety of dilutions, giving to understanding of the influence dilution has on the chemical structure of the formed gel.

On the Relation Between Texture Parameters and Double Layer Capacitance of Activated Carbons

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The porous textures of activated carbons and their electrochemical double layer capacitance (DLC) in organic electrolyte prepared on the basis of spent coffee waste ground were investigated by using low-temperature nitrogen adsorption and constant electric current cycling methods. It was found out that the double layer capacitance of activated carbons did not have a linear relationship with their BET specific surface area.

A modified version of H. Shi's model [1] is proposed. Thereupon it is presumed that the DLC per unit of internal surface area (C_{INT}) is different from that per unit external surface (C_{EXT}) instead of using one fixed DLC for all sample porous surface

On the basis of the experimental data, the modified model is examined. A linear relationship: $\frac{C}{A_{EXT}}$ vs $\frac{A_{INT}}{A_{EXT}}$ (where C, A_{EXT} and A_{INT} are respectively the sample capacitance, external and internal surface areas) is observed on the basis of which relation C_{INT} and C_{EXT} of samples are calculated.

Thus calculated values of C_{INT} and C_{EXT} of carbon samples are considerable higher in comparison to the values of their capacitance per unit of BET specific surface area (i. d. specific capacitance C_0).

This fact gives evidence about the resultant character of C_0 as a ratio between respectively the sum of different capacitance per unit of constitutive parts of BET specific surface area (not of unity fixed DLC for all the porous surface of activated carbon) and the integral surface parameter, A_{BET}.

An assumption has been made that it is possible or not a linear relationship between double layer capacitance of activated carbons and their BET specific surface areas from arise in the dependence of the capacitances per unit of constitutive parts of BET specific surface area contributions.

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Model Calculation of the Effectiveness of Tb^{3+} Containing Glass as a Wavelength Converter in Thin Film Solar Cells

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As a way to achieve higher efficiency of third generation solar cells wavelength converters have been proposed as one of the ways forward. The idea is to shift the wavelength of the light which is absorbed by the solar cell to the spectral region where the device is most efficient. Higher energy photons are often absorbed unproductively near the front contact of the solar cells or the carriers generated by them recombine before being separated. By the application of photoluminescent materials these photons are transformed into longer wavelength ones, which contribute more effectively to the generated photocurrent.

In this contribution the improvement that a wavelength converter containing Tb^{3+} ions can effect on the efficiency of a thin film silicon single junction solar cell under AM 1.5 solar radiation is assessed by model calculations. The absorption and emission of a specified number of Tb^{3+} ions in a fluoride glass layer or plate is calculated on the basis of literature data. It is presumed that such a plate is placed in front of the solar cell and modifies the solar spectrum falling on it. This modified solar spectrum is used to calculate the efficiency of two model solar cells, an amorphous silicon and a microcrystalline silicon one, using the program Afors-Het 2.2. The amount of Tb^{3+} ions per unit area in the wavelength converter layer is varied. In the best case the efficiency of the a-Si:H solar cell improves by 1% and that of the microcrystalline silicon cell – by 2.3%, in comparison to that calculated with the unmodified AM 1.5 spectrum.

Tantalum-Based Ceramics for Microwave Applications

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Dielectric materials with a high permittivity (ε_r), a high quality factor (Q) and a low temperature coefficient of resonant frequency (τ_f) have become very important for the miniaturization of microwave devices such as filters or antennas [1]. Their properties are directly influenced by the cation ordering, grains size [2] and second phases formation. About 39% of the resonator materials are based on tantalates or niobates.

In this work, we have studied three different tantalum-based compositions: $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Y_{1/2}Ta_{1/2})O_3$. The ceramic bodies were obtained via a modified Pechini method [3] or by the solid-state reaction method. The influence of 0.50 % (gr.) Nb_2O_5 as sintering aid has been investigated.

The Pechini powders, as well as the final ceramics were compositional, structural and morphological characterized by thermal analysis, infrared spectroscopy, X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The dielectric properties of the ceramic bodies were measured in the microwave range.

Pechini powders are nanosized and show cubic structure. In the case of $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Ta_{2/3})O_3$, the sintering process makes possible the transition from a disordered cubic perovskite structure to a 1:2 ordered trigonal structure specific to this type of ceramics.

The prevention of zinc oxide volatilization and the achievement of relative good dielectric properties by processing the ceramics for short period of time at high temperatures represent the advantages of the Pechini method.

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Reducibility of $LaNi_xCo_{1-x}O_3$ and $LaFe_xCo_{1-x}O_3$ Perovskites ($0 \le x \le 0.5$)

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Nickel and iron substituted lanthanum cobaltates with perovskite-type structure ($LaCo_{1-x}Ni_xO_3$ and $LaCo_{1-x}Fe_xO_3$) are considered as promising cathode materials for solid oxide fuel cells, as well as automotive exhaust catalysts. One of the factors determining their performance is the reduction stability at high operating temperatures. The reduction of the perovskites is a complex process involving the formation of oxygen-deficient perovskite-type phases before the final reduction to metal and La_2O_3. Irrespective of the intensive studies devoted to the reducibility of perovskites, the appearance of different intermediate phases at the initial stages of reduction is still under controversial discussions.

The purpose of this contribution is to study in details the reducibility of nickel and iron substituted perovskites. In addition, the effect of the synthesis procedure on the reducibility of the perovskites is also examined. For the preparation of $LaCo_{1-x}Ni_xO_3$ and $LaCo_{1-x}Fe_xO_3$ with $0 \le x \le 0.5$, two methods were used: (i) thermal decomposition of La-Co-Ni/Fe citrates obtained by freeze-drying of the corresponding solutions, and (ii) the method of Pechini. Both methods allow preparing between 600 and 900 ^oC well-crystallized $LaCo_{1-y}Ni_yO_3$ and $LaCo_{1-x}Fe_xO_3$ with rhombohedrally distorted crystal structure. The reducibility of the perovskites was tested by thermal programmed reduction with hydrogen (TPR). The products of the partial and complete reduction were determined by *ex-situ* XRD experiments.

The complete reduction of $LaCo_{1-x}Ni_xO_3$ with H_2 proceeds to Co/Ni metals and La_2O_3. Both the Ni content and the synthesis procedure affect the formation of intermediate products. For the Ni-rich perovskites ($x>0.1$) annealed at 900 ^oC, the reduction proceeds via the formation of Brownmillerite-type phases (Ni substituted $La_nCo_nO_{3n-1}$), while for the perovskites obtained at low temperatures the reduction process is more complex and includes the formation of both oxygen-deficient perovskite-type oxides and transition metal. The more non-stoichiometric $LaCo_{1-x}Ni_xO_3$ in respect of oxygen, the easier the Brownmillerite type-phases are stabilized as intermediate products. The loosely bonded nanometric particles and the inhomogeneous distribution of Ni and Co ions favour the one-step reduction of M^{3+} to M^0.

The interaction of $LaCo_{1-x}Fe_xO_3$ with H_2 is not complete up to 700 ^oC. The reaction proceeds by preferential oxidation of Co^{3+} to Co^{2+} without affecting the Fe^{3+} ions. The reduction of $LaCo_{1-x}Ni_xO_3$ and $LaCo_{1-x}Fe_xO_3$ is less sensitive towards the synthesis procedure as compared to unsubstituted $LaCoO_3$. Iron substituted perovskites display higher reduction stability.

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Thermoelectric Properties of Nickel and Iron Substituted Lantanum Cobaltates

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Lantanum cobaltates with a perovskite type structure, in particular $LaCoO_3$, are recently considered as materials with potential application in thermoelectricity. The state-of-the-art research is mainly devoted to the improvement of the thermoelectric efficiency of $LaCoO_3$ by lanthanum or cobalt-substitution.

The aim of this contribution is to study the effect of Co substitution with iron and nickel on the thermoelectric properties of $LaCoO_3$. Metal-organic precursor method is used for the preparation of $LaCo_{1-x}Ni_xO_3$ and $LaCo_{1-x}Fe_xO_3$, where $0 \leq x \leq 0.5$. This method is based on the formation of mixed La-Co-Ni(Fe)-citrate complexes by freeze-drying of the corresponding solutions. Structural and morphological characterization was made by X-ray powder diffraction and SEM analysis. The thermoelectric power of perovskites was determined by independent measuring of the Seebeck coefficient and the conductivity.

The formation of $LaCo_{1-x}Ni_xO_3$ and $LaCo_{1-x}Fe_xO_3$ starts at 400°C by the reaction between $La_2O_2CO_3$ and a spinel phase after the decomposition of the citric complexes. The solid state reaction proceeds at a nano-scale regions, as a result of which well-crystallized $LaCo_{1-x}Ni_xO_3$ and $LaCo_{1-x}Fe_xO_3$ with a rhombohedrally distorted perovskite type structure are formed at 600 °C. The replacement of Co by Ni and Fe led to lattice expansion of the perovskite structure. For perovskites annealed at 900 °C, there was a random Ni, Fe and Co distribution. The nickel containing perovskites are slightly oxygen deficient in comparison with pristine $LaCoO_3$.

The electrical conductivity increases substantially during the progressive replacement of cobalt by nickel. At the same time, the Seebeck coefficient decreases smoothly. As a result, the lanthanum cobaltate with 10 mol % of nickel displays better thermoelectric power, which is an order of magnitude higher than that of $LaCoO_3$. The replacement of cobalt by iron leads to a decrease in the electrical conductivity, while the Seebeck coefficient slightly increases. Using the specific effect of Ni and Fe doping on the electrical conductivity and the Seebeck coefficient, new perovskite-type thermoelectric materials with double substitution (i.e. $LaCo_{0.8}Fe_{0.1}Ni_{0.1}O_3$) are prepared. All perovskites exhibit p-type conductivity.

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Matrix-Infrared Spectroscopy as a Tool to Monitor Admixtures in Minerals

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Matrix-infrared spectroscopy provides important information about the type of the admixtures included in minerals, either as isomorphous (isodimorphous) substitutions or as distinct phase inclusions. The vibrational spectra of distinct phase inclusions are similar to those of the respective neat compounds. However, the vibrational spectra of isomorphously included guest ions are essentially determined by both the site-symmetry, which is assumed to be the same as that of the respective host ions (substitutional type of mixed crystals), and the potential at the lattice sites where the guest ions are located, as shown by the extend of energetic distortion of the matrix-isolated ions.

In the present study, several phases belonging to the large number of natural and synthetic compounds with kröhnkite-type chains have been synthesized as model phases. The crystal structures of $Na_2Me(SeO_4)_2 \cdot 2H_2O$ (*Me* = Co, Ni, Zn, Cd) and $K_2Me(CrO_4)_2 \cdot 2H_2O$ (*Me* = Zn, Cd) were determined from X-ray single-crystal diffraction data and those of $K_2Me(CrO_4)_2 \cdot 2H_2O$ (*Me* = Co, Ni) by X-ray powder diffraction. The structures are build up from $MeO_4(H_2O)_2$ octahedra and XO_4 tetrahedra forming infinite kröhnkite-type octahedral-tetrahedral chains, which are linked by alkali cations to layers and further to a three-dimensional framework via hydrogen bonds. The sodium cobalt, nickel and zinc compounds as well as the potassium cobalt, nickel and cadmium compounds crystallize in the triclinic space group $P\bar{1}$ (type A), the sodium cadmium selenate in the monoclinic space group $P2_1/c$ (type D), and the potassium zinc chromate in the monoclinic space group $C2/c$, thus representing a new structural type (type H).

The vibrational behavior of SO_4^{2-} guest ions included in these chromate and selenate matrices has been studied by infrared spectroscopy. It has been established that the extent of energetic distortion of the SO_4^{2-} guest ions as deduced from the values of $\Delta\nu_{as}$ (site-group splitting) and $\Delta\nu_{max}$ (the difference between the highest and the lowest wavenumbered components of the stretching and bending modes), depends on both the electronic configurations of the Me^{2+} ions and the degree of covalency of the respective Me^{2+}–O bonds. The matrix-isolated SO_4^{2-} guest ions are stronger distorted in the selenates than in the chromates due to the smaller unit-cell volumes of the selenate host compounds as compared to those of the chromate ones and the different ionic radius of the K^+ and Na^+ ions. The smaller Na^+ ions cause a stronger electrostatic field (shorter Na–O bonds), thus leading to remarkably larger values of $\Delta\nu_{as}$ and $\Delta\nu_{max}$ of the guest ions in the sodium compounds.

Raman Study of the Composition and Structure of $Na_yMn_{1-x}Fe_xO_2$ oxides

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After the discovery of thermoelectric properties of layered sodium-cobalt oxides by Terasaki, the structural characterization of low-dimensional sodium transition metal oxides became one of the most widely investigated topics in materials chemistry. Several experimental techniques have been employed for their structural characterization. Raman scattering spectroscopy is often suitable for examination of the degree and type of cation ordering in complex oxide systems.

In this contribution, the structural characterization of layered sodium manganese-iron oxides with $Na_{2/3}Mn_{1-x}Fe_xO_2$ compositions (where x=0, 1/3, 2/3, y= 1/2, 2/3, 3/4) is reported using Raman spectroscopy. It makes it possible to distinguish between layered phases with orthorhombic (*Cmcm* space group) and hexagonal ($P6_3/mmc$ space group) distortion. It has been found that the crystal structure and the composition of $Na_{2/3}MnO_2$ display a strong dependence on the history of the thermal treatment. The orthorhombic distorted modification is stabilized at high temperatures (1000 ^oC). At lower quenching temperature, there is a phase separation into an orthorhombic and a hexagonal modification, concomitant with an increase in the oxidation state of Mn.

When Fe substitutes for Mn, the hexagonal modification is stabilized. The substitutional disorder is found to lead to a marked broadening of the Raman spectra and a shift of the A_{1g} band to lower energy. The broadening can be correlated with phonon scattering which would be beneficial for lowering the material's thermoconductivity.

The amount of Na in the hexagonal oxide is varied by an electrochemical extraction of Na at 3.8 V, as well as by an electrochemical insertion of Na at 2.35 V. A dependence of the position of the band assigned to the A_{1g} Raman mode on Na content is found in a similar manner to that in Na_yCoO_2 [1].

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Layered Manganese-Based Oxides as Cathodes for Lithium and Sodium Ion Batteries

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Lithium ion batteries are now established as electrochemical devices with high power density. However, lithium ion technology is in a great extent in an unconformity with environmental and cost requirements that impose the development of alternative rechargeable batteries. Sodium ion batteries offer some advantages over lithium-ion batteries in respect of the safety and the cost of raw materials. However, considerable further development is needed before the commercial application of sodium-ion batteries.

The aim of this contribution is to examine the layered manganese-based oxides as cathodes for lithium and sodium ion batteries. Two groups of layered manganese oxides are examined: nickel substituted $LiMnO_2$ with composition $LiNi_{1/2}Mn_{1/2}O_2$ and iron substituted $Na_{2/3}MnO_2$ with composition $Na_{2/3}Mn_{2/3}Fe_{1/3}O_2$. Both compositions are synthesized by co-precipitation reaction followed by the temperature treatment between 500 and 1000 °C. The composition and structure of oxides are controlled by the rate of cooling from the temperature of preparation. Structural characterization is carried out by powder XRD analysis and transmission electron microscopy (TEM). Electron paramagnetic resonance spectroscopy (EPR) is used for the analysis of local structure of Mn^{4+} in oxide systems. The electrochemical properties are studied in test electrochemical cells with lithium and sodium as anodes. The changes in local environment of Mn^{4+} ions during the electrochemical reaction were discussed on the basis of *ex-situ* EPR experiments.

$LiNi_{1/2}Mn_{1/2}O_2$ with a trigonal layered structure is formed in the temperature range of 800 and 950 °C. It is demonstrated that local cationic distribution in $LiNi_{1/2}Mn_{1/2}O_2$ is consistent with α,β-type cationic order with some extent of disordering that depends mainly on the precursors used. By quenching from 1000 °C, the orthorhombic distorted modification of $Na_{2/3}MnO_2$ is stabilized. A phase separation into orthorhombic and hexagonal modifications takes place when $Na_{2/3}MnO_2$ is slow cooled. The structure changes are concomitant with an increase in the oxidation state of Mn. The over–stoichiometric Mn^{4+} ions are accommodated in the hexagonal modification by creation of vacancies in the MnO_2–layers. The replacement of Mn by Fe leads to the stabilization of the hexagonal modification. The morphology and the local cationic distribution affect significantly the electrochemical performance of layered manganese-based oxides.

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Local Structure, Morphology and Electrochemistry of Mn^{4+}-Based Nanosized Spinels

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The increasing demands on high energy and high power Li-ion batteries lead the researchers to explore high voltage cathode materials. Nowadays research is turned to the improvement of their electrochemical performance by elaboration of nanosized composites and by metal substitution. A more detailed knowledge on the nano-scale effects in these materials is needed.

In this contribution we provide data on the local structure, morphology and electrochemistry of nanosized Mn^{4+}-based spinels. Two groups of spinels are examined: $LiNi_{0.5}Mn_{1.5}O_4$ and $Li_4Mn_5O_{12}$. The spinels were prepared using acetate-oxalate precursors, which were obtained mechanochemically at room temperature from metal acetates and oxalic acid. Acid treatment of the samples was used in order to modify their structure and morphology. XRD, HRTEM, ^{7}Li NMR and Mn^{4+} EPR are used for structural characterization. The electrochemical performance was tested in model lithium cells.

At 400 °C the acetate-oxalate precursor method yields a XRD single $LiNi_{0.5}Mn_{1.5}O_4$ phase with a mean particle size of about 20 nm. Low-temperature $LiNi_{0.5}Mn_{1.5}O_4$ displays a statistical cation distribution over the 16d spinel sites (*s.g. Fd3m*). At 600 °C a cationic redistribution takes place leading to a 1:3 cationic ordering (*s.g.* $P4_332$). At this temperature the particle size distribution becomes broader, but the mean particle size remains unchanged. Using acid treatment, $LiNi_{0.5}Mn_{1.5}O_4$ with an ordered structure and very close particle size distribution is obtained. Cationic distribution and size effects determine the electrochemical performance of $LiNi_{0.5}Mn_{1.5}O_4$.

At 400 °C, acetate-oxalate precursor method yields single a $Li_4Mn_5O_{12}$ phase with close particle distribution around 30 nm. According to HRTEM studies, the structure of nanosized $Li_4Mn_5O_{12}$ can be described as an integration of monoclinic Li_2MnO_3–like domains into a spinel matrix, $(1-a)Li_{1+x}Mn_{2-x}O_4.aLi_2MnO_3$ and $x<0.33$. Acid treatment leads to disappearance of the "Li_2MnO_3"-like domains, while the spinel matrix remains stable.

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Sol-gel synthesis of Nanosized Phosphoolivine Composites $LiCoPO_4$/CNFs as Cathode Materials for Lithium Ion Batteries

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The phosphoolivine $LiCoPO_4$ has been synthesized as a component for a composite cathode material in Li-ion batteries by a sol-gel ethanol-based method, similar to the technique previously applied for the synthesis of apatite [1]. The chosen method is found to be advantageous in producing nanocrystalline $LiCoPO_4$/carbon nanofibres (CNFs) with preferred physical and electrochemical properties as required for rechargeable lithium-ion batteries.

The starting reactants used were $LiNO_3$ (99.99%, Aldrich), $Co(NO_3)_2{\cdot}6H_2O$ (ACS, 98.0-102.0%, Alfa Aesar) and $P(OC_2H_5)_3$ (98%, Alfa Aesar). An as-prepared ethanol precursor solution (0.1M) was hydrolyzed and a stoichiometric amount of it was brought into contact with nanofibres (CNFs) for 24-72 h. After the solvents were driven off at 60˚C, the obtained gel was annealed at different calcination temperatures from 400 to 800˚C in Ar flow for 12h. X-ray powder diffraction (STOE STADI P) shows that the highest purity of the olivine phase is obtained in the 650˚C-750˚C temperature interval.

The particle size of the precursor particles during the sol-gel process depends on the concentration of the precursor solution and duration of the sol ageing period. Dynamic light scattering (DLS) was performed on the sols immediately after the reactants have been mixed. The observed general trend is that particle size of precursor increases only initially with time for about 6 hours and remains constant after that. The four times increase in concentration from 0.1M to 0.4M results in approximately twice as large particle sizes. The full-profile Rietveld analyses of the X-ray patterns of sample obtained from 0.1M precursor solution reveal after final annealing at 650˚C $LiCoPO_4$ as the main phase with volume-weighted average crystallite diameter of 60 nm, while at 700˚C $LiCoPO_4$ is obtained with crystallites of 400 nm.

