

Microstructure and Metal-Insulator Transition in Single Crystalline KM_4O_6

Margareth Andrade, Mariana Lanzoni Maffei, Leandro Marcos Salgado Alves,

Carlos Alberto Moreira dos Santos*, Bento Ferreira, Antonio Fernando Sartori

Departamento de Engenharia de Materiais, Escola de Engenharia de Lorena,
Universidade de São Paulo – USP, CEP 12602-810, Lorena, SP, Brazil

Received: March 1, 2012; Revised: July 17, 2012

High quality KM_4O_6 single crystals with tetragonal structure (space group $P4/mbm$) have been prepared by fused salt electrolysis. The crystals were studied by scanning electron microscopy (SEM), X-ray diffractometry, electrical resistivity, and magnetization measurements. X-ray powder diffraction patterns and SEM have given some information on the growth of single crystals. Electrical resistivity as a function of temperature shows that the KM_4O_6 compound is a bad metal with resistivity change of approximately 30% in the temperature range from 2 to 300K. A metal-insulator transition (MIT), observed at approximately 110K, has been also confirmed for this material. Magnetization as a function of temperature agrees with previous report, however a magnetic ordering has been observed in $M(H)$ curves in the whole temperature range.

Keywords: KM_4O_6 , single crystal, low-dimensional system

1. Introduction

During the last years great attention has been given to the low-dimensional (D) conductors¹⁻³. There are several reasons for that. Three of them are: *i*) low-D conductors are good models for comparison with theory of electrical conductivity such as Pierls transition⁴ and Luttinger liquid (LL) theory⁵, *ii*) they allow the study of several anisotropic properties, and *iii*) they are closed related to the existence of superconductivity.

In particular, molybdenum oxides form one of the largest families with high anisotropic behavior. One good example is the $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ purple bronze compound which is known to be the best example for the 1D LL theory^{3,6}. Furthermore, it shows a crossover from metal to insulator at low temperatures and becomes an anisotropic superconductor below 1.9 K⁷. Recently, our group has found anisotropic properties in a new phase with stoichiometry $\text{K}_x\text{MoO}_{2-\delta}$ ¹⁸. This compound has an anomalous metallic behavior at low temperatures which is related to a weak magnetic ordering. Also, some samples display superconducting behavior with surprisingly critical temperature (T_c) as high as 10 K⁸.

Additionally, molybdates have attracted great attention due to the existence of many valences of the Mo ions (from 2+ to 6+)⁹. Recently, the study of the Mo valences in the $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ compound unambiguously showed an interesting connection with the formation of 1D channels in this compound¹⁰.

Due to these characteristics of the molybdates, our group has studied the preparation and characterization of many anisotropic molybdenum oxides. In particular, this paper deals with the KM_4O_6 phase which is reported to be a quasi-low dimensional system¹¹⁻¹⁵. In fact, KM_4O_6 can

crystallize in two different phases, one is orthorhombic with space group $Pbam$ and another is tetragonal with space group $P\bar{4}$ or $P4/mbm$ ^{12,13}. The most reported phase is the tetragonal $P4/mbm$ which has high anisotropic electrical conductivity and shows a metal-insulator transition (MIT) near 110 K¹¹. Ramanujachary and co-workers have argued this compound is paramagnetic and no magnetic ordering is related to the MIT¹¹. The anisotropic low-D behaviors of the KM_4O_6 compound have been attributed to the metal-metal bonding along *c*-axis of the crystalline structure^{13,15}.

This paper reports some information on the microstructure of single crystals and additional physical properties of the tetragonal KM_4O_6 phase. It is reported for the first time details about the mechanism of the crystal growth during the fused salt electrolysis. Furthermore, magnetization measurements show a magnetic ordering in the whole temperature range from 2 to 300 K.

2. Experimental Procedure

Single crystals of the tetragonal KM_4O_6 phase have been prepared by fused salt electrolysis using K_2MoO_4 and MoO_3 in 6 to 1 molar ratio, respectively. The synthesis was performed during 52 hours at 930 °C applying an electrical current between 20 to 25 mA. Black single crystals with rectangular shape grew attached to the platinum cathode. To have a better idea about the cathode in Figure 1 is shown a typical platinum cathode before and after the electrolysis.

