

and cation vacancies were found at the octahedral cation site (B site). Change in cell dimension was smooth and monotonous, while structure refinements utilizing only high angle data (147 out of 182 Bragg points with $\sin\theta/\lambda \geq 0.6$) showed that the most of structural parameters have different trends with Ti doping higher and lower than 2%.

Anisotropy in ADPs at the octahedral cation site (B site) was high in the stoichiometric specimen [1] and this high anisotropy was kept in Ti 2% specimen. This anisotropy, however, got smaller with increasing Ti doping as it was reported on cation-deficient magnetite [2]. ADPs at the tetrahedral cation site (A site) and that at the oxide ion site along $\langle 111 \rangle$ increased steeply with Ti doping at concentrations higher than 5%.

As it has been repeatedly reported, the A-O and B-O distances in magnetite are longer and shorter than ${}^{\text{iv}}\text{Fe}^{2+}$ -O and average of ${}^{\text{vi}}\text{Fe}^{2+}$ -O and ${}^{\text{vi}}\text{Fe}^{3+}$ -O distances, respectively, in hitherto reported Fe-bearing spinels [3]. The A-O distance increased moderately with Ti doping, indicating transfer of remnant electron from the B site due to substitution of Fe^{2+} by Ti^{4+} . Change in the B-O distance showed convex feature with an amount of Ti: the B-O distance abruptly increased with Ti doping from 0 to 2%, then it turned into moderate convex trend with further Ti doping. Intercept at $\text{Ti} = 0\%$ extrapolated from Ti 5% and 10% data [$d(\text{B-O}) = 2.0610(6) \text{ \AA}$ at $\text{Ti} = 5\%$ and $2.0607(6) \text{ \AA}$ at $\text{Ti} = 10\%$] was 2.0615 \AA . While the value (2.0615 \AA) was still smaller than the average of $d({}^{\text{iv}}\text{Fe}^{2+}\text{-O})$ and $d({}^{\text{vi}}\text{Fe}^{3+}\text{-O})$ estimated from bond-valence scheme (2.078 \AA), this trend itself indicated change in nature of Fe-O bonding in the B-O bond (semi-metallic to ionic nature) with a little amount of Ti doping.

Difference Fourier synthesis on the stoichiometric specimen showed positive residues on B-O bonds, particularly in the vicinity of the B site (at $1/2, 1/2, 1/2$), and also positive residues on non-bonding directions in the vicinity of the A site. These features, however, were not clearly seen on Ti 2% and 5% specimens and vanished on Ti 10% specimen.

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Keywords: ferrite, spinel, configuration

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Structural properties of gahnite doped with cobalt, manganese or titanium

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Oxide spinels include a very large group of structurally related compounds having a considerable technological importance. Among them, zinc aluminate (ZnAl_2O_4), known by the mineral name gahnite, is of interest due its good combination of semiconducting and optical properties which makes it useful in various photoelectronic devices [1]. When doped with some transition-metal cations or rear-earth cations, it exhibits luminescence and can be used as a cathodoluminescence material [2]. Gahnite possesses a cubic spinel-type structure, space group $Fd\bar{3}m$ [3]. Although gahnite doped with various cations already has wide applications, some cases of doping are not completely elucidated.

Three series of nanocrystalline powder gahnite samples were

prepared by a sol-gel technique: (i) samples doped with 0-100 at% Co (substituted for Zn), (ii) samples doped with 0-60 at% Mn (substituted for Zn), (iii) samples doped with 0-12.5 at% Ti (substituted for Al). Structural changes due to Co, Mn and Ti incorporation in the gahnite lattice were studied by XRD. Crystal structures were refined by the Rietveld method [4], including the analysis of diffraction line broadening. Valence state and location of dopant cations in the gahnite lattice were determined by EPR spectroscopy.