Different concentrations of CNFs/$LiCoPO_4$ composites containing 30, 50 or 70% of active material were obtained from 0.05-0.1M precursor solutions (700˚C) and used for the electrochemical characterization. The best result was obtained with a discharge capacity of 68 mAh/g for the composite with 30% of active material, this is ca. 40% of the theoretical capacity of 167 mAh/g for $LiCoPO_4$ [2]. The discharge capacity decreases with increasing amount of active material (50, 70%), probably due to the accompanied increase of particle sizes. In conclusion, the presence of CNFs in combination with their coating by electrochemically active $LiCoPO_4$ nanoparticles can result in enhanced electrochemical properties of this hybrid material, but the specific sizes and amounts must be further optimized.

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Carbon Coated Nano-Crystalline $LiFePO_4$ as Electrodes for Lithium Ion Batteries

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Lithium iron phosphate, $LiFePO_4$, is the most promising cathode materials for high-power lithium-ion batteries with potential application in hybrid electric vehicles. Nowadays the research efforts are mainly devoted to the improvement of the rate capability of $LiFePO_4$ electrodes by engineering of nanosized phosphates, by coating with carbon and by doping with alien cations.

The purpose of this contribution is to examine the electrochemical performance of carbon-coated nanocrystalline $LiFePO_4$ prepared by a new phosphate-formate precursor method. This method is based on the thermal decomposition of homogeneous phosphate-formate precursors. Structural and morphological characterization of $LiFePO_4$ is carried out by powder XRD, BET measurements, SEM and XPS analyses. The electrochemical behaviour is tested in model lithium cells using galvanostatic mode. By changing the solution concentration, the freeze-drying method allows preparing $LiFePO_4$ with mean particle sizes between 60 and 100 nm and different particle size distributions. The content of carbon (appearing mainly on the particle surface) depends on both the solution concentration and the annealing temperature. The effect of particle size distribution on the voltage profile of $LiFePO_4$ is also demonstrated. The specific capacity is mainly determined by the quantity of carbon deposited on the particle surfaces. The higher capacity and the best capacity retention are observed for $LiFePO_4$ obtained from a diluted solution and annealed at 500 ^{o}C. This sample is characterized by lower particle dimensions (about 85 nm), a narrow particle distribution (about 40 nm) and a carbon content of about 2.3 mass %.

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High-Pressure Synthesis of $Li_{1+x}Co_{1-x}O_2$ with Extra Lithium in the Co-Site

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Cathode materials for lithium-ion batteries are based on lithium-transition metal oxides that can intercalate large amounts of lithium reversibly at potentials higher than 4V vs. Li. In terms of battery applications, oxides with layered and spinel crystal structures are of considerable interest. Despite of the high cost and toxicity of Co, $LiCoO_2$ with a layered crystal structure is still used as the main cathode material in lithium-ion cells. Recently, complex solid solutions of monoclinic $Li[Li_{1/3}M_{2/3}]O_2$ (M = Mn, Ti, Zr) with other layered compounds $LiMO_2$ (M ≡ Cr, Co, Ni) were reported as promising cathode materials.

In this contribution we report new data on the formation of novel $Li_{1+x}Co_{1-x}O_2$ compositions with a Li-to-Co ratio higher than 1 ($x \approx 0.12$). For the preparation of $Li_{1+x}Co_{1-x}O_2$, we have considered a new synthetic procedure involving a solid-state reaction between Li_2O_2 and Co_3O_4 spinel under high-pressure in an oxygen-rich atmosphere, intending to incorporate more than one Li in the structure and to stabilize Co ions in higher oxidation states. The new structural feature of these compositions as compared to the well-known layered $LiCoO_2$ is the incorporation of Li in the Co-site in addition to the nearly pure Li-site. The structure and the lithium distribution in these compositions were characterized by powder XRD analysis and ^6Li MAS NMR spectroscopy.

The target compositions were prepared by solid state reaction between Li_2O_2 and Co_3O_4 spinels under high-pressure (up to 3 GPa) using a piston cylinder type apparatus. The use of Li_2O_2 ensures an oxygen-rich atmosphere during the formation of $Li_{1+x}Co_{1-x}O_2$. When the Li-to-Co ratio in the precursor mixture is lower than 1.2, $LiCoO_2$ with a layered crystal structure is obtained. The incorporation of extra Li in $LiCoO_2$ leads to an increase in the mean Co(Li)-O bond length. By increasing the Li-to-Co ratio in the precursor mixture, a new structural modification is obtained. The crystal structure is described in terms of a spinel modification, where Li and Co occupies the *16c* and *16d* spinel positions ($Li_2Ti_2O_4$–type structure). The structural formula determined from the Rietveld refinement is $[Li]_{16c}[Li_xCo_{1-x}]_{16d}O_2$. The accommodation of Li^+ in the $Li_{1+x}Co_{1-x}O_2$ spinel is limited up to x=0.12. The different environment of Li in layered $LiCoO_2$ and $Li_{1+x}Co_{1-x}O_2$ spinel is demonstrated by ^6Li NMR spectroscopy.

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Mehanochemical Synthesis of Nanosized $Li_{1+x}Co_{1-x}O_2$

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In the last 15 years lithium cobaltate, $LiCoO_2$, has been considered as a material of great scientific importance due to its application as a cathode material in high-power lithium ion batteries. There are four structural modifications of $LiCoO_2$, the best electrochemical performance is established for $LiCoO_2$ with layered *O3*-type structure. Commercial $LiCoO_2$ consists of particles with dimensions of about 5 μm and displays a limited rate capability. To overcome this drawback, there is a need to elaborate specific methods for the preparation of nanosized $LiCoO_2$.

In this contribution we have studied the mechanochemical interaction of CoOOH and LiOH in order to prepare nanosized $LiCoO_2$ with a layered *O3*-type structure. The Li-to-Co ratio in the precursor mixture was varied from 1 to 2. The interaction of CoOOH and $LiOH.H_2O$ was monitored by DTA and TGA analysis. XRD powder analysis, TEM and ^{6}Li MAS NMR spectroscopy were used for structural characterization of lithium cobaltates.

The mechanochemical treatment of the CoOOH - LiOH mixture leads to a lattice expansion along the *c*-axis of the layered structure accompanied with a preservation of the intralayer distance between the metal ions. In addition, a partial transformation of CoOOH into lithium-containing Co_3O_4 spinel takes place. Thermal treatment at 400 °C yields *O3*-type $LiCoO_2$ with small amounts of spinel-type $LiCoO_2$ (less than 2 %). The spinel modification of $LiCoO_2$ is able to accommodate extra Li forming $Li_{1+x}Co_{1-x}O_2$ oxides with a Li-to-Co ratio higher than 1. The layered modification of LiCoO2 exhibits a Li-to-Co ratio equal to 1 and remains rigid with respect to the insertion of Li^+ in the CoO_2-layers. Both phases display thin particles with sizes varying between 10 and 50 nm. There is no intergrowth between the two structural modifications.

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Size-Dependent Specific Heat of Nanoclusters

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The contribution of surface energy to overall thermodynamic properties of the system is crucial for small, finite size phases [1]. A very telling example is the experimental evidence of size-dependent heat capacity of nanoparticles, recently reported for metallic nanoclusters and nanostructured dielectrics [2,3]. Despite of its clear physical background this phenomenon is still subject to a limited number of theoretical models. This is the reason to focus our study on the impact of the interface energy on specific heat of nanocrystals. In the framework of classical Gibbs thermodynamics, the Einstein-Debye model for heat capacity of solids is extended to clusters with comparable number of bulk and surface atoms. We introduce surface heat capacity that accounts for surface free energy contribution. Defined as a difference, between the surface and bulk terms, the excess heat capacity reveals temperature gap and size limits of nanoclusters where the contribution of surface energy is essential. Considering the role of surface Debye temperatures, we evaluate the deviation of specific heat for nanoclusters having different surface atomic density and surface orientation. We found that specific heat of nanocomposite systems can be enlarged by: (i) decreasing the size of nanocrystals and (ii) increasing the relative part of high index surfaces that facet the nanocrystal. Being in agreement with recent experimental findings, the present model opens up a way to predict basic, size-dependent thermodynamic properties of nanocomposite systems [4,5].

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Synthesis, Characterization and Catalytic Application of Au/ZnO Nanocomposities, Prepared by Coprecipitation

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As a bulk material the gold (Au) hasn't got significant catalytic activity. In the form of the nanoparticles (NPs) on the surface of different oxide supports the gold reveals surprising high activity even at room temperature. According Haruta the best catalysts are those containing ~8% Au-NPs with diameter 5-8 nm.

In the present study the Au/ZnO nanocomposit~~i~~es with different gold content were synthesized via coprecipitation method. For comparison the pure ZnO was obtained at the same experimental conditions. The samples were characterized by XRD, SEM, TEM and XPS. The catalytic activity of Au/ZnO nanocomposit~~i~~es was tested to the CO oxidation reaction.

The real gold content in the nanocomposites prepared, determined by AAA is 0.8, 2.5 and 9 wt %. The specific surface area values of the samples are similar and vary between 40 and 46 m^2/g. The TEM observation shows a homogeneous incorporation of gold nanoparticles in the ZnO matrix and narrow nanoparticle size distribution. The average diameter of Au-NPs in the samples, estimated from TEM-micrographs is 4 ± 0.3 nm.

The catalytic performance of Au/ZnO nanocomposites to the CO oxidation shows that the catalytic activity increases 8 to 11 fold after the incorporation of Au-NPs in the ZnO matrix and the temperature of 50 % CO conversion degree decreases with about 50-60ºC. However, there is not a strong correlation between the dopant content and catalytic activity of Au/ZnO nanocomposites..

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Preparation and Characterization of Nanoscale $LiVMoO_6$ via Soft-Mechanochemical Synthesis Method

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This study is a continuation of our previous synthesis and structural characterization of lithium transitional-metal oxide $LiVMoO_6$, which recently attracted special attention as an electrode active material in rechargeable lithium ion batteries [1, 2]. Several methods for the $LiVMoO_6$ preparation are described in the literature, including solid state reaction and wet chemistry techniques (sol–gel, soft-combustion synthesis and rheological phase reaction). There is no data for the application of mechanochemical synthesis. Especially soft-mechanochemical synthesis method developed by Senna [3] posses some advantageous because highly reactive compounds containing oxygen-hydrogen groups are used as a precursors. A mixture of LiOH. H_2O, V_2O_5 and MoO_3 in 1:1:2 molar ratio of oxides were subjected to intense mechanical treatment in air for different periods of time using a planetary ball mill (Fritsch-Premium line-Pulversette № 7). Powder XRD data indicate the formation of a single phase $LiVMoO_6$ with brannerite-type structure after 30 min.milling time. The IR spectrum contains absorption bands characteristic for the Me_2O_8 (Me=V, Mo) units present in the crystal structure of $LiVMoO_6$. TEM and XRD reveal that the as-obtained $LiVMoO_6$ consists of crystallites mostly in the 25–50 nm size range with spherical shape. XPS analysis shows that $LiVMoO_6$ product contains vanadium and molybdenum ions in a higher oxidation state only - V^{+5} and Mo^{+6}, while the data of the EPR indicate the existence of traces of isolated VO^{2+} species in the as-prepared material.

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Copper(II) Coordination Polymers with Dimethyl(methylenoxyaryl) Oxides-Based Ligands: Synthesis, Structure and Properties

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The coordination polymers are polymers whose repeating units are metal complexes. Recently, research in the field of design and synthesis of novel coordination polymers with predictable properties received particular attention due to their application as novel materials in various areas of industry. The ligands used for the synthesis have a polydentate nature and their characteristics such as nucleophilisity of the donors, bond angles, ligand length, bulkness, etc. play a crucial role in constitution of the supramolecular compounds. In addition, tendency of metal ions to adopt certain geometries also influences of the coordination polymer's structure and properties.

In the paper presented here, we describe the synthesis, single-crystal structure and physicochemical properties of three novel one dimensional copper(II) coordination polymers obtained with bis(dimethylphosphinylmethylenoxy)benzenes [1], Fig.1.

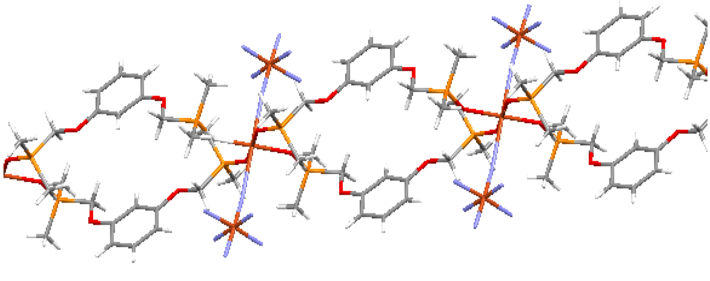

Fig. 1. Copper(II) coordination polymer of 1,3-bis(dimethylphosphinylmethylenoxy)benzene.

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Simple Prediction of Physical Properties of Ionic Liquids: The Residual Volume Approach

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A new method for the prediction of fundamental physical properties of ionic liquids (ILs) is proposed. The *residual volume approach* allows the estimation of density, viscosity and ionic conductivity of unknown ILs, using a simple linear correlation between a given property and newly defined substituent parameters – β^X. The proposed method has been developed for the density estimation of 50 *n*-alkyl substituted imidazolium and tetraalkylamonium ILs homologous series and has been extended for the estimation of viscosity and ionic conductivity which also correlate linearly with the corresponding β^X. In addition, the parameters β^X are temperature and pressure independent, which allows the prediction of these values at any temperature and pressure. The results demonstrate the influence of *n*-alkyl substituents on the property changes, which show the possibility for fine-tuning density, viscosity and ionic conductivity of ILs by slight variation in the structure of a given anion-cation combination.

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Synthesis of Pd-Containing Catalysts Promoted by NiO for Reduction of NO with CO

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Promotion of catalysts, containing noble metals with oxides of Ni, Cu, Zn, Mn and other metals leads to obtaining a new type of highly active and stable catalysts for purification of waste gases.

The aim of present investigation is synthesis of catalysts with minimal content of Pd in the presence of promoter NiO using modified alumina supports. This way high activity in reduction of NO and good mechanical strength and thermo stability of the contact is reached, which is necessary for application of the catalyst in neutralizers in automotive transport [1-3].

The synthesized supports have following content in wt. %: corundum 98÷20; aluminium hydroxide up to 62; bentonite – 15, MgO – 2. The supported active phases are Pd – 0.3-2 % and NiO – 12% in all samples. The final temperature of calcination of the contacts is 400°C for 3 h. The main physicochemical parameters of the catalysts after formation are in the range: specific surface area – S = 56÷2m^2/g, porosity Θ ~ 40% and mechanical strength σ up to 500 kg/cm^2. Highest catalytic activity toward reduction of NO with CO shows catalyst with active phase containing 0.3% Pd and 12% NiO on support containing 62% aluminium hydroxide as precursor (Fig. 1).

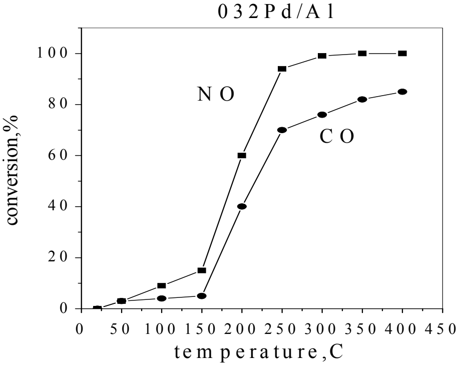

Fig. 1 Catalytic activity tests performed at RO = 1± 0.05 and space velocity, W= 26 000h^{-1}

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Structural Elements of Cobaltates with Potential Application as Thermoelectric Materials

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The ability of thermoelectric materials to convert heat into electricity determines them as a key source of the “clean” energy of the future. The wide potential application of thermoelectric materials is due to the possibility of generating electric energy not only by utilizing exhaust heat, but also by using geothermal or solar heat as an energy source. The conventional thermoelectric materials comprise the metals and semiconductors based on bismuth and tellurium. Their economic importance is restricted because of the low efficiency in energy conversion, as well as their low chemical and thermal stability at high temperatures. In 1997, new class of thermoelectric materials based on layered sodium cobaltates was introduced by Terasaki [1]. Nowadays, the state-of-the-art research is mainly directed to identifying oxide materials with higher thermoelectric efficiency. In this contribution we review our previous and ongoing studies on the synthesis and structural characterization of cobalt-based oxides with potential application as thermoelectric materials. Two classes of cobaltates are considered: cobaltates with layered and perovskite-type structure. The common feature in these oxides is the presence of cobalt in mixed oxidation state: 3+ and 4+. The modulation of properties of cobalt-based oxides is discussed on the basis of selective replacement of cobalt ions with manganese, nickel and iron ions. For layered oxides, the adaptation of specific methods of synthesis of nanostructured materials is considered with a view to reduce the resistance of polycrystalline oxides.

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On the Preparation of Olivine-type $LiMnPO_4$ as a Cathode in Lithium-Ion Batteries

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Lithium transition metal phosphates, $LiMPO_4$ (M = Fe, Mn, Co, Ni), with olivine-type structure have attracted the research interest as promising cathode materials for high-power lithium ion batteries with potential application in HEV. The main drawback of phospho-olivines is their low electronic conductivity, which determines the lower rate capability. To improve the rate capability, it is necessary to elaborate specific methods that allow controlling the morphology and nano-crystallinity of the phospho-olivines.

In this contribution we report new methods for the preparation of nano-crystalline $LiMnPO_4$ with controlled morphology. The first method is based on the formation of homogeneous precursors by freeze-drying of mixed phosphate-formate solutions. The thermal decomposition of the precursors at temperatures above 400 °C yields pure $LiMnPO_4$ with isometric particles and close particle distribution in the range of 60−120 nm, which do not form aggregates. The Rietveld analysis evidences that $LiMnPO_4$ are characterized with a low extent of Li-to-Mn disorder (below 1%). The particle sizes of $LiMnPO_4$ are varied by the concentration of the solutions subjected to freeze-drying and by the annealing temperature.

The second method is based on ion-exchange reactions using dittmarite-type host matrices with composition $MMnPO_4.H_2O$ (M = NH_4 and K). The structural similarity between the dittmarite- and olivine-type structures facilitates the ion-exchange process at low-temperatures. The ion exchange reaction was performed at 270 ^oC in an eutectic mixture $LiCl$:$LiNO_3$ for a short time (90 min). The exchange of potassium with lithium results in the formation of $LiMnPO_4$ with platelet-like aggregates composed by nearly isometric nano-particles (about 90 nm). The exchange of NH_4^+ with Li^+ takes places with NH_3 release, which destroys the pristine dittmarite particles. As a result, nearly isometric particles with dimensions in the range of 70 - 110 nm are formed. The particle shape and dimensions are preserved during further annealing up to 500 ^oC.

The results obtained demonstrate that the ion-exchange and the phosphate-formate methods are effective for the synthesis of nano-sized $LiMnPO_4$ with a controlled morphology, which is favourable for its application as cathode material in lithium-ion batteries.

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Topic B.

Materials for Environmental Protection

Doping of TiO_2 for Improving its Photochemical Activity

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Titanium dioxide has emerged as the celebrated material for numerous applications, among which the photocatalysis is one of the most studied. TiO_2 is a wide band-gap energy (>3.0 eV) semiconductor, therefore, only UV light (< 400 nm) can be utilized for generation of electron-hole pairs in its pristine form(s). On the other hand, there are also evidences that, defects created within the band-gap, either on purpose or through the preparation routes, lead to remarkable photochemical activities. Numerous physical (vapor and/or sputter deposition, etc.) and wet-chemical (sol-gel, and/or layered deposition, etc.) routes have been heavily investigated to create materials with controlled defects, which can simply be categorized as n- or p-doping processes. Similarly, there has also been an immense activity for reliable characterization of the resultant materials, using electrical, electrochemical, and/or spectroscopic tools. In this contribution, a brief review of the preparation routes, and characterization techniques will be given with a special emphasis on the use of X-Ray Photoelectron Spectroscopy, XPS, for harvesting chemical and electrical properties of various doped TiO_2, and similar materials, by utilizing electrical and/or optical modulation techniques.