Some of the crystals were removed from the cathode, ground, and characterized by powder X-ray diffractometry. The cathode and some crystals were analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). In order to measure the electrical

*e-mail: cams@demar.eel.usp.br

and magnetic properties some crystals were cleaned using diluted HCl solution. Electrical resistivity measurements were performed in a Physical Properties Measurement System (PPMS) from 2 to 300 K using the standard four-probe method along c-axis of the single crystal. Magnetization measurements were carried out in Vibrating Sample Magnetometer (VSM) coupled with 9T PPMS. The measurements were performed attaching several single

crystals on the sample holder and applying magnetic field parallel and perpendicular to the longest axis of the crystals.

3. Results and Discussion

X-ray powder diffraction pattern of the ground single crystals removed from the cathode is shown in Figure 2. The peaks agree very well with those of the simulated for the P4/mbm phase¹². Peaks marked with * symbols are due to the MoO_2 phase despite the overlaps with the (220), (211)

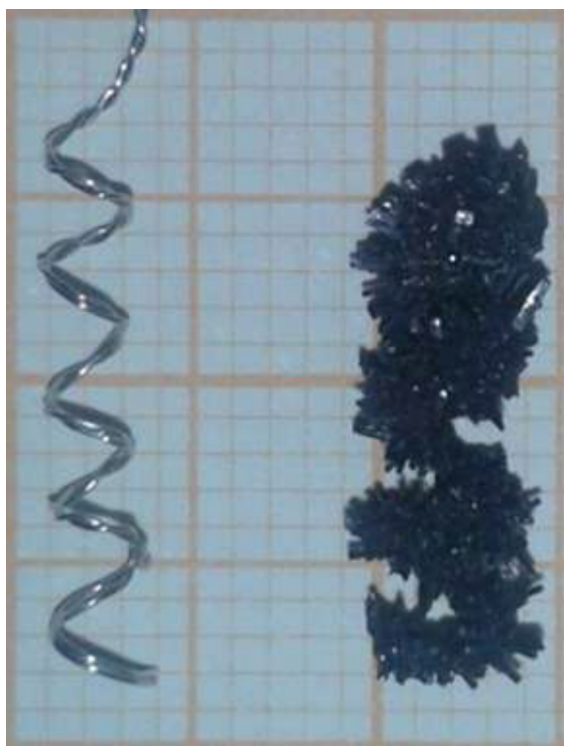


Figure 1. Shape of the cathode used in the fused salt electrolysis. It is shown the platinum cathode before (left) and after the electrolysis (right).

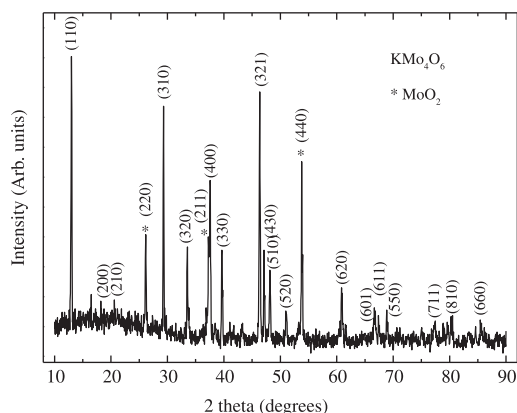
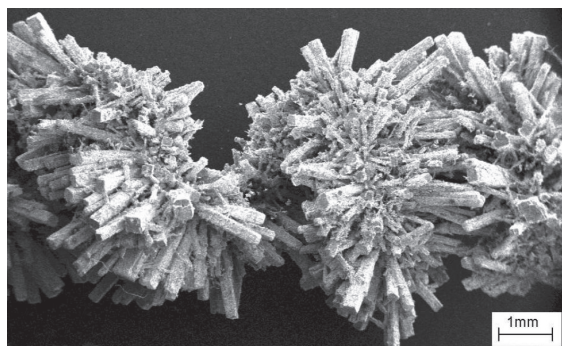
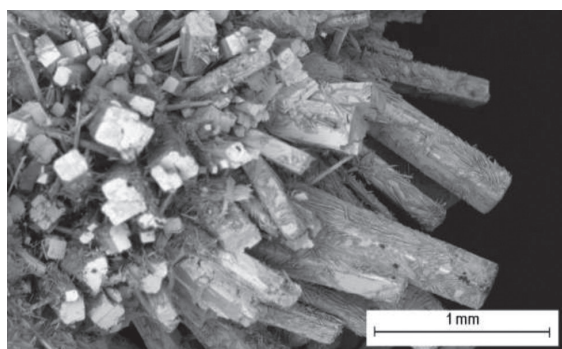


