Thermoelectric Properties of Nickel and Iron Substituted Lantanum Cobaltates

Vassil Vulchev[1], Ludmil Vassilev[1] , Sonya Ivanova [2], Ekaterina Zhecheva[2] and Radostina Stoyanova [2]

[1] Faculty of Physics, University of Sofia, 1164 Sofia, Bulgaria.
[2] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria. *E-mail:* vdv@phys.uni-sofia.bg

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 $LaCoO_3$. A 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^{o}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 ^{o}C. The replacement of Co by Ni and Fe led to lattice expansion of the perovskite structure. For perovskites annealed at 900 ^{o}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.

Acknowledgments: Authors are grateful to the financial support from the National Science Fund of Bulgaria (IDEAS No D0-02-309/2008) and National Centre for New Materials UNION (Contract No DO-02-82/2008).