Receptor Modeling of Nanofine Air-borne Particulate Matter

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Receptor models are mathematical or statistical procedures for identifying and quantifying the sources of air pollutants, including nanofine air-borne particulate matter, at a receptor location. Unlike photochemical and dispersion air quality models, receptor models do not use pollutant emissions, meteorological data and chemical transformation mechanisms to estimate the contribution of sources to receptor concentrations. Instead, receptor models use the physiochemical characteristics of particles measured at source and receptor to both identify the presence of and to quantify source contributions to receptor concentrations. The most widely used models are the chemical mass balance (CMB), principal components analysis (PCA)/absolute principal components scores (APCS), positive matrix factorization (PMF) or UNMIX model. All of them posses both many advantages and limitations. For example, in contrast to other receptor models, which extract source compositions from the data, CMB model requires detailed knowledge of source emission type. Furthermore, CMB is applied separately to each observation, rather than operating on the entire set of data. Applying PCA/APCS, PMF and UNMIX one can analyze a series of observations simultaneously in an attempt to determine the number of sources, their chemical composition and their contributions to each observation [1].

In this lecture some theoretical basis of the most popular models accompanied by several case-studies will be considered since the role of the modeler is extremely important not only as an information provider but as a designer of understandable visual material for those who are responsible for the clean environment and sustainability.

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Environmetric Interpretation of Different Size Fractioned Aerosol Monitoring Data

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The rapid development of the research and study in the field of nanomaterials and nanotechnologies still lacks the answer of the question about the possible environmental hazards which could happen when the scale of nanomaterials production becomes massive. Although there are already series of publications concerning the problem, no detailed studies or scenarios are available for real assessment of the environmental quality in the moment of turning nanotechnologies into a routine industrial activity.

The main goal of the present study is to perform classification and modeling of aerosol monitoring data by the use of environmetrics methods in order to better understand the specificity of the nanoparticles as air pollutants as well as their seasonal behavior. It is well known that the air-borne particles are the major atmospheric pollutant and small-sized aerosols are serious danger for human health. That is why in the study the collection of aerosols was performed by the use of cascade impactor in order to separate the dust into 6 different size fractions – from 0.01 to 25 μm. The different samples were analyzed for the content of 16 chemical parameters (major ions, carbon content and heavy metals). The sampling sites were located in an Alpine region of Austria near to the Slovenian border. Advanced environmetric methods such as N-way Principal Components Analysis, PARAFAC and Self-Organizing Maps (SOM) were involved in the classification and modeling study.

The study has indicated that there is a specific relationship between each aerosol fraction and the chemical content, season of sampling and sampling location. None of these relationships could be reliably interpreted without application of environmetrics which turns to be one of the major metrics for risk assessment and sustainable development.

Gold Catalysts Supported on Ceria Doped by Al(III) and Sm(III) for Water Gas Shift Reaction

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Gold catalysts supported on ceria doped by Al(III) and Sm(III) have been characterized by XRD, Raman spectroscopy, XPS and H_2-TPR. The WGS activity of the materials has been tested and the mechanism of the $CO+H_2O$ surface reaction has been investigated by in situ FT-IR spectroscopy. The WGS activity of Au/CeO_2-Sm_2O_3 is higher than that of the Al_2O_3-containing catalyst. The difference in the catalytic behavior is explained by differences in the structural properties of the catalysts. In the gold catalyst doped by Al(III), the oxygen vacancies are found within the bulk of ceria, whereas in the Au/CeO_2-Sm_2O_3 sample the vacancies are located most likely around Sm(III). The Au 4f XP spectra of fresh samples reveal higher contribution of dispersed form of Au on the Sm-containing catalyst than on the Al-doped one. The Ce 3d XP spectra disclose also higher concentration of Ce(III) before the catalytic operation in the case of the Sm(III)-modified catalyst as compared with the fresh Al(III)-containing sample. There is no distinct correlation between the reducibility and WGS activity of the studied catalysts.

The amount of formate species, generated during the surface $CO+H_2O$ reaction and detected by in situ FT-IR, is higher on the Sm(III)- than on the Al(III)-containing catalyst and parallels the catalytic activity. It is concluded that the high activity of Au/CeO_2-Sm_2O_3 is related with the high dispersion of Au nanoparticles leading to large number of active Au-support interface sites, which results in high concentration of formate species. According to the FT-IR data, the Au/CeO_2-Sm_2O_3 and Au/CeO_2-Al_2O_3 samples behave differently with regard to the adsorption of water at room temperature: water adsorbs dissociatively on the former catalyst and molecularly adsorbed water has been observed on the Al(III)-doped sample. It can be proposed that the higher concentration of oxygen vacancies on the surface of the Sm(III)-containing catalyst facilitates the dissociation of water. This demonstrates the active role of defective ceria in the latter process. The facile dissociation of water on the Au/CeO_2-Sm_2O_3 catalyst accounts also for its better performance in the WGS reaction.

Microporous Carbon Nanostructures Derived from $Cr(C_5H_5)_2$ and $Cr(C_6H_6)_2$

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Organometallic compounds have been widely used as precursors to produce shaped carbon materials because their chemical composition provides the carbon source and the metal catalyst [1,2]. Their final characteristics (purity, shape, surface area and pore size distribution) make them potential candidates for hydrogen and methane storage materials, supercapacitors and catalysts. In this work, we present the synthesis and characterisation of microporous carbon nanostructures obtained by chlorination of $Cr(C_5H_5)_2$ (chromocene) and $Cr(C_6H_6)_2$ (chromobencene). Precursors, powder purity of 97% Aldrich, were heated in a tubular furnace at 900 ºC (heating rate of 50 ºC/min) during 30 min, in a continuous flow of high purity chlorine gas (25 mL/min) following the next possible reactions:

$$Cr(C_5H_5)_{2(s)} + (13/2)Cl_{2\,(g)} \rightarrow 10C_{(s)} + CrCl_{3\,(g)} + 10HCl_{(g)}$$
$$Cr(C_6H_6)_{2\,(s)} + 7Cl_{2\,(g)} \rightarrow 12C_{(s)} + CrCl_{2\,(g)} + 12HCl_{(g)}$$

Transmission Electron Microscopy (TEM) images were done with a JEOL 3000 F (acceleration voltage of 300 kV) microscope (point resolution of 1.7 Å) equipped with an ENFINA spectrometer for Electron Energy Loss Spectroscopy (EELS) measurements. Solid and hollow carbon nanospheres were found in both samples (Figure 1a, 1b); additionally, amorphous carbon nanotubes-like (α-CNT) structures were observed in the sample prepared from chromocene. On the High Resolution-TEM images we observe that the structures are formed by highly disordered graphene layers. Quantification of bonding type, obtained by EELS, indicates sp^2/sp^3 content higher than 95 %. The mass-density (1.3 – 1.8 g/cm^3), obtained from the low-loss region of the EEL spectra, shows values bellow graphite density. The N_2 adsorption measurements at 77 K showed, isotherms shape which can be assigned to Type I (Figure 1c) due to small contributions of mesoporosity and textural porosity ($p/p_0 > 0.8$); however, high surface areas were developed (694 and 1761 m^2/g) and pore size distribution in the range of 0.58 – 1.35 nm (see inset in Figure 1c).

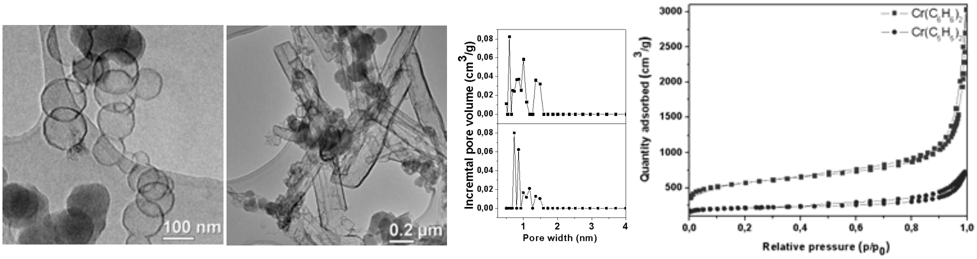

Fig. 1. Shaped carbon nanostructures derived from (a) $Cr(C_5H_5)_2$ (b) $Cr(C_6H_6)_2$ and (c) BET measurements.

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UV and Visible Light Active TiO_2/WO_3. Powder and Film for Water and Air Purification

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Powder nanocomposites of TiO_2/WO_3 are prepared by a simple solid-state thermal procedure from commercial oxide powders and cast after that as a film on a substrate. The WO_3 content in the powder composites is varied from 0.5 to 50 %. The phase composition and morphology of titania/tungsten composites and films is characterized by SEM and X-ray analysis. The photocatalytic action of TiO_2/WO_3 powders is tested with respect to the degradation of malachite green in water solutions under UV light irradiation. The effect of preparation temperature on the photocatalytic activity is also investigated. It is found that the mixed powder of 5%WO_3 is of best photocatalytic performance. The prepared powder photocatalyst is successfully deposited as a film for gas-phase application. The as-obtained composite films with 5%WO_3 are investigated in air purification from ethylene under UV and visible light illumination. The TiO_2/WO_3 films show always a better activity than the pure TiO_2.

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The photocatalytic and Optical Properties of ZnO Nanoparticles Synthesized by Mechanochemical Activation

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T. Tsuzuki et al. [1,2] have used mechanical activation of solid - state displacement reaction $ZnCl_2 + Na_2CO_3 \rightarrow ZnCO_3 + 2NaCl$ for ZnO nanoparticles manufacturing. In order to avoid the additional thermal decomposition of intermediate $ZnCO_3$ and washing of NaCl we applied mechanically activation directly on $ZnCO_3$. The initial trade $ZnCO_3$ (Fluka) which is a mixture of $Zn_5(CO_3)_2(OH)_6$ and $Zn_4(CO_3)_2(OH)_6.2H_2O$ was subjected to intense mechanical treatment in air using a planetary ball mill (Fritsch – Premium line – Pulversette №7) up to 120 min. Stainless steel vials and balls with 5 mm in diameter were used. The balls to powder weight ratio was 10:1. The phase and structural transformations were investigated by X-ray diffraction (XRD) and infrared spectroscopy (IR). The optical properties of the ZnO powders were characterization by UV-VIS spectroscopy. Nanoparticles of ZnO single phase was obtained after 90 min milling time. Additional mechanical treatment did not lead to any phase and structural changes of ZnO. The ZnO powder synthesized by mechanochemical activation exhibits a photocatalytic activity in the degradation of Malachite Green (MG) under UV-light irradiation. According to UV-VIS spectra the obtained sample exhibits transparency above 360 nm.

Acknowledgements: Thanks are due to the Financial Support of Bulgarian National Science Fund, Ministry of Education and Science Grants: TK-X-1702/07 and the National Science Fund of Bulgaria, National Centre for New Materials UNION, Contract No DO-02-82/2008.

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Nonhydrolytic Sol-Gel Synthesis and Antibacterial Properties of Nanosized TiO_2

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The titanium dioxide (TiO_2) is one of the most studied metal oxides during the last 20 years due to its technological and environmental importance. Although a wide variety of approaches for its synthesis have been reported it still remains a particularly active research field. The nonhydrolytic sol-gel methods have been developed for the synthesis of TiO_2 with controlled particles size [1]. Among the various applications of this oxide, its antibacterial properties are one of the most investigated topics [2]. It is known that the photocatalytic activity of TiO_2 strongly depends on the particles size and the type of the precursors. For this reason, many researchers have extensively investigated the relation between the synthesis conditions and the properties of nanosized TiO_2 powder [3]. This motivates our study to synthesize TiO_2 by a nonhydrolytic sol-gel route and to examine its antibacterial properties. In the present work the reaction between $TiCl_4$ and benzyl alcohol was performed at 80°C under continuous stirring for 8 hours, followed by calcinations at 500°C. The structure and morphology of the resulting particles were characterized by XRD, IR and SEM. The average particles size of synthesized TiO_2 (anatase) was 10-20 nm.

The antimicrobial action of the as-prepared TiO_2 was investigated using *Escherichia coli* as test microorganism. The bacteria growth was examined by the effect of UV light alone, in the presence of TiO_2 at dark conditions and in the presence of both – TiO_2 and UV radiation. The experiments were done in suspension containing initial cell concentration of 185000 colony forming units $(CFU)ml^{-1}$ and TiO_2 concentration of 1 gL^{-1}. It was found that the photocatalytic activities of TiO_2 and UV light alone were roughly the same – approximately 50% of bacteria were killed for 3 hours, while the combination of TiO_2 and UV radiation led to the complete killing of bacteria in 30 min. It was concluded that the as-obtained nanosized TiO_2 (anatase) could be successfully used for disinfection of water.

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Preparation and Characterization of Ni-Doped ZnO Thin Films as Photocatalysts in the Degradation of Organic Dye

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Nanostructured ZnO thin films with different concentrations of Ni^{2+} doping (0, 1, 5, 10 and 15 wt%) are prepared by the sol gel method for the first time. The films comprise of ZnO nanocrystallites with hexagonal crystal structure, as revealed by means X-ray diffraction (XRD). The film surface is with characteristic ganglia-like structure as observed by Scanning Electron Microscopy (SEM). Furthermore, the doped films are tested with respect to the photocatalysis in aqueous solutions of malachite green upon UV-light illumination, visible light and darkness conditions. The thin films are prepared from $Zn(CH_3COO)_2.2H_2O$, 2-methoxyethanol and monoethanolamine on glass substrates using the dip coating technique. The initial concentrations of malachite green and the amount of catalyst are varied during the experiments. It is found that increasing of the amount of Ni^{2+} ions with respect to ZnO generally lowers the photocatalytic activity in comparison with the pure ZnO films. Neverthess, all films exhibit a substantial activity in both visible light and darkness, which is promising for the development of new ZnO photocatalysts by the sol-gel method.

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Effect of Manganese on the Photocatalytic Performance of ZnO Thin Films

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The photodegradation of organic pollutants in air or aqueous medium, catalyzed by various semiconductors, is a promising remediation technology especially at lower concentration of the pollutant. Among the various semiconductors used, ZnO has been recognized as one of the attractive materials for its biological and chemical inertness, high catalytic efficiency, low cost and environmental sustainability. On the other hand, ZnO is used as a UV-blocker agent because it adsorbs light in the whole region of the UV-spectrum (UVA and UVB). Depending of the application, the photocatalytic properties of ZnO should be promoted or suppressed. This can be achieved by changing the particle size and/or by doping.

In the present study, the effect of manganese on the photocatalytic performance of ZnO thin films is investigated. The activity of ZnO and Mn/ZnO thin films is tested in the reaction of photoassisted bleaching of the organic dye Malachite green. The thin films are synthesized via the sol-gel method from $Zn(CH_3COO)_2{\bullet}2H_2O$, monoethanolamine for stabilization of the solution and 2-metoxyethanol like a solvent. For Mn-doping $Mn(CH_3COO)_2{\bullet}H_2O$ is used at the ratio of Mn^{2+} to Zn^{2+} in the solution being 1:99. The samples are characterized by XRD and SEM.

The XRD analysis shows the formation of ZnO with a wurtzite structure. The films possess ganglia-like morphology and the ganglia consist of separate grains. The photocatalytic tests show the effect of the dopant on the catalytic performance of ZnO. The results are compared with our previous data for the activity of doped ZnO thin films, obtained by different method and precursor.

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Preparation of ZnO on TiO_2 Multilayers Structures with Ganglia like Morphology. Decolouration effect on Malachite Green Dye under UV Light.

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Nanostructured ZnO on TiO_2 multilayer structures were prepared on glass substrate by sol-gel method using dip coating technique. Dense or porous TiO_2 films with different thickness were deposited as a bottom layer, after that it was covered by one or two ZnO films. Structures containing three ZnO layers were obtained in order to compare the photocatalytic properties with the multilayers structures. Titania dense films were obtained from $TiCl_4$ ethanol solutions, while for the the porous films was used ethylcellulose modified solution. The ZnO films are prepared from solutions containing $Zn(CH_3COO)_2.2H_2O$, 2-methoxyethanol and monoethanolamine.

The structures were characterized by X-ray Diffraction (XRD), Energy Dispersive X-ray Spectroscopy (EDAX) and Scanning Electron Microscopy (SEM). Only peaks of wurtzite ZnO crystalline phase were registered on X-Ray difractograms. Pure ZnO films have crystallites about 30 nm, while the ZnO on TiO_2 multilayers possess crystallite sizes in the range 40-55 nm. All oxide structures possess ganglia like morphology.

The photocatalytic degradation of Malachite Green dye is faster on the structures with bottom dense titania layers than those with porous titania films. The best photocatalytic activity of Malachite Green dye is registered for the structures with pure ZnO films (more than 77 % for 3 hours).

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Modified Sol-Gel Synthesis of $ZnTiO_3$ and its Antibacterial Properties

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From industrial perspective zinc titanate ($ZnTiO_3$) is an attractive material due to its various applications as paints pigments, fusion cast thermistors, sorbent, microwave dielectrics, dielectric resonators, catalysts, etc. It is well known that ZnO and TiO_2 posses antibacterial properties, but there is no data concerning the antibacterial properties of $ZnTiO_3$. This provokes our interest to study that compound in order to check these properties. There are several methods for preparing $ZnTiO_3$ powders, including conventional solid state reactions, mechanochemical activation and several variants of sol-gel technique [1, 2]. During recent years, the sol-gel method has been regarded as an advantageous method for synthesis of nano-powders. This method was selected in order to overcome the $ZnTiO_3$ decomposition (~ 945^0C).

The present study is based on a modified sol-gel method. The $Ti(OEt)_4$, Zn-nitrate and Zn-acetate were used as main precursors. The phase formation and structural transformation at every step of the synthesis routes were followed by X-ray phase analysis and IR spectroscopy. The agglomeration tendency and the crystals size were determined by Scanning Electron Microscopy. Submicron powders of pure $ZnTiO_3$ were obtained by heating up to 550^0C. It was established that $ZnTiO_3$ possesses photocatalytical activity against Malachite green organic dye. For first time it was shown that submicron powders of $ZnTiO_3$ possess strong antimicrobial activities against high concentration of *Escherichia Coli* bacteria.

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Influence of the Zinc Precursors Solutions on the Photocatalytic Activity of ZnO Sol-Gel Films

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Thin ZnO films are successfully prepared on glass substrates by the sol-gel method using both dip coating and spin coating techniques. Two different procedures are applied for preparation of the films: (i) polymer modified (zinc acetate and polyvinyl alkohol) and (ii) classical sol gel method (zinc acetate with complex agent monoethanolamine). The films are characterized by means of X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), Fourrier Transform Infrared Spectroscopy (FT-IR) and Thermal Analyses (TG-DTA).

The mean crystallite size, estimated by the Sherrer's formula for the polymeric-derived films, is 10-12 nm, while for the films obtained by procedure (ii) is about 30 nm. The films prepared by complex agent solution possess many ganglias on the surface, while the polymer modified solutions leads to a formation of some ganglia aggregates.

The as-obtained ZnO films are studied with respect to the photo-initiated bleaching of malachite green under UV illumination in aqueous solutions. It turns out that the films obtained by zinc acetate with complex agent solution have a better photocatalytic activity than those by polymer modified solution. It is proven that the films have also some activity in darkness, which is lower than the activities under UV light.

The results obtained show that the films morphology has more significant influence on the photocatalytic properties than the size of the crystallites. The ZnO thin films prepared by us are promising as efficient photocatalyst for degradation of malachite green dye.

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XPS Study of ZnO Nanolayers Prepared by Laser Deposition

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Nanosized ZnO has great potentiality for being used in gas sensors, photocatalysts, chemical absorbents, solar cells, electrical and optical devices. Hence, investigations on the synthesis and modification of nanosized ZnO have attracted tremendous attentions.

In this work, nanostructured ZnO films were produced by pulsed laser deposition on amorphous SiO_2 substrates. The nanostructured films were fabricated via a two step process. As a first step, thin ZnO layers were fabricated on SiO_2 substrates at different oxygen pressures in order to form different types of growth nuclei. As a second step, ZnO films were deposited on the as-created nuclei in an on-axis PLD configuration. The influence of the growth nuclei parameters on the morphology and physicochemical properties of the nanostructured films was investigated.

The surface morphology and structure of the nanostructured ZnO films were characterized with AFM in order to determine the optimum conditions of formation of different types of nuclei. XPS was used to investigate the composition and chemical state of the nanostructured ZnO. The changes occurring on the surface of the films after prolonged exposition in air are considered in the light of the nanostructure of the ZnO layers.