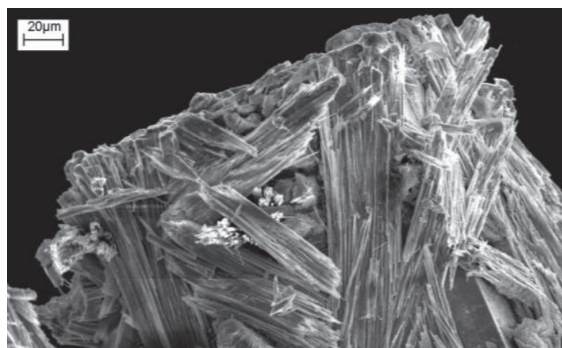
Figure 2. X-ray powder diffractogram of some ground singles crystals removed from the cathode. (hkl) indicate the peaks related to the KMnO_6 tetragonal (P4/mbm) phase. Peaks marked with * symbols are related to the MoO_2 phase. These peaks are attributed to the formation MoO_2 crystals on top of the KMnO_6 single crystals during the cooling procedure.



(a)



(b)



(c)

Figure 3. Scanning Electron Microscopy of the cathode after electrolysis. In (a) and (b) are shown a large view of the cathode using two different magnifications. One can see that KMnO_6 single crystals grow perpendicularly to the platinum wire. The crystals are rectangular bars 1 to 2 mm long. In (c) is displayed the Scanning Electron Microscopy for one typical as-grown single crystal. One can see many small crystals which are attributed to the MoO_2 grew during the cooling procedure. The flat surface of the KMnO_6 single crystal can also be seen on the lower right of the micrograph.

and (440) peaks of the KMnO_4O_6 phase. The comparison between powder diffractograms shows that the crystals are mainly due to the KMnO_4O_6 tetragonal $P4/mbm$ phase with some MoO_2 impurities. Results of SEM performed in some as grown-single crystals agree with that. Micrograph of the deposited crystals, displayed in Figure 3a, shows that the single crystals grow perpendicularly to the spiral shaped platinum cathode. In Figure 3b, one can see that the crystals

are rectangular bars 1 to 2 mm long with cross section up to $0.2 \times 0.2 \text{ mm}^2$.

One as-grown single crystal was selected and observed with higher magnification. Figure 3c displays the micrograph of a small part of the crystal. It is possible to observe several small impregnated crystals on the KMnO_4O_6 bar. These small crystals have been attributed to the MoO_2 impurities in agreement with the peaks of this phase observed in X-ray diffractogram shown in Figure 2. Probably, the small crystals on top of the KMnO_4O_6 single crystal bars have grown during the cooling process in which MoO_2 and MoO_3 can exist in equilibrium at high temperatures¹⁶.

Figure 4 displays the electrical resistivity as a function of temperature for the longest axis of one single crystal (c-axis).

The electrical resistivity varies less than 30% in the range from 2 to 300 K. This is an indication that the KMnO_4O_6 compound is a poor conducting metal. Furthermore, a MIT occurs near 118 K. The general behavior of the electrical resistivity is in good agreement with previous report¹¹. The origin of this MIT is still under discussion. Ramanujachary et al.¹¹ pointed out that this transition is not associated with any magnetic ordering. In order to clarify that we have performed magnetization measurements in the crystals with magnetic field applied parallel and perpendicular to the longest axes of the crystals. In Figure 5 are displayed magnetization measurements as a function of temperature, $M(T)$. Main panel shows the $M(T)$ for magnetic field of 2 T applied parallel to the longest axes of the single crystals.

