Crystal Growth and Unusual Electronic Transport Properties of Some Reduced Molybdenum Oxides with Bi-Octahedral Mo$_{10}$ Clusters

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Single crystals of AMo$_5$O$_8$ (A = Ca, Sr, La-Gd), suitable for electrical conductivity measurements have been grown by high temperature and fused salt electrolytic techniques. The structures of all of these compounds are dominated by the presence of bi-octahedral clusters of Mo atoms joined together parallel to the monoclinic a axis, forming infinite chains. Temperature dependent electrical resistivity measurements on AMo$_5$O$_8$ (A = La, Ce, Pr, Nd, Sm) show anomalous metal-semiconductor transitions near 180 and 30 K. The resistivities of the Eu and Gd analogues are different, in that the former is semiconducting while the latter shows a weak anomaly ~ 110 K. The Ca and Sr analogues are also semiconducting in the range 20–300 K. The electrical conductivity of these phases appears to be closely related to the inter-cluster separation and the number of metal-cluster electrons. The magnetic susceptibility of these compounds show no anomalies at the temperatures corresponding to the transitions seen in their electrical resistivities. The magnetic susceptibility of LaMo$_5$O$_8$ shows a small decrease in the $1/\chi$ (dχ/dT) *vs* T plot in the vicinity of ~ 150 K.

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INTRODUCTION

Reduced ternary molybdenum oxides featuring condensed clusters of molybdenum atoms have been the subject of recent investigations because of their unusual structural chemistry and interesting physical properties. Since the discovery of $NaMo_4O_6$ by Torardi and McCarley,[1] in which the Mo_6 octahedral clusters share their *trans*-edges forming infinite chains, there has been renewed interest in searching for novel ternary molybdenum oxides with low-dimensional, low-valent character. So far this effort has led to the discovery of a number of new phases with both extended metal-metal bonding as well as several compounds with isolated or quasi-isolated metal atom cluster configurations. Some of the more interesting cluster compounds include those with digonal Mo_2 clusters such as $La_2Mo_2O_7$, $La_5Mo_4O_{16}$ and $La_4Mo_2O_{11}$[2-4] which are respectively, metallic, semiconducting and insulating. More complex clusters are found in $LaMo_{7.70}O_{14}$ and $LnMo_8O_{14}$[5-7] (Ln = La, Nd) which contain Mo_8 clusters formed by capping 2 faces of an Mo_6 octahedron while $LaMo_5O_8$ and related compounds[8-12] contain Mo_{10} clusters where two Mo_6 octahedra share an edge in common. Several of these compounds display low dimensional electronic and magnetic behavior.

As a part of our current effort to understand the structure-property correlations among various reduced ternary molybdenum oxides with strong metal-metal bonds, we have recently reported the electrical and magnetic properties of KMo_4O_6,[13] $La_5Mo_4O_{16}$,[14] $La_2Mo_2O_7$[15] and $LaMo_{8-x}O_{14}$[16] phases. These investigations have revealed the importance of the inter-cluster distance as well as the low-dimensionality of electronic correlations in determining their transport behavior. For example, KMo_4O_6, which shows extended metal-metal bonding along the tetragonal c axis, with Mo-Mo distances of 2.794 and 2.879 Å, displays metallic behavior, while the corresponding inter-cluster distance of ~ 3.08 Å rendered $LaMo_8O_{14}$ semiconducting. Furthermore, in $La_5Mo_4O_{16}$, the quasi-two-dimensional electronic correlations have resulted in a significant anomaly in both the electrical and magnetic properties at ~ 180 K. The metal-semiconductor transition observed in $La_2Mo_2O_7$ near 120 K, appears to be due to the onset of a charge-density wave instability associated with the linear chains of edge and corner shared Mo atoms parallel to the orthorhombic c axis.

Although these studies are indicative of the complex nature of electronic interactions in oxides with Mo-clusters, because of their distinctly different crystal structures, it was not possible to correlate the structure and electronic properties in a unified model. The AMo_5O_8 system on the other hand, provides an excellent opportunity to probe into such correlations, because all the members of this family are iso-structural with a systematic variation of the inter-cluster distance and the number of metal-cluster electrons.

