

for $\text{BaBi}_{10}\text{B}_6\text{O}_{25}$ $a=6.434\text{ \AA}$, $b=11.763\text{ \AA}$, $c=29.998\text{ \AA}$, cell volume $V=2270.34\text{ \AA}^3$, $Z=8$.

[1] Barbier J., Penin N., Denoyer A., Cranswick L.M. *Solid State Sciences*, 2005, 7, 1055. [2] Egorysheva A.V., Kargin Yu.F. *Zh.Neorg. Khim.* 2006, 7, 2078. [3] Egorysheva A.V., Skorikov V.M., Volodin V.D., Myslitskiy O.E. & Kargin Yu.F. *Zh.Neorg. Khim.* 2006, 12, 2078.

Keywords: $\text{BaBi}_2\text{B}_2\text{O}_7$, $\text{BaBi}_{10}\text{B}_6\text{O}_{25}$, $\text{BaBi}_8\text{B}_2\text{O}_{16}$

FA2-MS14-P18

Isomorphic (Mg, K) Substitution in Triple Molybdate $\text{K}_{3+x}\text{Li}_{1-x}\text{Mg}_4(\text{MoO}_4)_6$, Tatyana Yu. Kardash^a, Zoya A. Solodovnikova^b, Sergey F. Solodovnikov^b, Evgeniya S. Zolotova^b. ^aBoreskov Institute of Catalysis, SB RAS, Novosibirsk, Russia. ^bNikolaev Institute of Inorganic Chemistry, SB RAS, Novosibirsk, Russia.
E-mail: kardash@catalysis.ru

Subsolidus phase relations in the ternary system $\text{Li}_2\text{MoO}_4\text{--K}_2\text{MoO}_4\text{--MgMoO}_4$ were studied at 480–570°C using X-ray powder diffraction (Bruker D8, $\text{CuK}\alpha$), which revealed the existence of a new nonstoichiometric triple molybdate $\text{K}_{3+x}\text{Li}_{1-x}\text{Mg}_4(\text{MoO}_4)_6$ formed in the quasi binary join $\text{K}_2\text{Mg}_2(\text{MoO}_4)_3\text{--Li}_2\text{Mg}_2(\text{MoO}_4)_3$. The compound was found to be decomposed at 730°C into a solid mixture of $\beta\text{-K}_2\text{Mg}_2(\text{MoO}_4)_3$ and $\text{Li}_2\text{Mg}_2(\text{MoO}_4)_3$. The homogeneity range $0 \leq x \leq 0.25$ was found from the dependences of the trigonal unit cell parameters on the composition for powder samples quenched in air from 500°C (see Table). Crystals of the compound were obtained by spontaneous crystallization of the molten ceramic mixture $\text{Li}_2\text{MoO}_4 + 2\text{K}_2\text{MoO}_4 + 2\text{MgMoO}_4 + 2\text{K}_2\text{Mo}_2\text{O}_7$ cooled from 610°C. The crystal structure of $\text{K}_{3.11}\text{Li}_{0.89}\text{Mg}_4(\text{MoO}_4)_6$ (Bruker X8 Apex, $a = 14.3541(2)\text{ \AA}$, $c = 19.7338(4)\text{ \AA}$, sp. gr. $R\bar{3}c$, $Z = 6$, $R = 0.0191$) is isotypical to that of the sodium-ion conductor $\text{II-Na}_3\text{Fe}_2(\text{AsO}_4)_3 = (\text{Na}_5\Box)^{\text{IX}}\text{Na}^{\text{VI}}\text{Fe}^{\text{VI}}\text{Fe}^{\text{VI}}_3(\text{AsO}_4)_6$ [1], and has the following cationic distribution: $(\text{K}_{0.5}\Box_{0.5})_6(\text{Mg}_{0.89}\text{K}_{0.11})(\text{Li}_{0.89}\text{Mg}_{0.11})\text{Mg}_3(\text{MoO}_4)_6$. The main interatomic distances (\AA) are: Mo–O 1.753(2)–1.768(2), K–O 2.771(2)–3.512(2), (Mg, K)–O 2.152(2) \times 6, (Li, Mg)–O 2.075(2) \times 6, Mg–O 2.034(2)–2.134(2). The structure comprises 3D framework built of MoO_4 tetrahedra and oxygen octahedra around three Mg-containing positions where each (Li, Mg) O_6 octahedron shares edges with three MgO_6 octahedra to form discrete octahedral tetra-clusters while the (Mg, K) O_6 octahedra are isolated. Large cavities of the framework are half occupied by K^+ ions. The unexpected feature of the structure is an isomorphic (Mg, K) substitution revealed for the first time. The analogous (Mn, K) and (Co, K) substitutions were early found in the isostructural compounds $\text{K}_{3.07}\text{Li}_{0.93}\text{Mn}_4(\text{MoO}_4)_6$ and $\text{K}_{3.30}\text{Li}_{0.70}\text{Co}_4(\text{MoO}_4)_6$ [2]. The open framework structures, the presence of defects in the $(\text{K}_{0.5}\Box_{0.5})$ position and a structural relation of these three triple molybdates with the solid electrolyte $\text{II-Na}_3\text{Fe}_2(\text{AsO}_4)_3$ make us to suggest ionic exchange properties and an elevated ionic conductivity for the compounds considered.