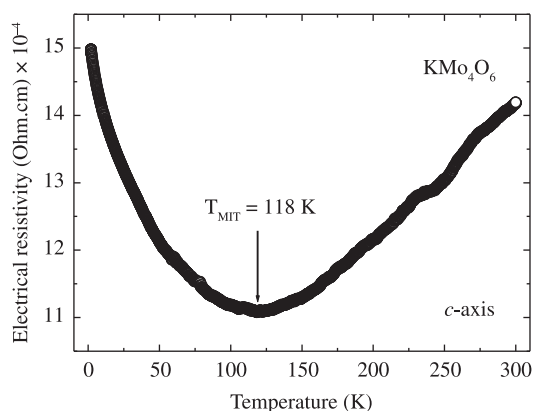


Figure 4. Electrical resistivity as a function of temperature for a KMnO_4O_6 single crystal. A metal-insulator transition near 118 K is observed. The electrical resistivity only varies approximately 30% within the temperature range of the measurement. This is a clear indication that the KMnO_4O_6 is a poor conducting metal.

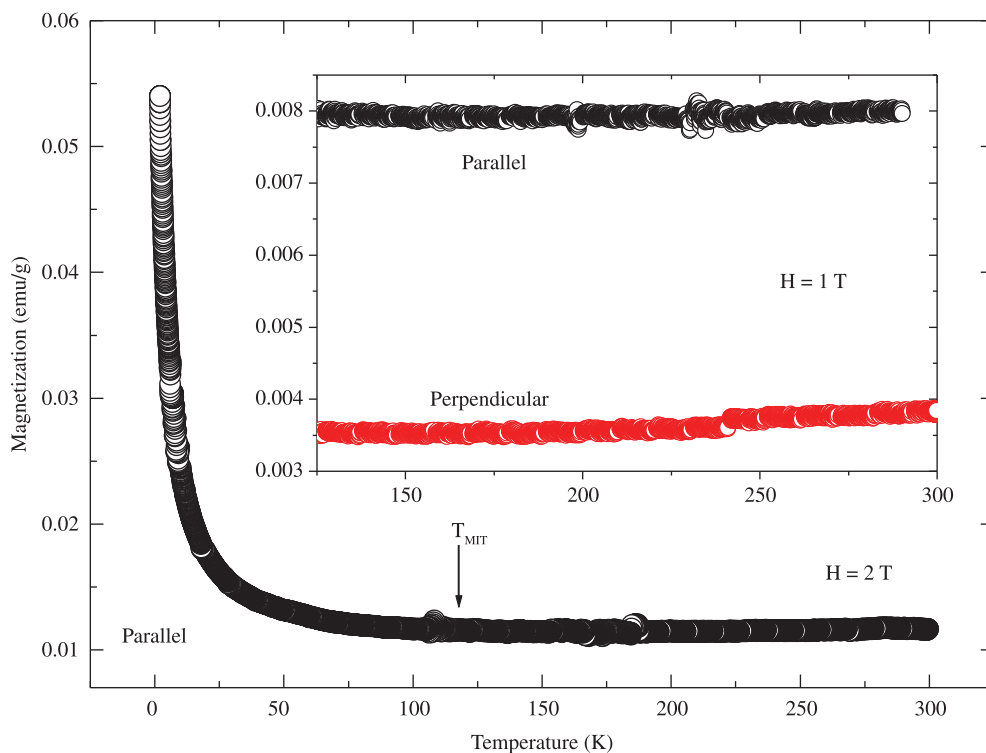


Figure 5. Magnetization as a function of temperature measured using several crystals. Inset shows the results for magnetic field applied in both parallel and perpendicular directions of the crystals. A clear anisotropic behavior can be observed. Above ~ 100 K the magnetization is almost constant. Below this temperature a Curie tail is observed.

