Bismuth Substitution Effects in Mg_3/Al_1 Layered Double Hydroxides

A. Kareiva[1], D. Sokol[1], M. Ivanov[2], A. N. Salak[3], R. Grigalaitis[2], M.G.S. Ferreira[3], A. Beganskiene[1], J. Banys[2]

[1]*Institute of Chemistry, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania*
[2]*Faculty of Physics, Vilnius University, LT-10222 Vilnius, Lithuania*
[3]*Department of Materials and Ceramic Engineering/CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*

Numbers of pairs of M^{II}-M^{III} cations were experimentally used to estimate the ranges of the relative sizes of the cations that can form an layered double hydroxide (LDH) structure. In a majority of the known M^{II}-M^{III} LDHs, M^{II} is cation of magnesium or a 4th-period transition metal from iron to zinc, and M^{III} is, as a rule, Al, Ga, Fe, or Cr [1]. In such combinations, the divalent metal cation is slightly bigger than the trivalent one. It should be pointed out that Bi-containing LDH are potentially of a great interest. Bi^{III} has a stereochemically active lone pair of electrons. This feature of bismuth is associated with onset of the unusual dielectric relaxation in oxygen octahedral phases that contain Bi^{III} coordinated by twelve (8+4) oxygens [2, 3]. Besides, polar (antipolar) orderings in oxygen octahedral multiferroics is typically resulted from parallel (antiparallel) displacements of Bi^{III} [4, 5]. Although trivalent bismuth is a relatively large cation, there are compounds with Bi^{III} coordinated by six oxygens [6, 7]. In those compounds, the BiO_6 octahedra are corner-linked; moreover, they are surrounded by the octahedra with smaller-size cations. Such alternation of the octahedra allows to accommodate Bi^{III} in the structure. Phenomenon of the cation ordering in LDH is rare and little investigated [8]. Taking into account a likely deformation of the BiO_6 octahedra in the hydroxide layers and the cation displacements, a Bi^{III} -containing LDH compound could appear to be an example of a 2-D multiferroic material that combines elastic and polar order parameters.

This work was aimed at investigation of feasibility of preparation of LDH compounds with M^{III}= Bi. LDH with the nominal compositions of $Mg_3Al_{1-x}Bi_x$-CO_3 (x=0 to 0.5) were prepared using co-precipitation and sol-gel methods. The mixed oxides were obtained either by calcination of the LDH or sol-gel precursor. All the LDH products were characterized using the methods of X-ray diffraction, scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy and thermogravimetry. We also present an initial study of dielectric and conductive properties of bismuth containing LDHs in this contribution.

Acknowledgements. The work has been done in frame of the project TUMOCS. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 645660.

[1] A.I. Khan, D. O'Hare, *J. Mater. Chem.* **12** (2002) 3191.
[2] A.N. Salak, V.M. Ferreira, *J. Eur. Ceram. Soc.* **27** (2007) 2887.
[3] A.N. Salak, V.M. Ferreira, J.L. Ribeiro, L.G. Vieira, R.C. Pullar, N. McN. Alford, *J. Appl. Phys.* **104** (2008) 014105.
[4] D.D. Khalyavin, A.N. Salak, N.M. Olekhnovich, A.V. Pushkarev, Yu.V. Radyush, P. Manuel, I.P. Raevski, M.L. Zheludkevich, M.G.S. Ferreira, *Phys. Rev. B* **89** (2014) 174414.
[5] D.D. Khalyavin, A.N. Salak, A.B. Lopes, N.M. Olekhnovich, A.V. Pushkarev, Yu.V. Radyush, E.L. Fertman, V.A. Desnenko, A.V. Fedorchenko, P. Manuel, A. Feher, J.M. Vieira, M.G.S. Ferreira, *Phys. Rev. B* **92** (2015) 224428.
[6] W.T. Fu, R. de Gelder, R.A.G. de Graaff, *Mater. Res. Bull.* **32** (1997) 651.
[7] P.E.R. Blanchard, Z. Huang, B.J. Kennedy, S. Liu, W. Miiller, E. Reynolds, Q. Zhou, M. Avdeev, Z. Zhang, J.B. Aitken, B.C.C. Cowie, L.Y. Jang, T.T. Tan, S. Li, C.D. Ling, *Inorg. Chem.* **53** (2014) 952.
[8] D.E. Evans, R.C.T. Slade, *Structure & Bonding*, Springer-Verlag, Berlin, Germany, 2005; Vol. 119, pp. 1−87.