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.

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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 MO₆ octahedra. The chromium hollandite $K_2Cr_8O_{16}$, which at room temperature is tetragonal and a paramagnetic metal (PM), becomes ferromagnetic with $T_{\rm C} = 180$ 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 $\sqrt{2a} \times \sqrt{2b} \times c$, 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 Cr₈O₁₆-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 K₂Cr₈O₁₆ at 20 K viewed from *c*-axis.

K. Hasegawa, M. Isobe, T. Yamauchi, H. Ueda, J. Yamaura, H. Gotou, T. Yagi, H. Sato, Ueda *Phys. Rev. Lett.* **2009**, *103*, 146403. [2] M. Sakamaki, T. Konishi, Y. Ohta, *Phys. Rev. B* **2009**, *80*, 024416.

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

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The investigation of the Li₂MoO₄-NiMoO₄-Fe₂(MoO₄)₃ quasi system led to the synthesis and characterization of a bi-dimensional lyonsitetype solid solution, delimited by the compositions: Li₂Ni₂(MoO₄)₃ $_{Li3}$ Fe(MoO₄)₃ and Li₂Ni_{1.2}Fe_{0.53}(MoO₄)₃, belonging to the Li_{2+x}Ni₂. $_{2x}Fe_{1+x}(MoO_4)_3$ 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 Xray 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 infinitive chains propagating along the [001] direction (Figure 3). The connection of the chains is ensured by MoO₄ 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.



Keywords: molybdate, structure, conductivity