Unit-cell parameter of gahnite increased on doping with Co, Mn and Ti. Doping with cobalt and manganese induced a partial inverse spinel structure, with Co^{2+} and Mn^{2+} cations residing on both tetrahedral and octahedral cation sites of the gahnite structure respectively. On the other hand, Ti^{4+} dopant cations occupied only octahedral sites substituting for Al^{3+} . In the latter case the excess Zn^{2+} cations (included during the synthesis procedure) were also situated on octahedral cation sites due to charge compensation. On cobalt doping as well on titanium doping, the metal-oxygen distances in gahnite structural tetrahedra decreased while in structural octahedra increased. In the case of manganese doping the situation is just opposite: metal-oxygen distances in structural tetrahedra increased and in structural octahedra decreased. Such behavior is a consequence of ionic radii of involved dopant cations and their contents on the respective cation sites.

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Keywords: doped gahnite, X-ray powder diffraction, rietveld structure refinement

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Structure and spectroscopic study of $\text{A}_{0.50}\text{SbFe}(\text{PO}_4)_3$ (A = Mn, Ca, Cd, Sr) Nasicon phosphates series

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The Nasicon-type family has been the subject of intensive research due to its potential applications as solid electrolyte, electrode material, low thermal expansion ceramics and as storage materials for nuclear waste [1-4]. The structure of such materials with general formula $\text{A}_x\text{XX}'(\text{PO}_4)_3$ consists of a three-dimensional network made up of corner-sharing $\text{X}(\text{X}')\text{O}_6$ octahedra and PO_4 tetrahedra in such a way that each octahedron is surrounded by six tetrahedra and each tetrahedron is connected to four octahedra. Within the Nasicon framework, there are interconnected interstitial sites usually labelled M1 (one per formula unit) and M2 (three per formula unit) through which A cation can diffuse, giving rise to a fast-ion conductivity. The crystallographic formula can be written as $[\text{M1}][\text{M2}]_3\text{XX}'(\text{PO}_4)_3$.

$\text{A}_{0.50}\text{SbFe}(\text{PO}_4)_3$ (A = Mn, Ca, Cd, Sr) samples were obtained by solid state reaction in air. The structural characteristics by powder X-ray diffraction (XRD) study using the Rietveld method show that $\text{A}_{0.50}\text{SbFe}(\text{PO}_4)_3$ (A = Mn, Ca, Cd, Sr) compounds are isostructural and crystallise in the $R\bar{3}$ space group. In all samples, A^{2+} cations occupied one-half of the M1 sites and the Sb^{5+} and Fe^{3+} cations are orderly distributed within the $\text{SbFe}(\text{PO}_4)_3$ framework. A globally structural comparison between $\text{A}_{0.50}\text{SbFe}(\text{PO}_4)_3$ phases are presented. In order to obtain further structural information about the nature of bonding in studied phosphates an assignment of Raman and Infrared bands was also realised.

[1] H.Y-P. Hong, *Mater. Res. Bull.* **1976**, *1*,1173. [2] R. Roy, E.R. Vance, J. Alamo, *Mat. Res. Bull.* **1982**, *17*, 585-589. [3] A. Aatiq, M. Ménétrier, A. El Jazouli, C. Delmas, *Solid State Ionics* **2002**, *150*, 391-405. [4] A.I. Orlova, V.A. Orlova, A.V. Buchirin, K.K. Korchenkin, A.I. Beskrovnyi, V.T. Demarin, **2005**, *47*, 235-240.

Keywords: Antimony and Iron phosphate, Rietveld refinement, Raman and IR spectroscopy

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Structural study of ferromagnetic metal-insulator transition in hollandite chromium oxide, $K_2Cr_8O_{16}$

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The hollandite oxides with the general chemical formula $A_2M_8O_{16}$ (A = alkaline metal; M = transition metal) are a kind of mineral. They are mixed valent oxides with $M^{3+}/M^{4+} = 1/3$ (an averaged valence of $M^{3.75+}$). The crystal structure consists of the tubular M_8O_{16} -framework and A -cations at the tunnel sites of the M_8O_{16} -framework. The M_8O_{16} -framework is constructed from the double chains (zigzag-chains) formed by sharing the edges of MO_6 octahedra. The chromium hollandite $K_2Cr_8O_{16}$, which at room temperature is tetragonal and a paramagnetic metal (PM), becomes ferromagnetic with $T_C = 180$ K [1], which is explained by the double exchange mechanism [2], but surprisingly this ferromagnetic metal phase undergoes a transition to an insulator at lower temperature, retaining ferromagnetism. The metal-insulator transition (MIT) at $T_{MI} = 95$ K is quite unique; it has a metal (or half-metal) to insulator transition in a ferromagnetic state and the resulting low temperature phase is a rare case of a ferromagnetic insulator (FI). In order to elucidate this unique ferromagnetic MIT, it is crucial to study the crystal structure across the MIT.