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Structure and Application of Organic-Inorganic Biomaterials on the Base of Natural Polymers and Silica

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The sol-gel method has definitely proved its exceptional perspective of the possibility to synthesize a significant number of new materials with specific properties. Organic-inorganic hybrids are a relatively new type of composites with interesting mechanical, optical, structural and thermal properties [1]. Natural polymers offer the advantage of being very similar, often identical, to macromolecular substances which the biological environment is prepared to recognize and to deal with metabolically [2].

The aim of the present study is to develop of new organic-inorganic biomaterials. Sol-gel method was used to synthesize biomaterials containing tetraethoxisilane, methylriethoxisilane and ethyltriethoxisilane as a source of silica and water soluble polymers as pectin from apple and methylcellulose. The biomaterials have been obtained as the quantities of the polymers have varied from 5 to 50 wt% to SiO_2.

The structural evolutions of prepared biomaterials have been investigated by X-Ray diffraction, Fourier transform infrared spectroscopy, BET and Atomic Force Microscopy. XRD patterns showed that all samples are in an amorphous state. IR spectra of prepared sol-gel organic-inorganic materials indicate characteristic peaks of polymers and silica network. Observed structure by AFM showed surface with random distributed aggregates. The size of aggregates varied in large range and depends of type of the natural polymers and silica source.

The application of obtained organic-inorganic materials were applied as matrices for immobilization of yeast cell *Trichosporon cutaneum* starin R 57. Obtained biofilms were used as a sorbents of heavy metals ions from polluted waters.

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Colour Stability of Red Wine after Treatment with Mesoporous Silica SBA-15

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The phenolic compounds are the most important components of wines and are directly related to colour, astringency, bitterness and oxidative level. The red colour of young wines is mainly due to: (a) free anthocyanins, principally as flavylium cation (red) and quinoidal anhydro-base (blue);(b) the self-association of anthocyanins; and (c) copigmentation of anthocyanins with other phenols present in wine (i.e., flavanols, flavonols and hydroxycinnamic acids).

The purpose of this work was to investigate the evolution of colour stability of red wine on treatment with mesoporous material SBA-15.

The purely siliceous molecular sieve SBA-15 was synthesized hydrothermally and the typical gel molar composition was 1TEOS : 0.017P123 : 5.95HCl : $194H_2O$.

Wine colour was evaluated by simple CIELab76 methods reflecting the colour visual appreciation. This method has been proposed as an OIV method for colour determination.

This CIELab76 colour or space system is based on a sequential or continuous Cartesian representation of 3 orthogonal axes: *L, a* and *b* (Fig.1). The chromatic characteristics were calculated by equations:

$L=116(Y/Yn)^{1/3}-16$; $b=200-[(Y/Yn)^{1/3}-(Z/Zn)^{1/3}$; $a=500[(X/Xn)-(Y/Yn)]$;
$C=(a^2+b^2)^{1/2}$;$H=tg^{-1}(b/a)$; $\Delta H=[(\Delta E)^2-(\Delta L)^2-(\Delta C)^2]^{1/2}$;
$\Delta E=[(\Delta L)^2+(\Delta a)^2+(\Delta b)^2]^{1/2}$;$\Delta E=[(\Delta L)^2+(\Delta C)^2+(\Delta H)^2]^{1/2}$

Mesoporous silica SBA-15 retains phenolic compounds from red wine, it is comparable with those obtained using active carbon as adsorbent and can be used as fining agent for red wine.

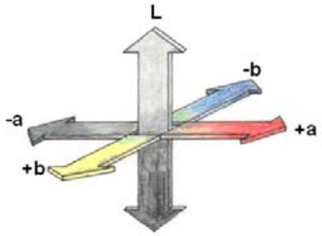

Fig. 1. Diagram of colourimetric coordinates according to *Commission Internationale de l’Eclairage* (CIE, 1976)

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PW Heteropoly Acid Supported on Al, Ti, Zr-MCM-41 Mesoporous Materials: Preparation and Characterisation

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The class of MCM-41 materials has been widely studied, because of its pseudo-crystalline and textural properties, such as the hexagonal arrangement mean pore diameters in the range of 20–100 Å and high surface area ~~s~~ (>1000 m^2/g).

In general, the structural and textural characteristics of such molecular sieves are directly related to the synthesis conditions under which they are prepared: the nature of the surfactant, pH, presence of electrolytes, temperature, solvents, aging/preparation time, etc. On the other hand, the incorporation of heteroatoms in the MCM-41 structure, transition metals or Al, promotes the appearance of active catalytic sites (both acid or redox), which may suit them for interesting applications in heterogeneous catalysis such as hydrocarbon catalytic cracking, isomerization, hydrodesulphurization, oxidation reactions, hydroxylation and epoxidation of aromatics, olefins and phenols, etc. In addition, MCM-41 material is an excellent support for acid catalysts like heteropoly anions, allowing a better dispersion of the active phase.

The aim of the current research is the synthesis of MCM-41 modified with Al, Ti or Zr. The tungsten heteropolyacid were dispersed on Al, Ti, Zr-MCM-41 using the impregnation method improving its oxidation potentials.

Characterization of materials has been made by means of X-ray diffraction, N_2 adsorption, ^{29}Si CP MAS NMR and Transmission Electron Microscopy.

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Single and Bi-metallic Silver Modified ZSM-5 for HC-SCR

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The emission of nitrogen oxides (NO_x) from internal combustion engines is one of the biggest environmental problems nowadays. The waste gases from traditional gasoline engines can be purified successfully by three-way catalysts, which operate under stoichiometric conditions. However, the more efficient diesel and lean-burn engines emit gases with a large excess of oxygen, which so far cannot be purified effectively from NO_x.

The selective catalytic reduction by hydrocarbons (HC-SCR) is an elegant technique for the abatement of NO_x emissions from lean-burn vehicles. In this method the unburned hydrocarbons in combination with added ones are used to reduce NO_x in the exhaust gases over a suitable catalyst. A catalytic system on the basis of silver supported on alumina, shows extremely high NO_x into N_2 conversion (maximum conversion of 90% at 450°C) in large excess of oxygen (6 vol.%) and water (12 vol.%), i.e. under real lean-burn conditions with low sulphur containing diesel fuel. However, a drawback of the Ag/alumina catalyst is its poor catalytic activity at low temperatures (below 300°C) and the strong CO formation during the conversion of NO_x with a maximum value at 450°C. A combination of Ag/alumina with commercial platinum oxidation catalyst for CO removal at a 33 mm distance resulted in a decrease of NO_x conversion by about 20% at 450°C. For that reason single and bi-metallic silver modified ZSM-5 catalysts, which has both oxidation and reduction activity were synthesized using three different methods of preparation, characterized by several techniques and tested in simulated diesel conditions. Additionally the catalytic behavior of the most active catalyst, containing 5 wt.% Ag and prepared by impregnation (5Ag(Imp)-H-ZSM-5), was studied over a broad temperature range with two reducing agents (octane and propene). To correlate the catalytic activity of the prepared catalysts with preparation parameters the materials were characterized by XRD, SEM, N_2-physisorption, octane/propene-TPD, EPR and ICP techniques. A dual bed system consisting of Ag/alumina and the most active zeolitic material (5Ag(Imp)-H-ZSM-5) was shown not only to substantially enhance the activity of Ag/alumina in the low temperature region (below 300°C), but also to completely oxidize the produced CO and unburned hydrocarbons. These two important features of the zeolite catalyst suggest it as a competitive candidate to replace the expensive noble metal based oxidation catalysts, which only oxidizes the produced CO and unburned hydrocarbons and decreases the high NO_x reduction activity of the Ag/alumina.

Silver Loaded Zeolites and Investigation of their Antimicrobial Activity

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Clinoptilolite, microporous zeolite can be used for dispersion of Ag^+ activity having permanent removal of coliforrm bacteria normally found in natural water. Findings of the clinoptilolite antibacterial effect of Ag^+ nanoparticles/clinoptilolite was made from two bacteria: *Escherichia coli ATCC 25922* and *Staphylococcus aureus ATCC 25923.*

To guarantee the microbiological quality of the water, which is been affected by the pollution of the bacterium, is necessary to implement a tertiary drinking system in the resident houses. A possible complementary system is the utilization of clinoptilolite for treatment of drinking water [1,2].

Modification of natural zeolite was carried out under various conditions with $H_2C_2O_4$ (P_a) and NaOH (P_b), respectively (with a liquid/solid ratio of 5:1). After treatment, the solids were vacuum filtered, washed several times with deionised water and dried at 105°C for 6 hours. The second stage consists of the obtaining of the Ag^+ (P_1-P_b treated with $AgNO_3$, P_2-P_a treated with $AgNO_3$) modified clinoptilolite.

After preparing inoculum and culture media, zeolitic species were put in contact with the surface agarizat environment. After 24 hours of incubation was followed by inhibition of bacterial growth phenomenon by the appearance of lysis zones around clinoptilolite with Ag^+ nanoparticles clinoptilolite (Fig.1 and 2).

Fig. 1: Antibacterial test results using *Escherichia coli* ATCC 25922 (P_1-P_b treated with $AgNO_3$, P_2-P_a treated with $AgNO_3$).

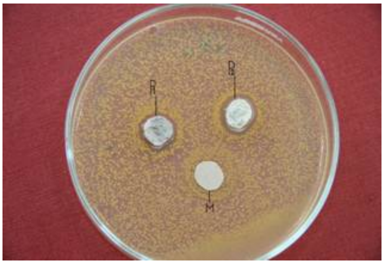

Fig. 2: Antibacterial test results using *Staphylococcus aureus* ATCC 25923 (P_1-$\mathbf{P_b}$ treated with $AgNO_3$, P_2-P_a treated with $AgNO_3$).

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State of Copper in Different Cu-ZSM-5 Samples: An FTIR Study

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Due to the particular importance in catalytic reactions of environmental interest, Cu-ZSM-5 is among the most studied materials during the last two decades. Nevertheless, there are still unresolved questions, concerning the coordination chemistry of copper ions in different location and oxidation states. The present study is based on a comparative investigation of four Cu-H-ZSM-5 samples with different copper loading and based on two parent zeolites, having Si:Al ratios of 12 and 25, respectively and differing in the particle size. We used mainly IR spectroscopy of adsorbed probe molecules (CO and NO), but some additional techniques were also utilized.

The main results obtained are summarized in Table 1.

Table 1. Main results of the spectroscopic studies.

Sample	Concentration of Cu, wt %[a]	Si : Al	Relative Cu^{2+}/Cu^{+} ratio[b]	Associated Cu^{2+} sites [c]	Fraction of Cu$_{3c}^{+}$ [d]
Sample 1	0.77	25	0.72	few	45 %
Sample 2	1.01	25	3.5	not detected	35 %
Sample 3	1.16	12	0.56	not detected	45 %
Sample 4	1.55	12	0.63	important	60 %

[a] *Data from AAA analysis.*

[b] *Ratio between the intensities of the Cu^{2+}-NO (2000-1850 cm^{-1}) and Cu^{+}-NO (1850-1760 cm^{-1}) bands.*

[c] *Estimated by DR UV VIS spectra and the existence of Cu^{2+}-NO bands at 2000 – 1950 cm^{-1}.*

[d] *Fraction of the Cu^{+} sites able to coordinate up to three CO molecules.*

To prove the polycarbonyl structure coadsorption of $^{12}C^{16}O$-$^{13}C^{18}O$ was utilized and it was demonstrated that this isotopic mixture is advantageous as compared to $^{12}C^{16}O$-$^{13}C^{16}O$.

Finally, the effect of Si:Al ratio and copper concentration on the reducibility and coordination state of the copper ions in Cu-ZSM-5 is discussed.

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Mesoporous Alumina Obtained in the Presence of Different Surfactants

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The organized mesoporous alumina has many environmental applications as catalysts support, adsorption or separation material. This type of applications requires materials with well-controlled textural properties [1,2]. Our work has been focus on the obtaining of mesoporous alumina with large surface area and narrow pores size distribution by sol-gel method in the presence of different surfactants. We have studied the synthesis conditions for mesoporous alumina formation from aluminum isopropoxide in the presence of anionic (lauric and stearic acids) or cationic surfactants (cetyltrimethylammonium bromide, CTAB), respectively. To establish the thermal treatment conditions, alumina precursors were investigated by thermal analysis (DSC-TG). The crystalline phase evolution was studied by X-ray diffraction (XRD). Alumina samples were further investigated by FTIR spectroscopy, adsorption-desorption isotherms and transmission electron microscopy (TEM).

The alumina precursors were calcined at different temperatures and durations to obtain mesoporous γ-alumina. The XRD data show that the alumina samples obtained at 500 °C or 550 °C in the presence of carboxylic acid have amorphous walls, whereas the samples prepared at 500 °C, in the presence of CTAB, in alkaline medium are crystalline with γ-alumina structure.

It is observed that a high concentration of carboxylic acid determines a decrease of the specific surface area values. We have prepared mesoporous γ-alumina with specific surface area values in the range of 200 - 450 m^2/g and the best results have been obtained when stearic acid has been used as template agent.

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Effect of Nickel Particle Size on the Catalytic Performance of Ni/SiO_2

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The particle size effect in catalysis is a well-known phenomenon [1]. However, due to the difficulties in the preparation of uniformly distributed metal particles, there are only few unambiguous data in this respect. Earlier we elaborated a method for preparation of well-defined nickel nanoparticles on SiO_2 with a pre-set size [2]. In this communication we report on the effect of nickel particle size on the catalytic performance of Ni/SiO_2 in the decomposition of methanol. This reaction proceeds in two stages: (i) methanol decomposition to CO and H_2 and (ii) methanation of CO (above 500 K).

The catalysts were synthesized by successive adsorption-reduction as reported earlier [2] and after each reduction nickel was passivated. The metal surface area and the particle size were measured by hydrogen adsorption and the data were confirmed by TEM and XRD measurements. The main results obtained are summarized in Table 1.

Table 1. Main results of the characterization of the Ni/SiO_2 samples

sample	Ni concentration [a], %	Metal surface area [b], $m^2 g^{-1}$	Mean particle size [b], nm	TOF, h^{-1} conversion [c]	TOF, h^{-1} methanation[d]
Ni/SiO_2-1	3.63	147.2	4.6 nm	6.26	0.96
Ni/SiO_2-3	7.61	123.6	5.5 nm	4.52	0.80
Ni/SiO_2-5	12.62	90.2	7.5 nm	3.22	0.95

[a] *Data from AAA analysis;*
[b] *Data from hydrogen adsorption;*
[c] *CH_3OH conversion to CO and H_2 at 476 K;*
[d] *Selectivity to CH_4 at 520 K.*

Conclusions: Methanol decomposition on Ni/SiO_2 catalysts is characterized by structure sensitivity, while CO methanation is not structure sensitive reaction.

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Degradation of 2,4-dichloridephenol from Wastewater on SnO_2 – Montmorillonite Nanocomposites

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Recently, attention has been given to the use clays, microporous and mesoporous materials with special properties and features in environmental photocatalysis. Successfully used in the degradation and mineralization of many organic pollutants, heterogeneous photocatalysis, is based on irradiation of a catalyst, usually a semiconductor, which through photoexcitation, leads to the formation of electron donor sites (reducing sites) and some electron acceptor places (oxidizing sites).

It is known that tin dioxide is a versatile material, applicable in many physico-chemical processes, being one of the most intensively studied semiconductors.

In this study the SnO_2 – clay nanocomposites having photocatalytic activity in terms of mineralization of 2,4-phenol dichloride from wastewater were analysed. These studies have followed a performance evaluation of catalysts synthesized in the mineralization of 2,4-phenol dichloride, which is why the initial parameters: concentration of 2,4-dichloridephenol, and hydrogen peroxide, as well as the solution pH, temperature were kept constant.

In figure 1 a comparative study of evolution of degree of mineralization in time on synthesized catalysts, is presented.

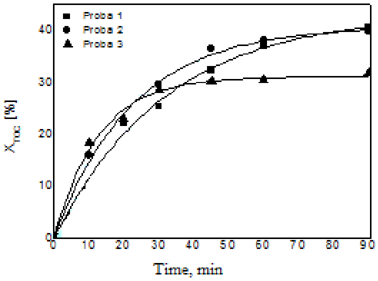

Fig. 1. Time dependence of the degree of mineralization of 2,4- phenol dichloride: duration of balance determining - 30 min, 10 mM H_2O_2

Although at certain moments/phases of the process, the degree of mineralization achieved in the presence of these catalysts has been higher at 90 min., it is noticed that its values were very close. In case of sample 1, whose concentration of SnO_2 is greater efficiency was significantly higher than other catalysts, the degree of mineralization being 40.63%, at 90 min.

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Solid Acid Catalysts for Dehydration of Glycerol to Acrolein in Gas Phase

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The biodiesel production is accompanying with one problem - increase the production of glycerol as a by-product. Therefore the increase of biodiesel production results in the accumulation of glycerol, which leads to a price decline. Unfortunately, the current application of glycerol is mainly confined to pharmaceuticals and cosmetics and hence the demand is somewhat limited. The availability of large amounts of cheap glycerol is the driving force to develop new processes for its energetic or chemical utilization. Finding value-added alternatives to glycerol incineration would improve economic viability of biodiesel manufacture and the biofuel supply chain. One possibility is to perform an acid-induced dehydration of glycerol to acrolein.

Catalytic conversion of glycerol to acrolein by a double-dehydration reaction could be an important route for using glycerol resources and could offer a sustainable alternative to the present acrolein technology based on propylene. Increasing attention has consequently been paid to the selective dehydration of glycerol to produce acrolein using solid acid catalysts. The as-synthesized alumina and W- modified SBA-15 supported heteropolyacid catalysts using $H_3PW_{12}O_{40}.xH_2O$ and $(NH_4)_6H_2W_{12}O_{40}.xH_2O$ as precursors compounds were characterized by nitrogen adsorption, XRD, TG/DTA, Raman spectroscopy, UV-Vis DRS and TPD of NH_3.

In particular, the influence of selected support materials, catalyst loading, nature of precursor compounds and temperature on acrolein formation was studied at standard reaction conditions.

Mechanochemical Synthesis of Nanosized Fe_2O_3-TiO_2 Mixed Oxides

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Fe_2O_3-TiO_2 nanosized mixed oxides with Fe_2O_3/TiO_2 ratio of 1:1 and 3:1 were synthesized using mechanical activation of hematite and rutile in high-energy ball mill in argon atmosphere and varying the milling procedure. Similarly, mechanochemically activated pure hematite and rutile materials were also prepared as references. The obtained materials were characterized by low temperature nitrogen physisorption, powder X-ray diffraction, infrared and diffuse-reflectance spectroscopies and TPR with hydrogen. Methanol decomposition was used as a test reaction for the catalytic activity.

The reflection lines in the XRD patterns of all activated samples were broad and of low intensity indicating the presence of nanocrystalline particles with average size of 30-50 nm. The prolonging of the milling time at low milling intensity facilitates the formation of materials with fine particles and high specific surface area. The infrared spectra of the obtained bi-component materials represented the typical absorption bands of pure α-Fe_2O_3 only in the case of the sample with Fe_2O_3/TiO_2 ratio=3:1. The decrease in intensity of these bands for the other samples is an evidence for increased interaction between TiO_2 and hematite nanoparticles. The UV-vis spectra of all bi-component samples were superposition of characteristic bands of rutile and hematite spectra. The presence of isopropyl alcohol during the mechanochemical activation strongly affects the position of the absorption bands near 350 nm, which is assigned to $^6A_1 \rightarrow {}^4E(^4D)$ ligand field transitions of Fe^{3+} ions. The shift of the band to higher wavelength is an indication for the changes in their environment probably due to the formation of a new bi-component oxide phase. This suggestion is also confirmed by the TPR results.

Methanol decomposition is observed above 525-550 K, CO, methane and dimethyl ether being the main registered carbon-containing products. The highest conversion combined with high selectivity to CO (above 85 %) was registered for the bi-component sample, prepared by mechanochemical activation in isopropanol.

The physicochemical and catalytic results reveal a facilitated effect of the wet milling with isopropanol for mechanochemical preparation of Fe_2O_3-TiO_2 mixed oxides.