Composition of sample	a , \AA	c , \AA
$\text{K}_{2.9}\text{Li}_{1.1}\text{Mg}_4(\text{MoO}_4)_6^*$	14.350(1)	19.703(2)
$\text{K}_{3.0}\text{Li}_{1.0}\text{Mg}_4(\text{MoO}_4)_6$	14.350(1)	19.703(2)
$\text{K}_{3.1}\text{Li}_{0.9}\text{Mg}_4(\text{MoO}_4)_6$	14.353(1)	19.704(2)
$\text{K}_{3.2}\text{Li}_{0.8}\text{Mg}_4(\text{MoO}_4)_6$	14.358(1)	19.706(2)
$\text{K}_{3.3}\text{Li}_{0.7}\text{Mg}_4(\text{MoO}_4)_6^{**}$	14.360(1)	19.709(2)

* $\text{Li}_2\text{Mg}_2(\text{MoO}_4)_3$ impurity. ** $\beta\text{-K}_2\text{Mg}_2(\text{MoO}_4)_3$ impurity.

[1] D'Yvoire, F.; Bretey, E.; Collin G. *Solid State Ionics*, 1988, 28-30, 1259. [2] Solodovnikov, S.F.; Khaikina, E.G.; Solodovnikova, Z.A.; Kadyrova, Yu.M.; Khal'baeva, K.M.; Zolotova, E.S. *Doclady Chemistry*, 2007, 416, Part 1, 207.

Keywords: triple molybdate, nonstoichiometry, structure

FA2-MS14-P19

Nanostructured Random Type MgFe_2O_4 Spinel Prepared by Soft Mechanochemical Route. A. Kremenovic^{a,b}, B. Antic^b, N. Jovic^b, M. Vucinic-Vasic^c. ^aUniversity of Belgrade, Belgrade, Serbia. ^bThe "Vinča" Institute, Belgrade, Serbia. ^cUniversity of Novi Sad, Novi Sad, Serbia.
E-mail: akremen@EUnet.rs

Results of structural, spectroscopic and magnetic investigations of MgFe_2O_4 nanoparticles prepared by soft mechanochemical synthesis will be reported. MgFe_2O_4 nanoparticles crystallize in $Fd\bar{3}m$ space group with mixed cation distribution and reduced percentage of Fe^{3+} at tetrahedral (8a) sites. Discrepancy in the cation distribution compared to that in the bulk Mg–ferrite is one of the highest known. X–ray line broadening analysis reveals crystallite size and strain anisotropy. The average apparent size is 10(1) nm and the average maximum strain is 27(2) $\times 10^{-4}$. The projection of three-dimensional bodies representing “average apparent crystallite size” and “apparent maximum strain” on crystallographic (001) plane are given in Figure 1.

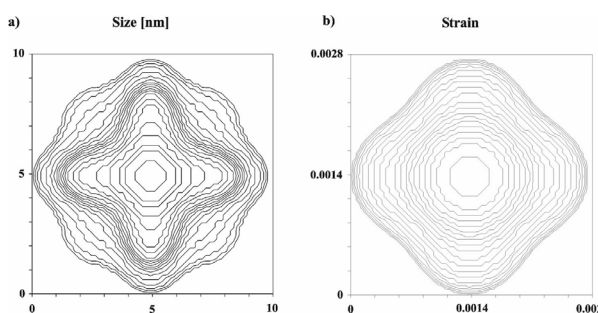


Figure 1. The projection of three-dimensional bodies representing (a) average apparent size and (b) maximum strain in crystallographic plane (001).

The saturation magnetization, $M_{\text{sat}} = 62\text{ emu/g}$ measured at 5 K is twice higher than that found in the bulk counterparts. Such high value of M_{sat} is attributed to the low value of cation inversion parameter ($\delta=0.69$), to the core/shell structure of the nanoparticles and to the surface/volume ratio. Mössbauer spectrum collected at room temperature reveals ferrimagnetic ordering between Fe^{3+} ions in 8a and 16d sites, while zero-field-cooled (ZFC) and field-cooled (FC) $M(T)$ measurements were shown SPM state above 350 K.

Keywords: nanocrystals, microstructure analysis, magnetism