The synchrotron X-ray diffraction study for the single crystal has revealed the structural distortion from tetragonal to monoclinic with $\sqrt{2}a \times \sqrt{2}b \times c$, where a , b and c are the lattice parameters in the PM phase (Fig.1). In the FI phase, four Cr sites, two K sites and eight O sites become crystallographically inequivalent. Four Cr sites form the coupled four-chains running in the c -direction by sharing corner oxygen in the Cr_8O_{16} -framework. In this geometry, the alternations of Cr-Cr bond and Cr-O bond along the c -direction exist in the coupled four-chains, resulting in a weak tetramerization of the Cr ions. Such bond alternation could be responsible for the opening of band gap.

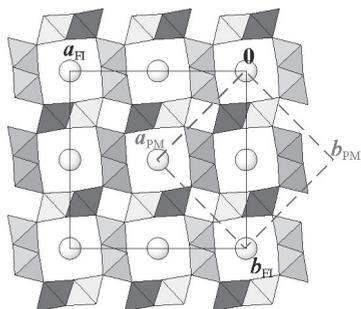


Fig.1 Crystal structure of $K_2Cr_8O_{16}$ at 20 K viewed from c -axis.

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Keywords: synchrotron x-ray diffraction, single crystal, phase transition

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Synthesis and characterization of a new solid solution with lyonsite type structure

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The investigation of the Li_2MoO_4 - $NiMoO_4$ - $Fe_2(MoO_4)_3$ quasi system led to the synthesis and characterization of a bi-dimensional lyonsite-type solid solution, delimited by the compositions: $Li_2Ni_{2x}(MoO_4)_3$, $Li_{1.3}Fe(MoO_4)_3$ and $Li_2Ni_{1.2}Fe_{0.53}(MoO_4)_3$, belonging to the $Li_{2+x}Ni_{2x}Fe_{1+x}(MoO_4)_3$ and $Li_2Ni_{2-x}Fe_{0.33x}(MoO_4)_3$ systems. The samples were synthesized by a glycine soft-combustion process and characterized by ICP analysis, IR spectroscopy, DTA and powder X-ray diffraction. The cation distribution was established from a single crystal X-ray study of the $Li_2Ni_{1.5}Fe_{0.33}(MoO_4)_3$ composition. In terms of the $M(1)M(2)_2M(3)(XO_4)_3$ general formula of the lyonsite, the following occupancies were found: 0.87 Li in M(1), (0.34 Li + 0.50 Ni + 0.16 Fe) in M(2) and (0.48 Li + 0.52 Ni) in M(3). All these sites are six coordinated. The M(1) sites form zig-zag chains of edge-sharing trigonal prisms that run along the [100] direction (Figure 1). The M(2) sites are edge- and corner-sharing to form layers perpendicular to the [001] direction (Figure 2). The M(3) sites are face sharing to produce infinite chains propagating along the [001] direction (Figure 3). The connection of the chains is ensured by MoO_4 tetrahedra leading to the formation a three-dimensional network.

The existence of vacancies within the M(1) sites, suggests a high mobility of lithium along the chains of edge-sharing M(1) O_6 prisms. However, ionic conductivity measurements, performed by the impedance spectroscopy technique showed the material to be a poor ionic conductor, with activation energy of 1.08 eV. This behavior is attributed to the fact that the mobility of lithium is attenuated due the one-dimensional character to a one-dimensional pathway.

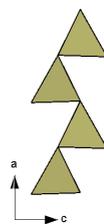


Fig. 1 : chain of $M(1)O_6$ prisms



Fig. 2: layer of $M(2)O_6$ octahedra



Fig. 3: chain of $M(3)O_6$ octahedra

Keywords: molybdate, structure, conductivity