At high temperature (above $\sim 100\text{K}$), the magnetization is almost constant and at low temperatures it shows an upturn. Although the $M(T)$ curve looks like a conventional paramagnetic behavior, $1/M$ versus T plot (not shown) does not display any linear behavior in whole temperature

range measured. The constant magnetization at higher temperatures can be more properly observed in inset of the Figure 5 for magnetic field of 1T applied parallel (black symbols) and perpendicular (red symbols) to c -axis of the single crystals. A magnetic anisotropy

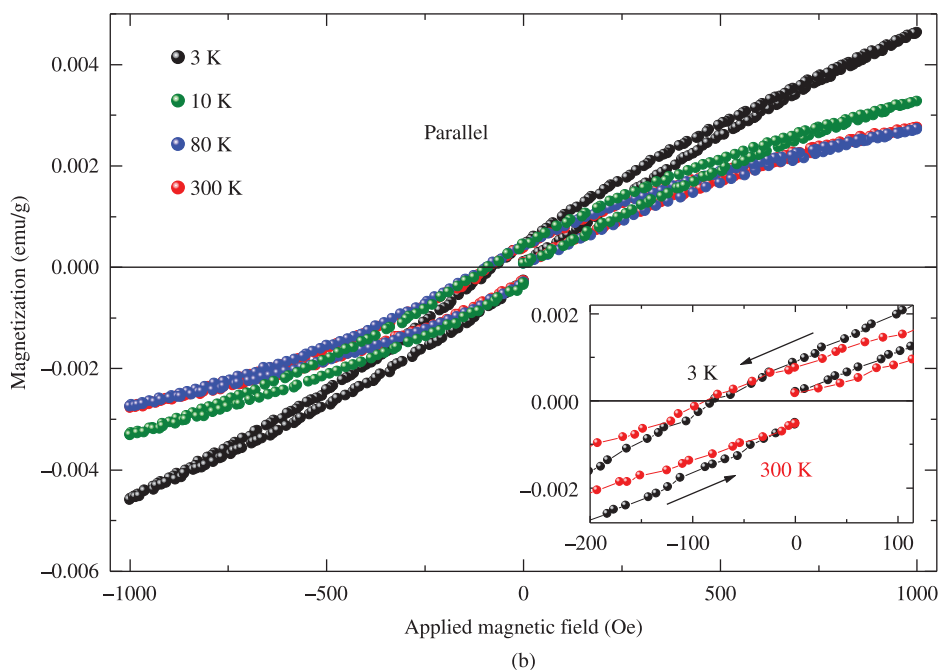
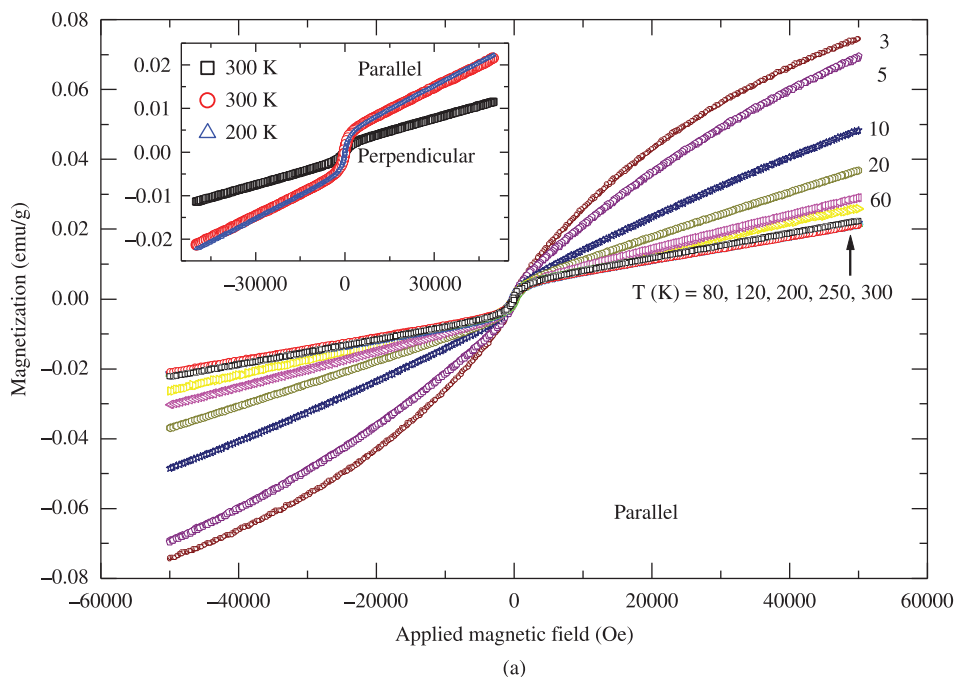