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Synthesis of $Zn_3(VO_4)_2$ – a Comparative Study

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Different synthesis methods were applied in order to prepare $Zn_3(VO_4)_2$ compound: melt quenching technique, conventional solid state synthesis and mechanochemically assisted solid synthesis. The phase and structural transformations were monitored by X-ray diffraction (XRD). The formation of $Zn_3(VO_4)_2$ was also confirmed by infrared spectroscopy (IR). Applying melt quenching method two different techniques were used: i) pouring the melt and press between two copper plates (cooling rate 10^2 K/s) and ii) roller technique (cooling rate 10^4–10^5 K/s). In both cases several phases ($Zn_4V_2O_9$, $Zn_2V_2O_7$, ZnO, V_2O_5, $Zn_3(VO_4)_2$) were detected on x-ray diffractograms. XRD patterns of mechanochemically activated precursors for different time (from 0,5 to 4 hours) shown presence of amorphous phase together with diffraction peaks of $Zn_4V_2O_9$ as dominated phase and Zn_2VO_4. Pure $Zn_3(VO_4)_2$ was prepared after heat treatment at 700 ^oC of mechanochemically activated sample. Using conventional solid state reaction $Zn_3(VO_4)_2$ was obtained as main crystalline phase. ZnO (3.5 wt.%) is also detected on diffractogram. It was established that mechanochemically assisted solid synthesis is more appropriated method for synthesis of $Zn_3(VO_4)_2$. The photocatalytic measurements were carried out on the $Zn_3(VO_4)_2$ powders obtained by both methods. Photocatalytic activity was evaluated by degradation of a model aqueous solution of Malachite Green (MG) upon UV-light irradiation.

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Complete Oxidation of n-Hexane and Toluene on Perovskite-type Catalysts

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A series of perovskite-type catalysts ($LaFeO_3$, $LaCoO_3$, $YFeO_3$ and $YCoO_3$, supported on α-Al_2O_3 spherical particles) were synthesized via sucrose assisted solution combustion method. A catalytic activity with respect to the complete oxidation of hydrocarbons (n-hexane and toluene) was studied. The phase formation stages as well as the surface morphology and catalyst evolution were studied before and after the reaction using different instrumental methods as XRD and XPS. In order to establish the reaction mechanism, an additional experiments on so-called “depletive” oxidation were performed. Based on the experimental results the mechanisms of Elley – Rideal and Mars – van Krevelen were considered as non probable. Power law kinetic and four mechanistic models (Langmuir – Hinshelwood, bimolecular reaction, surface reaction being the rate-determining step) were fitted with the experimental data by applying of an integrated computer program for simultaneous solving the material balance in an isothermal PFR (plug flow reactor) and numerical nonlinear optimization procedure, based on iterative reducing the gradients. Aliphatic hydrocarbon (n-hexane) was found to be difficult to oxidize, while with aromatic compound (toluene) a promising activity was observed with $LaFeO_3$ sample, while the lowest activity being observed with $YFeO_3$. This fact is associated with the lowest crystallite size of $LaFeO_3$ catalyst assuming highest surface area of the active phase. It was concluded that the reaction proceeds via LH – mechanism with dissociative adsorption of oxygen.

Synthesis and Characterization of Magnetic Nano-sized Fe_3O_4 and $CoFe_2O_4$

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Nano-sized materials made of magnetite (Fe_3O_4) and cobalt ferrite ($CoFe_2O_4$) are attractive both from fundamental point of view and for various physical, chemical and biological applications. The synthesis of Fe_3O_4 and $CoFe_2O_4$ nanomaterials was performed by co-precipitation of corresponding metal hydroxides and their further decomposition to oxides under ultrasonic irradiation. Mean crystallite size was determined from the line broadening of the X-Ray diffraction peaks. The crystallite sizes were about 6-7nm for the Fe_3O_4 sample and from 1.9 to 20 nm for the $CoFe_2O_4$ depending on synthesis conditions. Specific surface area of Fe_3O_4 material of 180 m^2/g was calculated from the results of low temperature adsorption of nitrogen. Mössbauer spectra of Fe_3O_4 and $CoFe_2O_4$ with different crystallite size were measured at room temperature and 77 K. They revealed that samples with crystallite size of 7 nm (Fe_3O_4) and of 1.9 nm, 3.4 nm and 19.7 nm ($CoFe_2O_4$) show superparamagnetic behavior. The Mössbauer spectrum of 19.7 nm $CoFe_2O_4$ also reveals that this nano-material is an inverse spinel with Fe^{3+} ions distributed over the tetrahedral and octahedral cation positions in the spinel structure. The particles were also characterized by high resolution transmission electron microscopy (HRTEM) and vibration scanning magnetometer (VSM) that complements the X-ray and Mössbauer means of characterization.

We are going to use these types of nano-materials for biomedical [1, 2] and sensory [3] applications. The specific absorption rate (SAR) is an important property for hyperthermia. This value was determined for Fe_3O_4. For sensory applications, the magnetite-particles were embedded into a hydrogel and tested as an element in a new type of magnetic based swelling sensor.

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Catalytic reduction of NO with CO on Ce-Added Alumina Supported Cu-Co Catalysts

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NO_x removal from exhaust gases still remains one of major challenges in the area of environmental catalysis. The most common approach is the reaction with residual reductants (unburned or partially burned hydrocarbons and CO) in the exhaust. Various catalysts have been extensively studied containing noble metals, ion-exchanged zeolites, and metal oxides. The metal-supported alumina catalysts have received one of the most attentions due to its high activity and stability. The mixing of two different oxides offers an opportunity not only to improve the performance of the involved metal oxide, but also to form new stable compounds that may lead to totally different physicochemical properties and catalytic behavior from the individual components. Doping of ceria by divalent or trivalent ions can increase the concentration of oxygen vacancies or improve its thermal stability

In the present work we investigate the effect of cerium addition to alumina supported copper, cobalt and copper-cobalt oxides with low loadings on the catalysts efficiency in NO reduction with CO. We suggest that the combination of the supported metal oxides will lead to formation of active phases with physicochemical properties suitable for the studied reaction. The attention is also focused to varying the impregnation procedure in the ternary supported catalysts in order to determine the best catalyst as well as the reasons for the enhanced catalytic activity.

Ternary Co-Cu-Ce and binary Co-Ce, Cu-Ce and Cu-Co supported alumina were prepared and characterized by ICP, XRD, adsorption studies, XPS, H_2-TPR and catalytic investigations.

The ceria promoted alumina supported copper and cobalt catalysts with metal loadings up to 4 wt. % total metal are effective in reduction of NO with CO. The ternary supported samples are more active than the binary ones, where the catalyst prepared by simultaneous impregnation with the three active metals is the most active in the temperature range. The addition of cerium in the binary systems affects the activity at temperatures over $130^{o}C$, whereas the activity of the ternary supported catalysts is enhanced even at room temperature. The higher activity of the ternary and the binary catalysts is determined by the favorable influence of the added cerium on the dispersion of the copper and cobalt active phases. The presence of ceria contributes the formation of appropriate active phases, resulting in catalytic sites on the surface of the samples that promote the reduction of NO with CO.

Modification of Bulgarian Natural Zeolite (clinoptilolite) and it use as Catalyst in Some Environmental Protection Reaction.

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Ozone is used as an oxidant for waste water treatment and drinking water sterilization The exhaust gases contain residual ozone, which is above the acceptable value, and an additional air pollution problem must be solved. The most effective method for nullification of ozone is via heterogeneous catalytic decomposition [1]. The Bulgarian clinoptilolite is a natural zeolite with HEU–type framework. As a member of the zeolite class, clinoptilolite can be used as catalyst support, adsorbent and ion-exchange medium [2]. Ion-exchanging process of natural zeolite clinoptilolite (CL) with Zn, Mn, Cu and Ag ions was made; the existence of mentioned transition metals in the samples (Zn-CL), (Mn-CL), (Cu-CL) and (Ag-CL) was detected by D.C. arc-AES. XRD patterns show that after exchanging the HEU zeolite structure is kept (Figure1). These samples were tested as catalysts for ozone decomposition at ambient temperature. Zn-CL was not active, Cu-CL shows about 15 % and Mn-CL about 32 % conversion at the beginning of ozonation. Deactivation of these investigated samples was observed. Very high catalytic activity Ag-Clinoptilolite showed - up to 89%.(Figure 2)

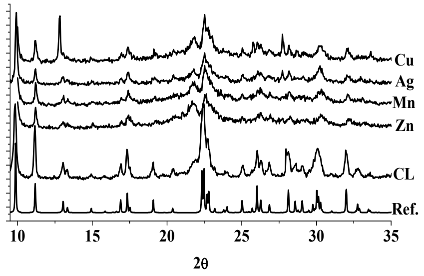

Fig. 1. XRD of samples and reference diffraction (Ref.) generated from http://www.iza-structure.org/databases/

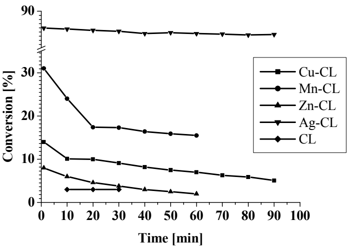

Fig. 2. O_3 conversion over natural (CL) and different ion- exchanged media.

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The Valorification of Waste Red Mud of the Alumina Industry

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Red mud disposal is responsible for a large part of the cost of alumina production.

Valorification of the waste red mud of the alumina industry is an imperative to increase the sustainability of the process, by reducing both the environmental impact and the economic cost, with a more responsible use of natural resources. High content of valuable elements, specific morphostructural characteristics and the imperativeness to solve the environmental problems coming from the high alkalinity.

In order to evaluate the neutralization capacity and the alkalinity reduction, red mud samples, having pH 12,3- 12,8, from different heaps, were processed by a systematic thermal and chemical treatments (oven air stream calcinations in controlled temperature mode at 105°C, 400°C, 600°C, 800°C) and by a chemical treatment with HCl, CH_3COOH, CO_2 gaseous.

Neutralization tests have been done at 250° C, for 4 hours). The chemical characterization (pH, atomic absorption spectroscopy - AAS), thermal characterization (TG, DTA and DSC) and morphostructural characterization (XRD, FTIR, SEM and BET) of the initial and treated red mud samples proved phase composition and textural modifications

Generated during the Bayer process, it is characterized by strong alkalinity and high ion exchange capacity.The phase composition denote of mixed metallic oxides of ; Fe: 30-40%, Al: 10-18%, Si: 5-9%, Ti: 4-8%, Ca: 4-7%, Na: 3-6%, K: 0.5-1% , Mg: 0.5-1%.

The work contains the results of a study about the thermal and chemical stability of the red mud, resulted from the Romanian aluminum industry

Conclusions

Preliminary research has enabled the identification of possible solutions to neutralize the mud with CO_2, and it can be an effective option for sequestration of CO_2.

The action of HCl on the structure of the material is more pronounced than that of all the CO_2. The neutralized waste composition and texture characteristics are of interest for applications in catalysis alone or after addition of different active metals.

Kinetics of Crude oil and Oil Products Adsorption Using Carbonized Rice Husks

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Composite materials, having different C/SiO_2 ratio, have been obtained by pyrolysis of rice husks, carried out at different temperatures within the 250-700^{0}C temperature interval. The phase composition of the initial raw material and that of the samples, prepared from it, has been determined by complex thermal analysis, XRD and FTIR spectroscopy. The morphology of the surface of the samples has been studied using SEM in combination with elemental analysis of the surface. The materials have been characterized also with respect to the specific surface area (B.E.T. method), apparent density, sieve fraction composition and oil sorption capacity. The influence of the apparent density of the sorbent has been investigated as well as that of the density of the oil product on the kinetics of sorption by the sample, showing the highest oil sorption capacity (9 g.g^{-1}).

It was established, on the basis of the kinetic dependence of the amount of sorbed substance on the time that the adsorption of different oil products is occurring in two steps. The various values of the tangents of the slope angles for each linear section give evidence for changes in the rate of sorption on the separate steps of the process. The first step is characterized by a high adsorption rate, whereupon it depends on the density of the oil product and on the apparent density of the adsorbent. The second step is connected with reaching adsorption equilibrium and it is occurring at a lower rate not depending on the above mentioned two parameters.

In order to evaluate the kinetics of adsorption and its equilibrium nature various kinetic models have been applied. The values of the correlation coefficient showed that the kinetics of adsorption of the different oil products is best described by means of the exponential dependence of Elovitch. The sieve fraction of size below 0.4 mm is characterized by the highest adsorption rate. The data for the equilibrium adsorption on the various fractions are best described by Redlich-Peterson's isotherm, while the diffusion of the adsorbate between the particles of the adsorbent obeys the law of Gjuren.

Influence of the Hybrid Materials used for Immobilization of Fungal Cells for Lactic Acid Production

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The sol-gel materials belong the hybrid materials containing organic and inorganic components and possessing nanoscaled structure, multifunctional properties and possibilities for application in optics, electronics, medicine, pharmacology and biotechnology. [1]. In recent years the interest towards the microbial production of lactic acid is constantly increasing due to its broad application [2]. New biotechnological approaches are being sought to intensify the lactic acid production, one of them being the use of immobilized cells.

In this work the research results on the sol-gel synthesis and structure of silica nanocomposites, containing carrageenan and their application as carriers for cell immobilization were described. The samples were prepared at room temperature by replacing quantity of the inorganic precursor with κ-carrageenan and HEMA. For studying the structure of the synthesized hybrids the following methods were used: FT-IR, XRD, BET-Analysis, EDS, SEM, AFM and roughness analysis.

The obtained materials were applied for immobilization of spores of the model strain *R. oryzae,* performing fermentation of glucose aerobically to obtained lactic acid and tested at repeated batch and fed batch experiments. The production of lactic acid was estimated for both matrices with immobilized spores.

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Impact of Rhenium Phytomining on the Soils of Ore Dressing Regions

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Current technologies for producing the rhenium containing concentrates and for extraction of rhenium from them are not effective enough. At these processes, part of the rhenium is lost and dispersed in the surrounding soils as volatile Re_2O_7 and as ReO_4^- in the waste industrial solutions and waters. The unique property of rhenium to accumulate in the green over ground parts of vegetation could be use for collection of scattered in the environment rhenium and for its phytomining [1]. The best plant hyperaccumulators of Re discovered by us at laboratory conditions are alfalfa (*Medicago*) – 4.66 % Re and white clover (*Trifolium repens)* – 3.51 % Re in the dry mass [1].

The present work shows the application of alfalfa (*Medicago*) for collection of scattered rhenium in soil near the depot of Cu concentrate of mine Asarel. Experiments were carried out as follows: a) Determination of Re in an aqueous extract of the soil using direct catalytic DMDTO method. The results of the analysis showed that C_{Re}= 5µg Re/ g dry soil, pH=8-9**;** b) Planting the soil with alfalfa at laboratory conditions; c) Determination of accumulated Re in alfalfa in different periods.

The results of experiments showed that after 10 days the Re concentration in alfalfa was 2780 g Re/t ash while after 35 days reached the maximum value of 4870 g Re/t ash. In this case the concentration of Re in alfalfa is 974 times more than in soil. We can conclude that:

1. The alfalfa is suitable for real collection of scattered rhenium from ore dressing soils.
2. One simple calculation shows that 1 t ash from alfalfa could be obtained from 2937 m2 alfalfa crop. At concentration of Re=4870 g Re/t ash and current price of Re= 4 500$/kg the profit for producers will be 21 915 $.
3. Cultivation of alfalfa on the exhausted mine soils leads to their remediation. For example, 1000 m2 soil enriched with 7 kg P2O5, 12 kg Ca, 20 kg N and 9 kg K2O after plugging of 3 years old alfalfa crop. That is more than average norm for fertilization of agriculture soils [1].
4. Application of Re phytomining in ore dressing regions remediate and purify the environment of this districts.

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Cleaning Properties of Ionic Liquids

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One of the interesting discoveries in the chemistry in the last decades are the ionic liquids (IL). They are salts, which are liquids at low temperatures (at room temperature and below), composed by ionic pairs – organic ions with positive and negative charges. These liquids reveal many useful properties. One of them is their cleaning capacity. Our preliminary observations have shown that in general, by rolling off on inclined solid surfaces, IL droplets collect inside all impurities along its road, leaving no microscopic visible traces behind itself. Taking into account that ILs are powerful solvents it can be supposed that the cleaning action will include removing of greasy spots. The poster includes experimental results of wetting dynamics of well defined (on the degree of hydrophobicity and profile) solid surfaces: rate of three phase contact line as a function of dynamic contact angles. There is a comparison with similar data of water (pure and surfactant solutions) droplets at the same conditions. Important cleaning characteristics is the stability of the flowing down (on the solid surface) liquid film. The poster shows data on kinetics of such thinning films (at the moment for soap IL films), as well as data of the so-called critical thickness of rupture of IL films.

Application of Mass Spectral Analysis to the Studying of Decomposition Mechanism of Some Oxalate Specimens

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During the last years the interest in the utilization of 3d-transition metal oxalates of the so-called “magnesium series” (Mg, Mn, Fe, Co, Ni, Zn) as precursors for nanosized oxide materials and metal powder has been growing considerably. In this application the good knowledge of the mechanism of oxalate decomposition is very important. A specific feature of these systems is the liberation of CO_2, as well as CO, which is capable of reducing the obtained oxide. This way the oxide with a lower oxidation state of M^{n+} could be formed and even a metal phase could appear (at Ni, Co, Cu oxalates). The Evolved gas analysis with following mass spectrometry (EGA-MS) of the liberated H_2O, CO and CO_2 is very appropriate for tracing the oxalate decomposition mechanism. The proceeding of the examination in vacuum eliminates the possibility for any secondary oxidizing processes occurring in air medium and thus disguising the true mechanism.

The objects investigated are $CoC_2O_4.2H_2O$, $Ni_{0.34}Mn_{0.66}C_2O_4.2H_2O$ and $Ni_{0.11}Mn_{0.89}C_2O_4.2H_2O$. They were characterized by XRD and SEM analyses. The mass-spectral studies were carried out applying linear temperature program and this way the kinetic curve of the process was obtained.

For $Ni_{0.34}Mn_{0.66}C_2O_4.2H_2O$ and $Ni_{0.11}Mn_{0.89}C_2O_4.2H_2O$ system it was established that the Ni content influenced on the morphology of the sample, temperature of dehydration and decomposition, and on the amount of liberated CO. The decreasing in the CO amount upon increasing the Ni content suggests the reduction of Ni^{2+} in vacuum from liberated CO in accordance with Ellingham diagrams.

The EGA-MS examinations of $CoC_2O_4.2H_2O$ show that the dehydration process is uncompleted and overlaps with the oxalate decomposition. The dn/dT curves reveal almost equal amounts of CO and CO_2 released, but the CO-evolution proceeds somewhat faster than that of CO_2.

Combined Computational, Multiple-NMR and IR Study of New Phenylplatinum Complexes Containing Monodentate Silsesquioxane

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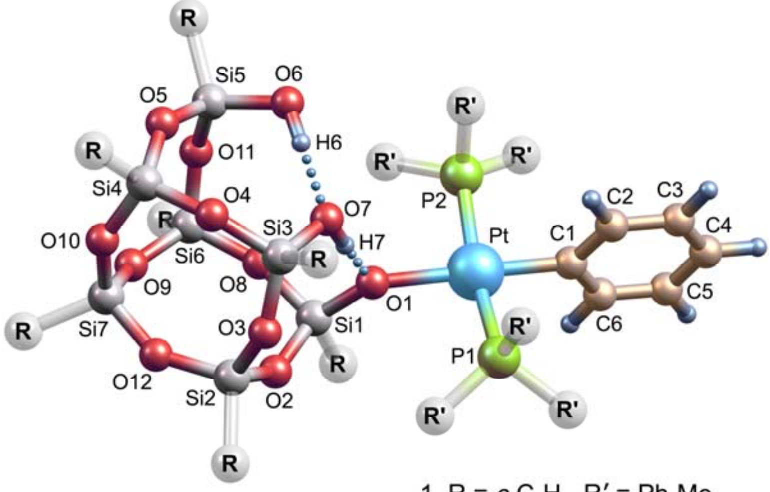
Silsesquioxanes are organosilanol compounds possessing –O–Si–O– bonds network and organic group attached to each Si atom. Incompletely condensed silsesquioxanes containing from one to four free silanol groups, Si–OH and their metal complexes are regarded as a molecular models of silica and metal silica supported catalysts.

