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The hollandite oxides with the general chemical formula $A_2M_2O_8$ ($A = $ alkaline metal; $M = $ transition metal) are a kind of mineral. They are mixed valent oxides with $M^{IV}/M^{III} = 1/3$ (an averaged valence of $M^{III}$. The crystal structure consists of the tubular $M_2O_8$-framework and $A$-cations at the tunnel sites of the $M_2O_8$-framework. The $M_2O_8$-framework is constructed from the double chains (zigzag-chains) formed by sharing the edges of $MO_6$ octahedra. The chromium hollandite $KCrO_3$, 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 half-metal (metal 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 $\gamma a = \gamma b = 12c$, 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 $CrO_6$-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 $KCrO_3$ at 20 K viewed from c-axis.

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

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

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The investigation of the $Li_xMoO_4-NiMoO_4(Fe_xMoO_4)$ quasi system led to the synthesis and characterization of a bi-dimensional lysite-like solid solution, delimited by the compositions: $LiNi_xMoO_4$, $Fe_xMoO_4$ and $LiNi_xFe_xMoO_4$, belonging to the $LiNi_{1+\delta}Fe_{1-\delta}MoO_4$ and $LiNi_{1+\delta}Fe_{1-\delta}MoO_4$ systems. The samples were synthesized by a glycine soft-combustion process and characterized by XRD analysis, IR spectroscopy, DTA and powder X-ray diffraction. The cation distribution was established from a single crystal X-ray study of the $LiNi_{1+\delta}Fe_{1-\delta}MoO_4$ composition. In terms of the $M(1)M(2)M(3)(XO_4)_2$ general formula of the lysite, 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 $[001]$ 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$_6$ 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 to 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