Figure 6. (a) $M(H)$ curves for several temperatures. Curves associated with temperatures above 80 K are almost temperature independent. Below 80 K, $M(H)$ curves have different magnetic moment at high magnetic fields. Inset compares the behaviors of $M(H)$ at high temperature with magnetic field applied parallel and perpendicular. Anisotropic magnetic behavior is confirmed in this inset. One can also see the small difference between the curves at 200 and 300 K for the parallel direction. (b) Magnetic hysteresis curves measured at low applied magnetic fields suggest a ferromagnetic ordering. The hysteresis behaves differently below and above 80 K. It is temperature dependent below 80 K and is constant above.

($M_{\text{parallel}}/M_{\text{perpendicular}}$) with a factor of 2 has been found near room temperature for $H = 1$ T. The general behavior seems to agree with previous measurements¹¹, but the magnetization versus applied magnetic field hysteresis curves, $M(H)$, measured at several fixed temperatures suggest a different interpretation. Figure 6 displays many $M(H)$ curves from 3 to 300 K. Above 80 K all the curves almost set on top of each other, show weak magnetic ordering at low magnetic fields, and linear behavior at magnetic fields above 2000 Oe. The $M(H)$ curves for temperatures below 80 K show non-linear behaviors and are strongly temperature dependent. This indicates a different magnetic behavior above and below 80 K. Furthermore, a weak ferromagnetic ordering is observed at all temperatures (see Figure 6b). Remanent magnetization and coercive field are weak temperature dependent. On the other hand, the hysteresis curves at low field follow the same trend for the curves measured at high magnetic fields above and below 80 K. The origin of the magnetic ordering in the KM_4O_6 is still under investigation but results performed in other molybdate compounds^{8,17} suggest that the presence of Mo ions with different valences could be responsible for the weak ferromagnetic moment observed in Figure 6.