The structure and spectroscopic properties of new synthesized platinum-silsesquioxane complex, *trans*-[Pt$\{O_{10}Si_7(cyclo\text{-}C_5H_9)_7(OH)_2\}(Ph)(PPh_2Me)_2$], 1 are characterized on the basis of computational, and multinuclear NMR (^{1}H, ^{13}C, ^{29}Si, ^{31}P) and IR data. Methodological DFT studies for reliable prediction of geometrical parameters, NMR chemical shifts and IR spectrum were performed for the complex *trans*-[Pt$\{O_{10}Si_7(cyclo\text{-}C_5H_9)_7(OH)_2\}(Ph)(PEt_3)_2$], reported in [1]. Density Functional Theory method at OPW91/6-31G(d) (6-31G(d,p)) level and small effective core potential (SDD) for Pt atom was found to be sufficient for obtaining accurate structural data, NMR and IR spectra in relatively reasonable CPU time. The theoretical approach could be further applied for better understanding of the structure and the properties of new platinum complexes of silsesquioxane.



1, R = c-C_5H_9, R′ = Ph_2Me
2, R = c-C_5H_9, R′ = Et_3

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XPS Characterization of Sn-Ni Layers Deposited on Quartz Plates

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Gas sensors play an important role in detecting, monitoring and controlling the presence of hazardous and poisonous gases in the atmosphere at very low concentrations. The present work is aimed at developing acoustic sensors for registration of NH_3 in the atmosphere. For that purpose, resonator structures are created by deposition of sorption Sn-Ni layers on quartz plates. The bimetallic layers are prepared by cathodic electro-deposition on quartz plates. After the electro deposition the coatings are treated at 200°C for one hour in air environment

The morphology and the chemical composition of the layers were studied by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). SEM micrographs of the coatings showed that they consist of a highly branching layer of bimetallic needles.

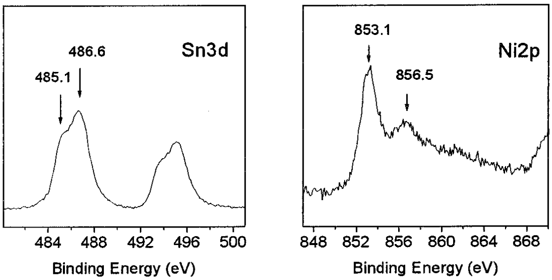

Fig. 1. XPS spectra of Sn3d and Ni2p of Sn-Ni layers on quartz plates

The surface composition of the Sn_xNi_y layer obtained from the XPS data is 12.9% Sn, 10.0% Ni and 77.1% O. The stoichiometry of the bimetallic layer is close to SnNi. The detected oxygen is due to formation of an oxide layer on the surface of the film, which is rather thin to screen the photoemission from the film under layers. Both photoelectron $Sn3d_{5/2}$ and $Ni2p_{3/2}$ peaks (Fig.1) are broad and contain two components. The low binding energy peak in both spectra is attributed to tin and nickel in SnNi alloy, while the peak with a higher binding energy is attributed to tin and nickel coordinated with oxygen atoms.

The gas sensing properties and selectivity of the bimetallic layers for registration of NH_3 will be further investigated.

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Adsorption Properties of Nanostructured Hybrid Materials Based on NHC=OO Functionalization Modified by Boron and Zirconium – a Comparative Study

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The adsorption properties of two new nanostructured hybrid materials containing B_2O_3 and ZrO_2 were studied and compared. The new organic-inorganic nanostructured materials were synthesized via a sol-gel method through hydrolysis and co-condensation reactions using trimethylsilyl isocyanate as a new silica source in the presence of tetramethoxysilane. As a modifying agent a quantity of 10 wt.% $Zr(OPr)_4$ or $B(OCH_3)_3$ was added. The structure of the hybrid materials was investigated by means of XRD and FTIR. Based on the data of the analyses pointed out the most probable cross-linking mechanism for the derived gels was proposed. The characterization of porous and texture parameters of both materials was carried out by low-temperature adsorption of nitrogen. The nitrogen adsorption isotherms were analyzed to evaluate the following parameters: the specific surface area, the total pore volume and average pore diameter.

Adsorption of Cu(II), Fe(III), Cr(III), Cd(II) and Pb(II) ions on both materials was investigated using multi-component solutions with different concentrations and acidity by means of the batch method. The adsorption was significantly affected by the pH value. Equilibrium modeling data were fitted to linear Langmuir, Freundlich and Dubinin-Radushkevich models and maximum adsorption capacities were calculated. In the present study, best fitting was observed by the Langmuir model, which showed correlation coefficients of greater than 0.95 for both systems studied. Thus we proved that Langmuir isotherm most adequately described the adsorption processes of the investigated ions. Kinetic of multi-component solutions at 0.5h, 1h, 5h and 24h was investigated. Pseudo-first order, pseudo-second order and intraparticle diffusion models were used to analyze kinetic data. The static capacities for multi-component solutions of the investigated ions were calculated. Both materials showed good adsorption properties towards Cu(II), Fe(III), Cr(III), Cd(II) and Pb(II) ions but the boron-containing material proved to be more suitable for their removal from aqueous solutions.

Removal of Mn(II), Fe(III) and Cr(III) from Aqueous Solutions Using Bulgarian Clinoptilolite

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Zeolites, which represent the largest group of microporous materials, are crystalline inorganic polymers based on a three-dimensional arrangement of SiO_2 and AlO_4 tetrahedra connected through their oxygen atoms to firm large negatively-charged lattices with Bronsted and Lewis acid sites. The use of zeolitic materials for the environmental protection is stimulated by good physico-chemical properties, e.g. selective sorption, by non-toxic nature, availability and low cost. A great deal of research on natural zeolites has been focused on the most commonly occurring types, especially clinoptilolite and mordenite. Natural zeolites are used in a wide range of environmental applications, including water purification, with the emphasis on the ammonia and heavy metal removal. Most technologies using natural zeolites for water and soil purification are based on the unique cation-exchange behaviour of zeolites through which dissolved cations are removed from water or soil by exchanging with cations on a zeolites exchange sites.

Adsorption of Mn(II), Fe(III) and Cr(III) from aqueous solutions onto natural and pretreated Bulgarian clinoptilolite from Beli plast deposit is studied. Batch adsorption studies are carried out to evaluate the effect of contact time, temperature, solution pH and initial concentration of investigated ions. The treatment with NaCl improves both the adsorption capacity and the removal efficiency of natural clinoptilolite. Comparison of the experimental data with Langmuir, Freundlich and Dubinin–Radushkevich isotherm models show the Freundlich model described the process more accurately. Pseudo-first-order, pseudo-second-order and intraparticle diffusion models are used to analyze the kinetic data. The values of adsorption standard free energy, enthalpy and entropy for Mn(II), Fe(III) and Cr(III on both adsorbents are determined. The removal of all investigated ions from multi-component aqueous solution is significantly affected by the presence of competing ions.

Based on the experimental results, it can be concluded that Mn(II), Fe(III) and Cr(III) ions can be effectively removed from aqueous solutions using natural and NaCl treated Bulgarian clinoptilolite. Hence, Bulgarian clinoptilolite may be used as a low cost source for the removal of Mn(II), Fe(III) and Cr(III) and it may be an alternative to more expensive materials.

Adsorption of Fe(III), Cr(III), Cd(II), Pb(II) and Cu(II) on a New Nanostructured Hybrid Material Containing Aluminium

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The adsorption properties of a novel nanostructured di-urethanesil hybrid material modified by aluminium towards Cu(II), Fe(III), Cr(III), Cd(II) and Pb(II) ions was studied. The material was prepared for the first time via new chemical precursor sol-gel method using tetraethylorthosilicate, trimethylsilyl isocyanate and aluminium sec-butoxide. From the XRD, SEM, FTIR, AFM and TEM results, the structure of the derived xerogel can be described as amorphous porous material built from Si-O-Al and Si-CH_3 repeated structural units covalently bonded onto the siloxane network by urethane (-NHC(=O)-) bridges to form a di-urethanesil backbone. The characterization of porous and texture parameters of the alumosilica oxycarbonitride material was carried out by low-temperature adsorption of nitrogen. The nitrogen adsorption isotherms were analyzed to evaluate the following parameters: specific surface area; total pore volume and average pore diameter.

Adsorption of Cu(II), Fe(III), Cr(III), Cd(II) and Pb(II) ions on this material was investigated using single- and multi-component aqueous solutions with different concentrations and acidity by means of the batch method. The adsorption was significantly affected by the pH value. Equilibrium modelling data were fitted to linear Langmuir, Freundlich and Dubinin-Radushkevich models. In the present study, best fitting was observed by the Langmuir model, which showed correlation coefficients of greater than 0.992 for all ions studied. Thus we proved that Langmuir isotherm most adequately described the adsorption processes of the investigated ions.

The removal of all investigated ions from multi-component aqueous solutions was significantly affected by the presence of competitive ions. For that reason the single-component adsorption for Pb, Cu and Cr was also studied. The maximum adsorption capacities for multi- and single-component adsorption were calculated. Highest adsorption capacity was achieved for Pb(II) ions. Therefore it is supposed, that the novel nanostructured hybrid material can be used for lead removal from aqueous solutions.

Modified Silica Gel with 5-Amino- 1, 3, 4 - Thiadiazole -2-Thiol for Heavy Metal Ions Removal

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Heavy metals presented in industrial wastewater, such as Cd(II), Pb(II), Cu(II), Co(II) ,Ni(II) and Hg(II) are hazardous to the aquatic ecosystem, which have posed possible human health risk. In recent years there is a trend to use surface modified inorganic supports.. In this way, new low-cost selective sorbents, which are effective catalysts and polymer fillers, have been obtained. Silica gels have a wide application as inorganic supports .The two sorbents was to synthesize for heavy metals removal: silica gel modified with 5-amino- 1, 3, 4 - thitadiazole 2-thiol (S5A) and pure silica gel. Modification of silica gel is achieved by tetraethyl orthosilicate (TEOS) preliminary hydrolyzed at room temperature. 5-amino-1, 3, 4- thiadiazole--2-thiol is added, with continuous stirring with a magnetic stirrer, to the hydrolyzed TEOS. Pure silica gel (sample SG) is obtained by the classical sol gel method using the same conditions and initial component ratios. The sorbents have been characterized as to their surface area, pore volumes, content of the functional groups, IR spectra, sulfur and nitrogen content. Their sorption properties to heavy (Cu (II), Co (II), Ni(II), Cd(II), Pb(II) and Hg(II) metals are investigated.. The investigations indicate that modified silica gel is characterized by a relatively higher sorption capacity than is the unmodified one. The highest sorption capacity belongs to Hg (II) in presence of unmodified silica gel due to which this sorbent can be used for selective extraction of mercury ions from aqueous solutions.

Spin Coated Copper Phthalocyanine Films for Room Temperature Odour Sensing Applications

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Hazardous effects of odour on environment and biological system makes it one of the important pollution issue. A number of techniques have been used for the detection of odour gases. In this direction, films of Copper Phthalocyanine (CuPc) (fig. 1) has been prepared by low cost spin coating technique under different experimental conditions on glass substrate and systematically studied for structural properties using FESEM, AFM and XRD techniques. Based upon these investigations, highly porous samples are selected for the detection of different primary amines. Various sensing parameters like sensitivity, selectivity, response and recovery times have been determined. Observations reveal that these gas sensors show an extreme high response to few parts per million level of primary amines with response time of 5 min. The interaction between sensor and analytes follows first order kinetics with rate constant $0.4 \leq k \leq 0.6$. This chemiresistive sensor shows very good stability at room temperature over a long period of time. The adsorption of analytes at film surface obeys the Elovich equation and a linear variation has been observed between analyte concentration and response rate.

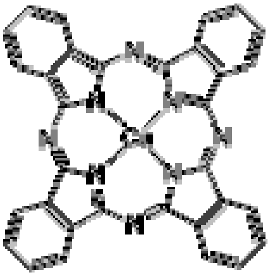

Fig.1. Molecular structure of CuPc molecule

Topic C.

Materials for Optics and Molecular Electronics

Nanostructured Optical and Ferroelectric Materials: Size-Dependent Changes of Physical and Chemical Properties

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Optical and ferroelectric materials are widely used in commercial products. Applications include computer memories, sensors, actuators, photorefractive devices, modulators, powder lasers etc. Since there is demand for the miniaturization of electronic and optical components, it is necessary to study size effects at the nanoscale.

It is well known that when dimensions of the crystallites approach the nanoscale their intrinsic properties change significantly. For instance, it has been shown that the ferroelectric properties disappear below a critical crystallite size [1,2]. The change in crystallite size may also lead to significant structural changes or even appearance of new phases not observed for the bulk material [2,3]. Furthermore, novel phenomena may arise from nanometer-size effects [1, 4].

I will discuss in this talk the size-dependent effects, which are most important for the application of optical and ferroelectric materials. I will also shortly discuss a few experimental methods, which probe these effects. The main focus will be on the application of spectroscopic techniques such as IR absorption, Raman scattering and luminescence. In the final part of the talk I will present a few examples of recent studies showing size-dependent effects in optical and ferroelectric materials such as perovskites, bismuth-layered compounds, yttria and tungstates.

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The Thermal Transformation from Lanthanum Hydroxide to Lanthanum Oxide

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Lanthanum hydroxide and lanthanum oxide are of great research interest because of their prospect as catalytic material and application in high-potential oxide ceramics [1]. The thermal transformation of $La(OH)_3$ was studied by high temperature XRD and thermal analysis (DTA/TG, DSC). A description of the experimental results is given by a two step reaction. Lanthanum hydroxide oxide is formed in a first step at ~330°C. It`s structure was characterized by X-ray powder diffraction and subsequent Rietveld refinement. LaOOH crystallizes in the monoclinic space group P21/m (no. 11) with the lattice parameters $a = 444.76(9)$ pm, $b = 397.10(7)$ pm, $c = 661.9(1)$ pm, and $\beta = 111.93(1)°$ [2]. In a second step lanthanum oxide is formed at ~500°C. The reaction enthalpies of the dehydration process were calculated by DSC to ~82 kJ mol^{-1} (transformation: $La(OH)_3$ to LaOOH) and to ~48 kJ mol^{-1} (transformation: LaOOH to La_2O_3) [3]. Kinetic analysis using multivariate non-linear regression gives insights into the mechanism of the dehydration reaction. A multi-step model provides an excellent description of the experimental TG results. The activation energies were calculated to $EA = 140.4 \pm 0.5$ kJ mol^{-1} (first reaction step) and $163.9 \pm 1{,}3$ kJ mol^{-1} (second reaction step). The corrosponding reaction orders indicate a complex mechanism for both reaction steps.

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Determination of Hard Alumina-Film Material Characteristics by Means of Nano-Indentation Measurements

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Four types of Al_2O_3 films were anodically formed on aluminium AD-3 in working electrolyte contained 180 g/l H_2SO_4. The electroformation of the two types of alumina films was realized at two different temperature of the electrolyte - at 0ºC (for “hard” anodization) and at 25ºC (for “normal” anodization). Part of the samples obtained in both temperatures was further treated in boiling water for one hour in order to seal the film pores.

The two mechanical characteristics of the films, the indentation (H_{IT}) and the indentation modulus (E_{IT}), were determined via nanoindentation tests. All measurements were done with G200 nanoindenter (Agilent Technologies) by diamond Berkovich tip. Time dependent effects were investigated by tests with different peak hold time and different loading rate. The change of the mechanical properties with indentation depth is also examined. The effect of the working temperature during the growth of the alumina layers and the influence of the pore sealing on the mechanical properties are evaluated via comparison of the average load-displacement curves. The role of the electrical regime (formation voltage and current density), the temperature of the electrolyte and sealing process) during the formation of the alumina films, with respect to possible changes of their chemical composition and structure, are discussed in order to explain the observed differences in the measured oad-displacement curves and the determined H_{IT} and E_{IT}.

Classification Order of Surface-Confined Intermixing. Nanoscale Pattern Formation on Stepped Crystal Surfaces

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The self-organization phenomena at epitaxial interface hold special attention in contemporary material science. Being relevant to the fundamental physical problem of competing, long-range and short-range atomic interactions in systems with reduced dimensionality, these phenomena have found exacting academic interest [1,2]. Besides this purely academic challenge, the motivation behind the present study relates also to the strong dependence of basic physical properties of electronic devices on the sharpness at atomic level of the interface between materials. On that physical background, the present report deals with two-dimensional (2D) surface alloy formation on stepped or vicinal crystal surfaces [3,4]. In specific temperature range, the high diffusion barrier for direct atomic exchange between adsorbed layer and substrate, completely block 2D intermixing on smooth, step-free surface domains. Hence, in a given energy gap the diffusion takes place exclusively via step terrace mechanism. In such systems, the dynamic competition between energy gained by mixing and substrate strain energy, results in diffusion scenario where adsorbed atoms form alloyed stripes in the vicinity of terrace edges. The stripe width, is step-anisotropy dependent and correlates with the relaxation ability of the terraces in specific direction. This phenomenon, considered as incomplete 2D alloying, opens a way various surface pattern to be configured at different atomic levels on the epitaxial interface. Refining important details of diffusion behavior of adsorbed atoms and accounting for the energy barriers at specific atomic sites (smooth domains, terraces, steps and kinks) located on the crystal surface, the presented model reveals a classification order of surface-confined intermixing: blocked, incomplete and complete [3].

Being in agreement with recent experimental findings, the observed stripe alloy formation can be applied to nanoscale surface design and preparation of regular interface patterns with exotic physical characteristics.

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Optical Properties and Crystallization of Glasses in the System MoO_3-Bi_2O_3-B_2O_3

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The bismuth-borate glasses have been widely studied over the years due to their high potential for use in applications such as nonlinear optical devices, laser hosts, tunable waveguides, tunable fiber gratings, etc. [1]. On the other hand, the presence of rare-earth ions can greatly improve the nonlinear optical properties of bismuth-borate glasses. This leads to increasing the melting temperature of compositions containing above 30 mol% rare earth oxides. In our previous studies we found that MoO_3 could be a suitable component to improve the melting conditions and modifying the properties of such type of glasses. But it was established that MoO_3 increases immiscibility tendency in the systems investigated [2, 3].

The purpose of this work is to study the optical properties of glasses in the ternary system B_2O_3-Bi_2O_3-MoO_3. The glasses were obtained by press quenching between two copper plates (cooling rate ~10^2 K/s). They were characterized by x-ray diffraction (XRD), differential thermal analysis (DTA), UV-VIS and scanning electron microscopy (SEM). According to the DTA data, the thermal stability drastically decreased in glasses with a high MoO_3 content. Most of the glasses were transparent in the visible region. It was established that the increase in the MoO_3 content led to decreasing the transmittance of glass compositions. Moreover, the absorption edge was shifts in the higher wavelength. The achieved results are directed for the preparation of novel low melting oxide glasses with possible applications in optics.

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5 Nm Structures in Fluorescent Photosensitive Glass-Ceramic Produced by Direct Laser Writing

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In this paper we present structural and optical properties of the fluorescent photosensitive glass-ceramics [1] doped with Sm. The properties were investigated by HRTEM and optical absorption spectroscopy. An application was dedicated to the recording of silver nanocrystal lines inside material by laser irradiation of a home built dynamic tester. 3D nanostructures produced by Direct Laser Writing could be useful for design and fabrication of 3D optical memory devices with an ultrahigh storage density [2-4], nanolithography, metamaterials, 3D photonic crystals in visible range, and plasmonic devices.. Using low power laser pulses and an adequate aperture of focusing lens, lines with 5 nm in diameter (Fig. 1) were written.

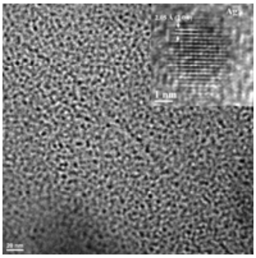

Fig. 1. HRTEM image of a silver nanocrystal line. Upper right insert presents the image of (2 0 0) lattice planes of a FCC silver nanocrystal.

A new fluorescent photosensitive glass-ceramic with Sm has been developed. Lines having an average width of 5 nm were produced, without annealing process, by a home built dynamic tester, using a low power laser. Measurements carried out by HRTEM sustain the presence of silver nanocrystal lines. 3D nanostructures realized in fluorescent photosensitive glass-ceramics, by Direct Laser Writing could be useful for design and fabrication of 3D optical memory devices with an ultrahigh storage density, nanolithography, metamaterials, 3D photonic crystals in visible spectral range, and plasmonic devices.

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Synthesis of Nanostructured Pure and Cr-doped NaAl$(WO_4)_2$

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An increasing interest in tunable and very short pulse solid-state lasers was observed during the last years due to their promising application in modern science and technology. This stimulated the studies on single crystal materials with a broadband emission in the near-infrared region. Cr-doped $NaAl(WO_4)_2$ is a potential laser active media because of high absorption, efficient pumping with the use of visible-range semiconductor diode lasers and broad laser emission. However, the production of single crystals as laser active media from this tungstate is related with a number of problems, first of all due to the low growth velocity and anisotropy. An effective approach to overcoming the crystal growth problems is to produce transparent ceramics, replacing the single crystals.

