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

Marushka Sendova-Vassileva[1], Miglena Nikolaeva-Dimitrova[1], Radostina Stoyanova[2], Dany Carlier[3], Meglena Yoncheva[2], Ekaterina Zhecheva[2] and Claude Delmas [3]

[1] Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria. *E-mail:* marushka@phys.bas.bg
[2] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria.
[2] ICMCB-CNRS, Université de Bordeaux, IPB-ENSCBP, 87 av. du Dr. A. Schweitzer, 33608 Pessac cedex, France.

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].

Acknowledgments: Authors are grateful to the financial support from the National Science Fund of Bulgaria (IDEAS No D0-02-309/2008).

References

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