References

- Tarkiainen R, Ahlskog M, Penttila J, Roschier L, Hakonen P, Paalanen M et al. Multiwalled carbon nanotube: Luttinger versus Fermi liquid. *Physical Review B*. 2001; 64:195412. <http://dx.doi.org/10.1103/PhysRevB.64.195412>
- Artemenko SN and Remizov SV. Low-temperature conductivity of quasi-one-dimensional conductors: Luttinger liquid stabilized by impurities. *Physical Review B*. 2005; 72:125118. <http://dx.doi.org/10.1103/PhysRevB.72.125118>
- Dos Santos CAM, White BD, Yu Y-K, Neumeier JJ and Souza JA. Dimensional Crossover in the Purple Bronze $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$. *Physical Review Letters* 2007; 98:266405. <http://dx.doi.org/10.1103/PhysRevLett.98.266405>
- Thorne RE. Charge-Density-Wave Conductors. *Physics Today*. 1996; 49(5):42. <http://dx.doi.org/10.1063/1.881498>
- Voit J. One-dimensional Fermi liquids. *Reports on Progress in Physics*. 1995; 58:977. <http://dx.doi.org/10.1088/0034-4885/58/9/002>
- Da Luz MS, Dos Santos CAM, Moreno J, White BD and Neumeier JJ. Anisotropic electrical resistivity of quasi-one-dimensional $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ determined by the Montgomery method. *Physical Review B*. 2007; 76:233105. <http://dx.doi.org/10.1103/PhysRevB.76.233105>
- Dos Santos CAM, Da Luz MS, Yu Y-K, Neumeier JJ, Moreno J, and White BD. Electrical transport in single-crystalline $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$: A two-band Luttinger liquid exhibiting Bose metal behavior. *Physical Review B*. 2008; 77:193106. <http://dx.doi.org/10.1103/PhysRevB.77.193106>
- Alves LMS, Damasceno VI, Dos Santos CAM, Bortolozzo AD, Suzuki PA, Izario Filho HJ et al. Unconventional metallic behavior and superconductivity in the K-Mo-O system. *Physical Review B*. 2010; 81:174532. <http://dx.doi.org/10.1103/PhysRevB.81.174532>
- Moshier WC, Davis GD and Cote GO. Surface Chemistry of Sputter-Deposited Al-Mo and Al-Cr Alloys Polarized in 0.1N KCl. *Electrochemical Society*. 1989; 136(2):356-62. <http://dx.doi.org/10.1149/1.2096635>
- Da Luz MS, Neumeier JJ, Dos Santos CAM, White BD, Izario Filho HJ, Leão JB et al. Neutron diffraction study of quasi-one-dimensional lithium purple bronze: Possible mechanism for dimensional crossover. *Physical Review B*. 2011; 84:014108. <http://dx.doi.org/10.1103/PhysRevB.84.014108>
- Ramanujachary KV, Greenblatt M, Jones EB and McCarroll WH. Synthesis and Characterization of a New Modification of the Quasi-Low-Dimensional Compound KM_4O_6 . *Journal of Solid State Chemistry*. 1993; 102(1):69-78. <http://dx.doi.org/10.1006/jssc.1993.1008>
- McCarroll WH, Ramanujachary KV, Greenblatt M and Marsch RE. On the Tetragonal Forms of KM_4O_6 . *Journal of Solid State Chemistry*. 1995; 117(1):217-18. <http://dx.doi.org/10.1006/jssc.1995.1266>
- Hughbanks T and Hoffmann R. Chains of trans-edge-sharing molybdenum octahedra: metal-metal bonding in extended systems. *Journal of the American Chemical Society*. 1983; 105(11):3528-37. <http://dx.doi.org/10.1021/ja00349a027>
- Jung D, Lee B-H, Kim S-J and Kang W. Synthesis, Characterization, and Electronic Structure of a New Molybdenum Bronze SnMo_4O_6 . *Chemistry of Materials*. 2001; 13(5):1625-29. <http://dx.doi.org/10.1021/cm000646q>
- Torardi CC and McCarley RE. Sodium tetramolybdenum hexoxide (NaMo_4O_6). A metallic infinite-chain polymer derived by condensation of octahedral clusters. *Journal of the American Chemical Society*. 1979; 101(14):3963-4. <http://dx.doi.org/10.1021/ja00508a043>
- Wold A, Kunnmann W, Arnott RJ and Ferretti A. Preparation and Properties of Sodium and Potassium Molybdenum Bronze Crystals. *Inorganic Chemistry*. 1964; 3(4):545-7. <http://dx.doi.org/10.1021/ic50014a022>
- Thakur P, Cezar JC, Brookes NB, Choudhary RJ, Prakash R, Phase DM et al. Direct observation of oxygen induced room temperature ferromagnetism in MoO_2 thin films by x-ray magnetic circular dichroism characterizations. *Applied Physics Letters*. 2009; 94(6):06250. <http://dx.doi.org/10.1063/1.3080679>

4. Conclusion

The following conclusions have been obtained:

- KM_4O_6 single crystals have been successfully prepared by salt fused electrolysis;
- Electrical resistivity measurement shows a similar behavior as reported previously and confirms the crossover from metal to insulating behavior near 118 K;
- Magnetization measurements as a function of temperature agree with the previous results;
- $M(H)$ curves at high magnetic fields ($H > 2000$ Oe) are temperature dependent and constant below and above 80 K, respectively;
- $M(H)$ hysteresis curves unambiguously demonstrate the presence of a ferromagnetic ordering at all temperatures from 3 to 300 K. The origin of this magnetic ordering is still under investigation.

Acknowledgements

This material is based upon work supported by FAPESP (2009/14524-6, 2009/54001-2, and 2010/06637-2) and CNPq (490182/2009-7 and 309084/2010-5). M. Andrade is a CAPES fellowship.