As a first step to this task nanostructured pure and Cr -doped $NaAl(WO_4)_2$ was synthesized by sol-gel (modified Pechini), solid state reaction as well as co-precipitation methods. The experiments show that sol-gel and solid state reaction methods are not suitable because of several secondary (mainly sodium tungstates) phases crystallize in parallel to $NaAl(WO_4)_2$. Co-precipitation method gives good possibilities pure nanosized $NaAl(WO_4)_2$ to be obtained. The dimensions, size distribution, morphology and reactivity of the particles were tested depending on conditions of powder preparation. It was established that the powder characteristic mainly depend on the thermal treatment conditions and Cr concentration. X-ray and TEM analyses show that the dimension of the particle could vary between 5 – 50 nm when different conditions for powder preparation are used.

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Preparation and Optical Properties of Zirconia Sol-Gel Materials

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The sol - gel technology is a low temperature method for preparation of different oxide materials like SiO_2, ZrO_2, Al_2O_3 or SnO_2 with interesting optical, electrical and mechanical properties from liquid precursors [1, 2]. In the present contribution the preparation and optical properties of sol-gel zirconia materials obtained via different schemes are described, which are potential candidates for doping with rare-earth complexes. The sol-gel materials are characterized with UV/Vis/NIR reflectance spectroscopy, SEM / TEM microscopy, IR and X-ray diffraction and molecular modeling with programs Gaussian09 and Turbomole. The use of chelating ligands like acetylacetone (AcAc) and acetic acid (AA) leads to transparent gels with high optical quality, materials prepared without modifying agents display a granule structure. Samples obtained with AcAc are yellow colored because of the formation of a complex between zirconium and AcAc with two characteristic peaks at 290 nm and 450 – 550 nm due to intra-ligand electronic transitions. The optical band gap of the prepared sol-gel glasses changes from 2.97 eV (AcAc addition) to 4.85 eV (preparation without chelating agents) depending on the doping conditions. Three potential Zr(IV)-AcAc complexes are modeled: $Zr(AcAc)_2(BuO)_2$, $Zr(AcAc)_2(OH)_2$ and $Zr(AcAc)_2(OH)_2 \cdot 2H_2O$ in order to understand their UV/Vis optical properties. The geometry optimizations and TDDFT calculations are performed at B3LYP/6-31++G(d) level and small effective core potential (SDD) for the Zr atom.

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Crystallization Kinetics of an Oxy-Fluoride Upconversion Glass Ceramic

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The rare earth doped oxy-fluoride glass ceramics showing anti-Stokes (upconversion) luminescence are of great interest due to the possible laser, amplifier, bio-pigments and IR imaging applications [1]. They combine the mechanical strength and chemical durability of the oxide glass matrix with the excellent luminescent properties of the rare earth doped fluoride crystals. If the crystals are with nano-scale dimensions the glass ceramics are transparent.

The aim of the present contribution is to study the kinetics of nano-crystallization in a boro-silicate glass containing PbF_2, CdF_2, YbF_3 and ErF_3. The x-ray diffraction (XRD) combined with a set of literature data revealed that a compound, $Pb_4Yb_3F_{17}$, crystallizes in glasses at temperatures 30K-80K above Tg. This phase is doped with a small amount of Er^{3+} ions and shows enhanced upconversion luminescence. A qualitative model is proposed to explain the formation of $Pb_4Yb_3F_{17}$ instead of a $Pb_xCd_{1-x}F_2$ solid solution, proposed by other authors.

The precipitation of the stoichiometric $Pb_4Yb_3F_{17}$ phase allowed us to use XRD (Scherrer's equation) to study the kinetics of isothermal crystal growth in glasses. During crystallization the Tg of the matrix glass increases with time, reaching the temperature of heat treatment while the mean size of the fluoride crystals reaches a constant value of 38 nm for prolonged heat treatment times. This crystallization behavior is consistent with the model of kinetically self-constrained crystal growth [2].

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Overcharging Process of Spherical Nanostructures

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Ionisable interfaces are present in many natural and industrial systems. In particular, numerous physical, chemical, and biological processes are governed by electrostatic interactions between charged colloids, surfactant monolayer, functionalized latex and oxide particles, polyelectrolyte, etc. In all these systems, the appearance of electrical forces is due to the surface charges developed on the interface by different charging mechanisms. Therefore, the presence of this surface charge implicates a distribution of ions around the charged surface, which is normally termed electric double layer (EDL).

The objective of our study is electrostatic properties of a model charged latex particle. In particular, we are interested to find the conditions needed to obtain the overcharging process for this modelled particle. The overcharging phenomenon or charge inversion occurs when the effective charge of a surface exposed to solution reverses polarity due to an excess of counter ions accumulated in the interface.

We have performed MD simulations with the GROMACS package. Different bulk conditions were obtained with different amounts of monovalent (Na+), divalent (Ca++) counterions. The Cl- ions were applied as co ions. The dependency of the colloids inverted charge on the concentration of the additional salt has been studied. The ionic strengths considered in our study were 1.0, 0.4 and 0.2 M.

MD simulations have been performed with GROMACS studying the density profiles and integrated charge distribution functions near nanoparticles bearing mobile unit charges at a variety of solution conditions. In particular, we analyzed the ability to generate particle charge inversion.

Influence of the Oligomer Chain-Length on the Optical Properties of Emeraldine Salt

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Conjugated organic polymers can be doped (via oxidation/reduction chemistry, or acid/base chemistry) to induce high electrical conductivity. After proton-acid doping polyaniline (PANI) increases remarkably its conductivity reaching values of the order of 10^2 S/cm [1]. This makes PANI particularly prospective for molecular-based electronics applications in electronic and opto-electronic devices. The conversion between the neutral semioxidized (emeraldine base) and the doped (emeraldine salt) form is a reversible and easily controllable process. Alongside with conductivity change, it is accompanied by notable variations of color and magnetic susceptibility. PANI allows a number of other applications and focuses incessantly the scientific interest. Major attention receive investigations searching for correlation between molecular geometry and electronic structure of the ground and excited states. However, the unambiguous interpretation of the emeraldine salt (ES) properties at the molecular level is still incomplete.

This study addresses the optical properties of model HCl-doped ES oligomers. The polaron and bipolaron configurations [2] at each chain length are considered. CC2/TZVP (Turbomole 6) and CIS/6-31G* (Gaussian 09) are employed. The choice of protocol is based on earlier findings [3], proving its potential for adequate description of the structure and electron distribution of ES. All calculations are carried out in implicit aqueous medium (COSMO/PCM). Parallel CC2/TZVP simulations in vacuum are performed in order to estimate the solvent effect on the electron spectra.

The results provide detailed information about the possible electron transitions in ES. The MO analysis affords description of the polaron/bipolaron states. The nature of the molecular orbitals involved in the electron transitions is discussed. The size dependence of the optical spectra is commented. The simulated spectra are compared to the available experimental data.

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Pyridine-Based Organic Radicals as Prospective Ligands in Hybrid-Spin Cu(II) Complexes

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A possible classification of the magnetic systems is: entirely inorganic, purely organic and organic-inorganic (hybrid-spin). The latter are the most promising candidates for novel magnetic materials, the organic component allowing fine tuning of the desired properties.

The present study is focused on investigation of different stable organic radicals, testing their suitability for ligands in Cu(II) hybrid-spin complexes. The radicals have as common feature a pyridine ring and they differ in the unpaired-electron-bearing substituents used and in the type and length of the π-conjugated system. Two of the positional isomers of the radicals are examined – meta- and para-substituted with respect to the N-atom of the pyridine ring. All stable conformers with respect to the dihedral angle between the radical moiety and the adjacent aromatic ring [1] are subject to full UB3LYP/6-31G* geometry optimization. The Mulliken atomic spin density distribution is assessed in order to monitor spin polarization and to quantify the atomic spin density at the N-atom of the pyridine ring – a key factor [2] for the efficiency of the exchange interaction with the copper ion: a high value being indication of a successful candidate. Several radicals are outlined as appropriate components of Cu(II) hybrid-spin complexes. Based on molecular orbital analysis, a prediction about the magnetic properties of model complexes is made derived from the pattern of coupling between the radicals and the metal ion. The sign and value of the energy difference between the high-spin and the low-spin states is used as measure of the type and amount of spin coupling in several designed complexes.

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Topic D.
Biology-Related Materials

Light Induced Reactions in Cryogenic Matrices

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The investigation of light induced reactions in cryogenic matrices is nowadays a hot topic in chemistry and physics. Interesting chemical systems with potential application as molecular optical devices have been described [1-3], and new materials, such as stable covalently bound noble gas containing molecules, have been produced and characterized [4,5]. In recent years, besides the more classic photochemical processes involving electronic excited states, studies have also included hot vibrational chemistry processes, in which vibrationally excited molecules in their ground electronic state undergo chemical transformations upon infrared excitation. Matrix-isolation spectroscopy has been the main technique used in these investigations, revealing itself to be specially powerful in the identification of reaction intermediates and establishment of reaction mechanisms. Interestingly, the success of this approach may also be ascribed to the concomitant development of computational chemistry, supported by an enormous quality jump regarding both hardware and software capabilities, which provided sound theoretical foundations for the interpretation of the experimental data, and the availability at relatively low cost of tunneable lasers that could be used as adequate irradiation sources to investigate specific processes in an elegant and powerful way.

In this lecture, both UV/visible induced photochemical processes and IR induced ground state hot vibrational chemistry will be considered. The described case studies will include photochemical reactions induced by UV/visible irradiation of matrix isolated organic compounds ranging from conformational isomerizations to complex bond-breaking/bondforming processes, a well as IR induced reactions and the intramolecular vibrational energy relaxation/redistribution processes involved in these reactions. Effects of the media on the chemical processes will also be addressed.

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Calcium Phosphate Biomaterials in Orthopaedic and Dental Applications

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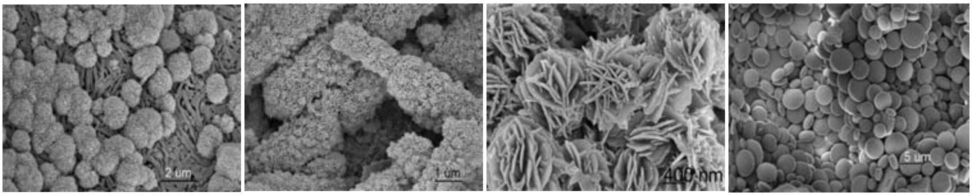
Given the bone tissue's superb ability to adapt its mass and morphology to *in vivo* functional requirements, its aptitude to repair itself without leaving a scar, its longevity, and its capacity to rapidly mobilize mineral supplies on metabolic demand, bone tissue is, in fact, the ultimate "smart" structural material present in biological systems.

Human bones (either *trabecular* or *cortical*) contain almost all the elements present in human blood plasma. Mineralized portions of bones can be oversimplified by the formula: $Ca_{10-x+\omega}Na_yK_z(PO_4)_{6-x}(HPO_4, CO_3)_x(OH)_{2-x+\omega}$. To start with a complex formula such as this, presents one of the many challenges facing the materials chemist synthesizing the bone mineral. However, acellular synthetic body fluids are shown to simulate the biomineralization and calcification processes. Over the last decade, biomimetic formation of nanocrystalline calcium phosphates has successfully been observed and investigated at numerous ceramic-metal, ceramic-polymer, and ceramic-ceramic interfaces in synthetic body fluid systems. Synthetic body fluids contain Posner's clusters. Understanding of biomineralization interactions with the organic matrix and the non-collagen bone proteins is also a principal aspect of biomimetic material synthesis. Understanding of the calcification processes taking place at the nano-scale will lead to important technological innovations and to the development of new biomedical devices with improved functionality.



Only the synthetic bone substitute materials of high BET surface areas, which closely mimic the Na- and K-doped, carbonated nature of human bones are found to readily take part in the bone remodeling processes. Non-cytotoxic calcium phosphate-based biomaterials do come in a variety of forms, such as, porous granules, porous prismatic blocks, bone mineral-coated metallic implants, polymer-blended bioceramics, self-setting injectable orthopedic cements, and nanowhiskers/single crystals. In order to preserve the above-mentioned delicate stoichiometry of the calcium phosphate-based human bone mineral in an ideal bone substitute, the development of novel, biomimetic synthesis techniques are still awaited. This presentation (with some picture highlights are shown above) will summarize our studies on the synthesis of porous CaP bioceramics and granules, CaP self-setting cements, biomimetic coatings on metals, ceramics and polymers, biomimetic powder synthesis procedures, synthesis of whiskers of calcium phosphates and the results of *in vitro* cell culture tests performed on such synthetic calcium phosphates, accompanied with IR spectroscopic and *X*-ray diffraction characterization studies.

Biomimetic Transformations of Calcium Phosphates - Thermodynamic and Kinetic Studies

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The biomimetic synthesis of XRD amorphous calcium phosphate (ACP) and dicalcium phosphate dihydrate (DCPD) and their further phase transformations into poorly crystalline apatite in three types Simulated Body Fluids (conventional (SBFc), revised (SBFr) and modified with glycine (SBFcg)) were studied by application of chemical, kinetic and spectral (XRD and IR) methods and thermodynamic simulations.

Several regularities were found:

- (i) Kinetic reasons determine the biomimetic precipitation of XRD amorphous calcium phosphate (ACP) and dicalcium phosphate dihydrate (DCPD) that are a less thermodynamic stable phases in comparison with calcium hydroxyapatite;
- (ii) The precipitated salts always contain impurities due to the parallel co-precipitation, ion substitution and maternal liquor incorporation. Their content depends on the nature and crystallinity of the precipitants;
- (iii) Both ACP and DCPD transform into poorly crystalline apatite in the studied SBFs microenvironments. An intermediate phase of octacalcium phosphate (OCP) was registered for DCPD only.
- (iv) The SBF composition influences the polymorphous phase transformation and its rate - HCO_3^- ions accelerate the transformation rates both of ACP and DCPD while the Glycine increases the transformation rate of ACP only.
- (v) The phase transformations of ACP and DCPD leaded to changes in the chemical compositions of solid and liquid phases. Thermodynamic simulations reveal that these phenomena could be explained by the processes of dissolution/crystallization/co-crystallization/ion-exchange.

These results elucidate some elementary processes of hard tissue mineralization and of the influence of micro-environmental surroundings on the transformation process.

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Molecular Design of Micelles for Drug Delivery Purposes

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The cell membrane is largely resistant to most of the present chemotherapeutics and to all alien proteins and DNA; therefore, the utilization of the endocytic pathway for intracellular transfer seems unfeasible. The design of reliable, effective and risk-free artificial systems for transport through the cell membrane will overlay the road to new pharmaceutical approaches for treatment of presently incurable diseases. Suitable candidates for such systems are micelles formed by ethers of oligo(ethyleneglycol)s and fatty alcohols (C_xEO_y) [1]. A change in the ratio of ethyleneglycol units and methylene groups modifies the hydrophilic-hydrophobic balance in the molecule and thereof the propensity to formation of supramolecular aggregates.

One of the purposes of the present study is to derive from first principles calculations and test molecular mechanics parameters for such ethers to be used in subsequent all-atom simulations of micelles formation. Monomers and dimers with two different types of periphery, which are short-chain prototypes of the amphiphilic surfactant $C_{12}(EO)_5$, were used as model systems. The geometry of low-energy conformers are obtained with modified OPLS and optimised with PBEPBE/aug-cc-pVTZ in vacuum and in implicit solvent. Convincing validation of the derived parameters provided the comparison between the density, molecular volume, enthalpy of solvation and vaporisation obtained from molecular dynamics (MD) simulations (Amber99/NPT/300 K) of diethyl ether and the existing experimental data.

On the other hand, the water solution of nonionic surfactants $C_{12}(EO)_5$ and their capacity to pack antimicrobial peptides (AMPs) and transport the latter across a bilayer are investigated on coarse-grained level with MARTINI coarse-grained (CG) force field [2]. The structural aspects of the amphiphilic organization in explicit aqueous medium is obtained from the simulation data for model micelles built of various number of $C_{12}(EO)_5$ molecules. Micelle shape, stability and water penetration into the hydrophobic core is acquired thereof. Examination of the results for the selected micelle permits the establishment of size-stability relationship. Finally, a small AMP is incorporated in one of the stable micelle and subject to CG MD simulation. Alongside with analysis of structural features, the stability of the formed $(C_{12}(EO)_5)_n$/peptide complex is evaluated by means of binding energy assessment.

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Development of Poly(*n*-butyl cyanoacrylate) Colloidal Nanospheres Loaded with Lipophilic Anticancer Drugs Intended for Targeted Drug Delivery

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The colloidal particles of poly(alkyl cyanoacrylate) are considered as one of the most perspective synthetic biomaterials for drug delivery applications, especially for improvement of cancer chemotherapy [1]. The classical method for their preparation is the emulsion polymerization in aqueous medium. Previously, we have used this method for the entrapment of the antibiotic ciprofloxacin [2] and the anticancer agent chlorambucil [3] in poly(*n*-butyl cyanoacrylate) nanospheres. Recently, we have demonstrated the successful utilization of the nanoprecipitation method for the entrapment of lipophilic drugs in poly(*n*-butyl cyanoacrylate) nanospheres [4].

Here, we report our recent results on the development of novel colloidal formulations of classical lipophilic anticancer drugs. The drugs are loaded into poly(*n*-butyl cyanoacrylate) colloidal nanospheres by the two methods – emulsion polymerization and nanoprecipitation. A presynthesized polymer is used in the nanoprecipitation approach, thus avoiding any chemical reactions during the entrapment of drugs in the colloidal nanospheres. Therefore, this method is preferred for the cases of chemically sensitive drugs, which are rather possible to be inactivated at the conditions of the classical emulsion polymerization. Drug-loaded colloidal nanospheres with various surface coatings are obtained and characterized for particle morphology, size distribution, ζ-potential, drug content and drug release kinetics in physiological phosphate-buffered saline. We suppose that the as-obtained drug-loaded colloidal nanospheres are suitable for future biomedical tests and evaluation of their potential application in targeted drug delivery.

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Derivation and Testing of Molecular Mechanics Model of Cy(EO)x Based on *ab initio* Estimates of the Structural and Electronic Characteristics

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The amphiphilic nature of surfactant molecules leads to their aggregation and selfassembly in a variety of micellar aggregates when exposed to solvent. These structures provide physical, chemical, and biological functions that make them well suited for various applications. In particular, their use for biomedical applications, such as drug delivery, has grown rapidly in recent years. Promising candidates for this aim are compounds with general formula ($C_y(EO)_x$) obtained by coupling of oligo(ethylene glycol) to fatty alcohols. Variation of the number of the ethylene glycol units and the methylene groups of the alcohol leads to different hydrophilic-hydrophobic balance of the molecule resulting in different aggregation propensity. On the other hand, there exist evidences that at very low concentrations the surfactant molecules preserve the selfassembly aptitude, especially in the subsurfacial layer [1]. These properties, together with the lipid compatibility of oligo(ethylene glycol) ethers, suggest that $C_y(EO)_x$ systems could be used as reversible micellar nanotransporters across biomembranes.

The present study includes the results of quantum-chemical calculations for the derivation and testing of molecular mechanical parameters for adequate simulation of amphiphilic alkanoid ethers to design materials of similar type. As short-chain prototypes of the soluble surfactant $C_{12}(EO)_5$ are used a monomer and a dimer of ethylene oxide (EO) with two different types of end-groups: CH_3- and OH-termini. The electrostatic potential of molecules is generated with SCF/HF/6-31G* on the optimized structures obtained from DFT calculation with PBEPBE/aug-cc-pVTZ in vacuum and in implicit solvent. The parameterization is tested by means of molecular dynamic simulations in the NPT ensemble of diethyl ether with Amber99 force field, implementing our parameters for the ether groups. Basic features of the system as molecular volume, density and characteristic thermodynamic quantities such as enthalpy of solvation and heat of vaporisation are calculated. The results are compared with experimental data for the model system, which enables the assessment of the relevance of the theoretical approach for reliable description of the behaviour of the target molecules in solution.

