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## MS54.P18

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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.

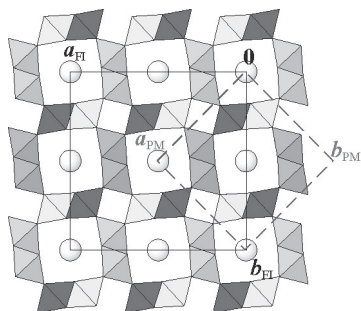


Fig.1 Crystal structure of  $K_2Cr_8O_{16}$  at 20 K viewed from  $c$ -axis.

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### 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.

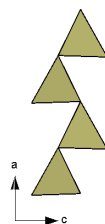


Fig. 1 : chain of  $M(1)O_6$  prisms



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



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

**Keywords:** molybdate, structure, conductivity