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Synthesis, Spectroscopic Investigation and Biological Activity of Encapsulated Metal(II/III) Complexes

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A new series of manganese(II), iron(III) and cobalt(III) Complexes of 14-membered macrocyclic ligand, (3.6.10.13,16,19-hexadentate bicycle(6.6.6)cosane) have been prepared and characterized by elemental analyses, IR, UV-VIS, ^{1}H- and ^{13}C- NMR spectra, X-ray single crystal (Cobalt(III) complex) magnetic susceptibilities, conductivities, and ESR measurements. Molar conductance measurements in DMF solution indicate that, the complexes are electrolytes. The crystal structure of cobalt(III) complex confirms that, the synthesis occurs with retention of the chirality of the $Co(en)_3^{3+}$ ion and show the hexadentate nature of the capsule with the tris-(methylene), second, each cobalt(III) atom is surrounded by six-nitrogen atoms belonging to the lattice to give octahedral geometry. The ESR spectra for cobalt (III) complex in CD_3OD+10%D_2O after exposure to ^{60}Co-γ-rays at 77 K using a 0.2217 M rad h^{-1} vicrad source shows $g_1 > g_{||} > g_e$, indicating that, the unpaired electron site is mainly present in the d_{z2} orbital with covalent bond character. However, in solid state after exposure to ^{60}Co-γ-rays at 77 K shows $g_{||} > g_1 > g_e$, indicating that, the unpaired electron site is mainly present in the d_{x2-y2} ground state. Manganese (II) complex shows six isotropic lines characteristic to an unpaired electron interacting with a nucleus of spin 5/2, however, iron(III) complex shows spectrum of a high spin ^{57}Fe (I = 1/2), d^5 configuration. On the basis of elemental analyses, IR, electronic and ESR spectral studies, an octahedral geometry has been assigned for the complexes. Cobalt (III) complex acts as a good electron capture reagent and has the ability to add to DNA molecules without any disruption of its native structure. It shows exploitation in reducing the amount of electron adducts formed in DNA during irradiation with low radiation products.

Role of Metal Complexes of 2-(benzothiazol-2-yl)-N\-(2,5-Dihydroxybenzylidene) Acetohydrazide as Antifungal

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The synthesis and characterization of Mn(II), Ni(II), Co(II), Cu(II) and Zn(II) of the 2-(benzothiazol-2-yl)-N\-(2,5-dihydroxybenzylidene)acetohydrazide are reported. Elemental analyses, IR spectroscopy, UV-Vis and magnetic susceptibility measurement, as well as, in the case of copper and manganese complexes, ESR spectroscopy have been used to characterize the complexes. Electronic and magnetic moments of the complexes indicate that, the geometries of the metal centers are either square planar or octahedral. The structures are consistent with the IR, UV-VIS, as well as conductivity and magnetic moments measurements. The fungicidal activities of the ligand and its complexes were investigated against Aspergillus nigar and Fusarium oxysporium. Complexes of cobalt (II) and copper (II) showed higher fungitoxic activity against Fusarium oxysporum than the ligand at all used concentrations. However, the manganese (II) complex shows a moderate toxic effect against Fusarium oxysporiurn in comparison to the ligand alone while the inhibitory effect of the complexes of nickel (II) and zinc (II) was not clearly manifested against this fungal strain. On the other hand, aqueous ions of the all tested metals showed a significant lower growth inhibition than that of the complexes being studied.

Synthesis and Characterization of Nano-Sized Ferrimagnetic Particles with Application in Medicine and Sensor Technology

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Oxide glasses with high concentrations of 3d-metals and based on them glass-ceramics containing ferrimagnetic nanocrystals are of both fundamental and practical interest due to their interesting electrical and magnetic properties. Depending on the phase composition, size and volume fraction of the formed particles, the precipitated crystals are applied as parts of ferrofluids in magnetic resonance imaging and in biomagnetic sensors for the detection of different chemical and biochemical substances.

In the present investigation, glasses from the system $Na_2O/MnO/SiO_2/Fe_2O_3$ are prepared using conventional glass-melting technique and after applying appropriate time-temperature programs, magnetic nanocrystalline phase is precipitated in them. The phase composition and microstructure of the formed glass-ceramics is studied by x-ray diffraction, scanning and transmission electron microscopy. Anomalous small-angle x-ray scattering experiments are used to gather information about the chemical composition and element distribution in the formed nanocrystals as well as to estimate their size-distribution.

FTIR Conformational Studies of Triclosan in an Argon Matrix

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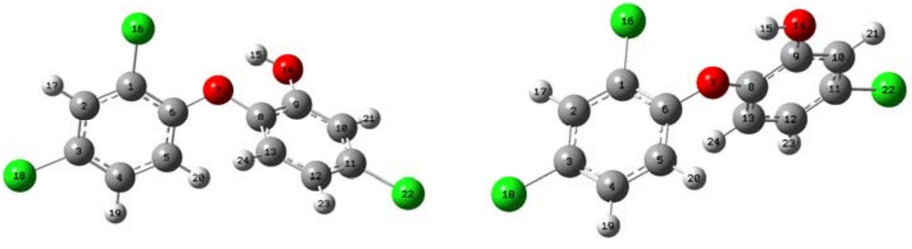
The preferred conformations of triclosan, a commonly used antibacterial and antifungal agent, and their vibrational spectra were studied by matrix-isolation Fourier transform infrared spectroscopy in argon matrix (T= 13 K), and interpreted on the basis of DFT(B3LYP)/ 6-311++G(d,p) calculations. The calculated ground-state potential energy surface of triclosan exhibits two low-energy minima (Figure 1), differing by orientation of the C1-C6-O7-C8 (β_1) and C6-O7-C8-C9 (β_2) dihedral angles. The most stable conformer I (β_1=160.3°, β_2=123.8º) was found to be lower in energy at 0 K, by *ca.* 1.4 kJ mol^{-1}, than conformer II (β_1=–93.1°, (β_2=177.7º). At room temperature, due to the higher entropy of conformer I, the order of conformational stability is reverse and is *ca.* 0.73 kJ mol^{-1} in favour of form II. Therefore, I and II are expected to constitute ca. 43% and 57% of the total population in gas phase, at room temperature. The barrier for conversion between forms I and II was calculated to be ca. 15 kJ mol^{-1}. The IR spectrum of the compound isolated in solid argon was obtained and interpreted. Preliminary photochemical experiments on the matrix-isolated triclosan were also undertaken. The compound was found to react upon UV irradiation (λ>200 nm) giving rise to a ketene, which is identifiable by observation of the ketene antisymmetric stretching characteristic intense IR band around 2140 cm^{-1}.



Conformer I (160.3º; 123.8º)

Conformer II (-93.1º; 177.7º)

Fig. 1. Calculated conformers of triclosan. Values in parenthesis are C1-C6-O7-C8 and C6-O7-C8-C9 dihedrals.

Novel B-Ring Modified Combretastatin A-4 Analogues: Synthesis and Cytotoxic Activity

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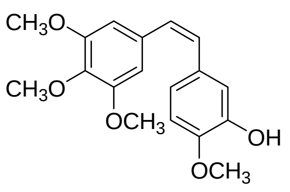
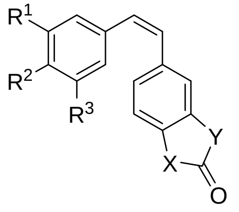
Combretastatins are a group of compounds with antimitotic activity isolated from the bark of the South African tree Combretum caffrum. The most promising of these natural products is combretastatin A-4 (CA-4). The CA-4 is a very attractive compound because of its simple structure and high cytotoxic activity against a variety of human cancer cell lines. The stilbene CA-4 is a potent anti-cancer drug and represents a new class of therapeutic compounds known as vascular disrupting agents.

We designed and synthesized 12 novel heterocyclic analogues of CA-4 containing benzothiazolone moiety, which could have important pharmacological properties. Compounds with general structure (**I**) were obtained in good yields and were evaluated for their cell growth inhibition activity on different human cell lines (HepG2, K562 and EA hy.926). The 3-methyl-6-(3,4,5-trimethoxystyryl)-2(3*H*)-benzothiazolone displayed potent cytotoxic activity against HepG2 cells with IC_{50} values in the nanomolar range. The ability of benzothiazolones to inhibit tubulin polymerization has been evaluated by fluorescent microscopy and flow-cytometry. The results showed that HepG2 were arrested at a pro-metaphase stage, with formation of condensed chromosomes and unnormal spindle formation. The arrest of cell cycle at G2/M phase also triggered the apoptotic cell death in HepG2 line. The heterocyclic analogues of CA-4 showed a potent antitumor activity and it is important because new anticancer therapeutics may emerge from these efforts.



CA-4



X = S, Y = NCH_3 *or* X = NCH_3, Y = S
$R^1 = R^2 = R^3$ = H, OCH_3

General structure I

Manufacturing and Bio-mineralization of Scaffold, Based on Polylactic Acid Fibrils

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Introduction: The main goal of this investigation is to offer a new technology for manufacturing of biodegradable scaffolds free from contacts with toxic solvents. For this purpose a modified concept for microfibrillar reinforced composites (MFC) was utilized. While tissue engineering has been proven in laboratories, the use of organic solvents in scaffolds fabrication precludes its implementation in a clinical setting. In the current investigation we have obtained polymeric fibrils as 3-dimentional (3D) scaffolds, using not toxic solvent.

Materials: PLA (Polylactic acid) supplied by Natureworks (Natur 2002B) and EVOH (Ethylene-co-vinyl alcohol), supplied by EVAL EUROPE (F101A). Not toxic solvent (mixture of propanol and water) was used.

Methods: The drawn PLA/EVOH (40/60 wt. %) blend bristles were manufactured according to the MFC concept on an industrially relevant production line [1]. A Soxhlet with temperature control was used for selective extraction of the EVOH fractions from the blend. For manufacturing of porous scaffolds from individual PLA fibrils a Freeze-dryer was used. The bio-mineralization of the samples was carried out at the Institute of general ond inorganic chemistry, BAS, Bulgaria. The microstructure, morphology and thermo-physical properties of the drawn bristles and of the scaffolds before as well as after biomineralizations were observed by WAXS, SEM and DSC.

Results: From WAXS and DSC investigations was found that after extraction the degree of cristallinity of the PLA fibrils increase as compared with this fraction in drown bristles. The SEM observations show 3D structure of the scaffolds. The diameter of the PLA fibrils are in the range of 150 nm to 1,5 μm, and the diameter of the scaffold pores vary between nano- and micro-scale. After bio-mineralization layers of Ca-Ph ions over the PLA fibrils were observed. This is maybe du to the nucleation ability of the fibrils.

Discussion and Conclusions: In this study, high porous 3D scaffolds from PLA microfibrils, using PLA/EVOH orientated blends, were successfully produced. In the best of our knowledge this study presents the first successful attempt for manufacturing scaffolds applying the MFC concept.

Acknowledgements: The authors gratefully acknowledge the financial support of the Bulgarian Ministry of Education and Science, Fund “Scientific Investigation” (Project DTK 02-70/09).

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Effects of the High –Energy Grinding of Bi-phase Calcium Phosphates on Their Cell Biocompatibility

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Synthetic bi-phase calcium phosphate ceramics are highly investigated in a view of materials for bone defect repairing. Thus the results of their cell biocompatibility are of a crucial importance. Studies are focused also on the elucidation of the relationships between bone-related cells (osteoblasts and osteoclasts) important for the formation of calcified tissues and nanosized calcium orthophosphates.

In the present study the effect of high-energy grinding of sintered bi-phased calcium phosphates consisting of HAP (hydroxyapatite) and β- TCP (tricalcium phosphate), on the phase modification and crystal size as well as on their biocompatibility was studied.

Chemical analysis, X-Ray, SEM and BET analysis were performed for product characterization.

It was found that the grinding (agate mill, 600 rpm, 20 hours) of sintered at 1100°C samples with about 70-80 nm crystal size of the particles leads to different decreasing of the crystal size of the both phases. The particles of the β-TCP phase were transformed into amorphous phase, while the crystal size of HAP was reduced from 2 to 3 times.

The specific area was increased about 10 times (from 2,5 to 28 m^2/g).

The biocompatibility of the samples was investigated using in-vitro test with SBF (simulated body fluid). and cell-culture test. No cytopathological changes were observed using double staining with acridin orange and propidium iodide.

The kinetic studies on maturation of the grinding and non-grinding samples in SBF reveal an increased ability for crystals growth of the grinding material in comparison with non–grinding material. This activity was bigger during the 1h and the equilibrium was reached for about 5- 7 days. No changes were found with the non-grinding materials.

The applied mechanochemical methods for phase and crystal size modification of bi- phased ceramics is an useful for preparation of materials prospective for biological application as the geometric characteristics of particles are important for contact osteointegration.

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Mg and Zn Modified Calcium Phosphate Ceramics

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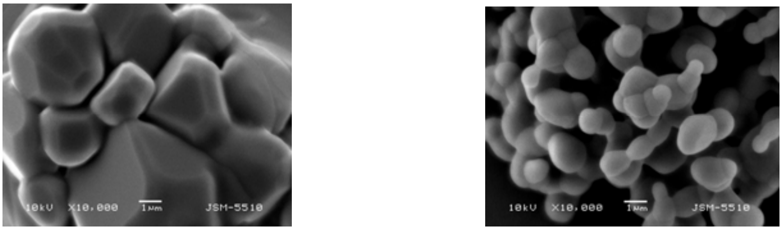
Ion modified calcium phosphate-based ceramics are designed to simulate the mineral composition of the hard bone tissues or to strengthen some specific biologically important behaviour. Thus the biological active Mg plays an important role in the formation and growth of the hard bone tissue and the Zn is extremely important mediator for more than 200 enzymes.

The present study aims to examine the effect of Mg^{2+} or Zn^{2+} ion substitutions on the phase composition of calcium phosphate ceramics, their morphologycal and structural changes. Chemical, XRD, FTIR and SEM methods have been applied for their characteristics.

Amorphous ion modified calcium phosphate precursors were precipitated in simulated body fluids modified by different amounts of Mg^{2+} or Zn^{2+} ions ($Me^{2+}/(Me^{2+}+Ca^{2+})$ was 0, 0.03, 0.07 and 0.13) at pH 8. Modified calcium phosphate ceramics with (Ca+Me)/P ratio of 1.3 - 1.4 were obtained after precursor lyophilization and sintering at 1000°C. Stabilization of β-tricalcium phosphate (β-TCP) structure occurs in the all cases of Zn^{2+} ions substitution for Ca^{2+} ions and formation of mono phased zinc-β-TCP ceramics with sizes (500–5000 nm) and idiomorphic crystals (Fig.1a) was registered. In the case of Mg^{2+} ions substitution for Ca^{2+} ions the concentration of Mg^{2+} ions is a crucial for the stabilization of β-tricalcium phosphate (β-TCP) structure. Mono phased magnesium-β-TCP ceramics with smaller size (100-500 nm) and spherical grains (Fig. 1b) were prepared when the $Mg^{2+}/(Mg^{2+}+Ca^{2+})$ ratio was 0.13. When this ratio was smaller (0.03 and 0.07) bi-phased ceramics consisting of magnesium-β-TCP and hydroxiapatite (HA) were obtained.



a b

Fig.1 SEM images of ion-modified mono-phased calcium phosphate ceramics:
a) zinc-β-TCP; b) magnesium-β-TCP.

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Nano-sized Porous Calcium Phosphate Ceramics

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Non-stoichiometric nano-sized apatites are one of the main components that build up the hard bone tissue. Thus nano-sized calcium phosphates with predetermined properties and structures obtained by varying their composition are of continuous interest in the field of the biocompatible materials as they could be used for bone repairing, reconstructive and remodeling applications.

The present study aims to investigate the crystallization of nano-sized precursors for calcium phosphate ceramics preparation. The influence of the reagents and the reaction environment on the composition, crystal size and morphology of the crystallized solid phase was followed in two types of experiments: (i) crystallization in polymer hydrogels by absorption of the reagents one by one and (ii) continuous precipitation. In the first type of experiments two natural polysaccharides (Xanthan Gum and Guar Gum) were used as polymer matrices. In these matrices K_2HPO_4 aqueous solution was pre-absorbed and than $CaCl_2$ solution diffused into the hydrogel. pH of medium was in the range of 3-6 for dicalcium phosphate dihydrate (DCPD) crystallization while for the amorphous calcium phosphate (ACP) formation pH was in the range of 10-12. The calcium phosphate crystallites obtained in Guar Gum were smaller in size than the ones obtained in Xanthan Gum due to the denser hydrogel that Guar Gum forms compared to Xanthan Gum at the same water content.

In the second type of experiments the precipitation was carried out at constant pH 8 but at varying composition of the reaction medium, respectively buffer aqueous solution, propylene glycol aqueous solution (1:5) and oil-in-water emulsion (1:20). The modification of the reaction medium allowed for crystallization of amorphous and small crystals calcium-phosphate precursors in contrast to the crystals obtained in an aqueous media. From thus obtained precursors two types of nano-sized, microporous ceramics were prepared: (i) mono-phased (calcium pyrophosphate) when the precursor was DCPD, and (ii) bi-phased (β-TCP and HA) when the precursor was amorphous or poorly crystalline calcium phosphates. The preparation of these ceramics included the following steps: (i) defined homogenous gel-forming of the precursor in polysaccharide matrix; (ii) lyophilization; (iii) washing; (iv) second lyophilization, and (v) sintering at $1000^{o}C$. The samples were characterized by chemical, XRD, FTIR and SEM methods.

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Calcium Phosphate Formation in Poly(methacrylic acid)-Polysulfobetaine Double Networks

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Double networks (DN) are a specific type of interpenetrating polymer networks that consists in a polyelectrolyte network with high crosslinking density (high density single network, HDSN) which is interlaced with a loose crosslinked network of a neutral polymer (low density single network, LDSN) [1]. This structure defines a very good mechanical performance of DN hydrogels – property which is a serious shortcoming in relation to hydrogels applications. Recently, we have observed a grain-like phase-separated morphology of DN made by polyacrylamide and polysulfobetaine (PSB) with grain size in the nanometer range which exact value strongly depended on DN composition [2]. In the present study we aim to explore this specific DN morphology in order to induce crystallization of calcium phosphates in the nanosized grains and to control this process via DN composition. The components of the new DN were chosen because poly (methacrylic acid) (PMAA), in the role of HDSN, is a polyelectrolyte that has many pending carboxylic groups (known to be nucleating sites for calcium phosphate crystallization) while polysulfobetaine, in the role of LDSN, is a neutral polymer with the very specific property to swell better in salty solutions than in pure water (that is the so called antipolyelectrolyte effect).

Three PMAA films have been synthesized differing in their crosslinking densities and these were further swelled into either 0.5 M or 1 M sulfobetaine solutions containing also small quantities of crosslinking agent and initiator (for both networks N,N'-methylene-bis-acrylamide was used as a crosslinking agent). Then the PSB network was obtained *in situ* after heating the samples at 60°C for few hours. The microhardness of thus obtained films was measured and their swelling kinetics in both pure water and 0.15 M NaCl was determined. The elastic modulus of the obtained hydrogels was obtained by using the Hertz's theory. The DN samples were used for in situ formation of calcium phosphates by using two alternative ways, namely, by swelling into simulated body fluids and by the sequential diffusion of HPO_4^- and Ca^{2+} ions. In both cases calcium phosphates were obtained as evidenced by scanning electron microscopy and X-ray diffraction.

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Size Effects in Mechanical Synthesis of Some Nickel-based Alloys

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Nickel-based alloys find large application in contemporary areas of industry for production of corrosion- resistant and thermo stable superalloys, high-loaded engine parts like turbine blades, medical instruments and implants etc. Here are demonstrated the possibilities of mechanochemical methods for synthesis of nanosized nickel-titanium shape-memory alloys having large application in instrument engineering and nickel-chromium alloys for application in dentistry. Using XRD, SEM/TEM are shown phase and structural transformations of reagents during mechanically-assisted and direct mechanical synthesis of Ni-Ti shape-memory alloys. It was shown that NiTi nanosized powders obtained by direct mechanical synthesis are appropriate to obtain structures with controlled porosity which is a precondition for their application in implantology. Some main mechanical characteristics of multicomponent Ni-Cr alloys are investigated. In synthesis of Ni-Cr alloys is used the simplest scheme of powder metallurgy: mechanical mixing/treatment of starting metal powders, their cold pressing and sintering. Technological, economic and ecological advantages of such approach in comparison with the traditional metallurgical method for thermal alloying of nickel-based alloys are also discussed.

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Author Index

Author Index

Author Index

Author Index

Author Index

Author Index

Author Index

Author Index

Author Index