A recent study of the magnetic properties of several $LnMo_5O_8$ (Ln = La, Ce, Pr, Nd and Sm) phases was reported by Gall et al.[17] The La compound displays a Pauli-type temperature independent susceptibility with an anomaly at 13 K which may be associated with a phase transition, while the Ce, Pr and Nd phases show susceptibilities essentially corresponding to the rare earth ions, except at low temperatures. In addition, the Sm compound gave some evidence of possible spin-glass behavior.

In order to further elucidate the properties of these interesting compounds we have investigated the temperature dependent electrical transport properties of single crystal specimens of several rare earth and alkaline earth members of this series and present the results of these investigations along with some additional magnetic studies.

EXPERIMENTAL

Synthesis Using Solid State Reactions

Crystals of $LnMo_5O_8$ (Ln = La, Ce, Pr, Nd, Sm, Eu and Gd) compositions were prepared by reacting stoichiometric, pelleted mixtures of Ln_2O_3, (Ln = La, Nd, Sm, Eu and Gd), CeO_2 or Pr_6O_{11}, MoO_3 and Mo metal in molybdenum crucibles which had been previously degassed at 10^{-5} Torr at 1500 °C. The pellets were placed in Mo crucibles which were then sealed by arc welding under a partial pressure of argon. The La and Ce compounds could be formed by heating at 1200 °C for 48 hrs., while a temperature of 1600 °C was required for the others. All products were found to be single phase on the basis of their X-ray powder diffraction patterns except for the Gd analogue which was estimated to contain about 20% of $Gd_4Mo_{18}O_{32}$.

Pure $SrMo_5O_8$ was obtained by reacting pelleted stoichiometric quantities of $SrMoO_4$, MoO_3 and Mo in evacuated sealed silica capsules at 1200 °C for 48 hours. Small black crystals of $CaMo_5O_8$ were obtained from reactions containing $CaMoO_4$, Mo and A_2MoO_4 (A = Na or K) in a molar ratio of 4:1:2 in a Mo-boat. The reaction mixtures were sealed in a double-jacketed quartz tube under a dynamic vacuum and heated at 1225 °C for 7 days. After washing with water to remove the unreacted A_2MoO_4 fluxes, the powder X-ray diffraction pattern of the ground crystals indicated a single phase of $CaMo_5O_8$.

While all other products obtained by the methods described above were microcrystalline, well faceted crystals of $CaMo_5O_8$ were obtained which were large enough for electrical measurements. To obtain relatively large single crystals of the other phases a high temperature regimen was followed in which products previously heated at 1600 °C in sealed Mo tubes were now heated to 1930 °C (1800 °C for $GdMo_5O_8$ at a rate of 5 °C/min and held there for 15 minutes followed by cooling at a rate of 100 °C/hr to 1000 °C at which point the furnace was shut down and allowed to cool to room temperature. Crystals obtained in this fashion typically were of the order of $0.1 \times 0.3 \times 0.5$ mm^3 in size.

Synthesis Using Fused-Salt Electrolysis

Single crystal specimens of $LaMo_5O_8$ and $SrMo_5O_8$ were also grown by fused salt electrolysis using molten Na_2MoO_4-MoO_3 mixtures to which La_2O_3 or $SrMoO_4$ respectively were added. McDanel 998 high density alumina crucibles were used to contain the melt. The largest crystals, of the order of 1 mm^3 were obtained by electrolyzing for 2 to 3 day periods with current densities between 30 and 50 mA/cm^2. A Pt spiral cathode and Pt foil anode were employed as electrodes. For the Sr compound a melt made from a mixture having the molar ratios Na_2MoO_4 : MoO_3 : $SrMoO_4$ = 10.0 : 1.00 : 3.00 was employed while ratios of Na_2MoO_4 : MoO_3 : La_2O_3 = 6.20 : 2.45 : 1.00 were used for the preparation of $LaMo_5O_8$. $SrMo_5O_8$ was prepared at 1070 − 1100 °C while the La analogue was prepared at 1000 °C. In both cases the desired product grew on the cathode and could be separated from the residual matrix by alternate washes in solutions of hot 5% K_2CO_3 and 2F HCl. In the case of the La compound a small co-deposit of prismatic MoO_2 was observed while small amounts of $La_2Mo_2O_7$ prisms and $La_9Mo_{13}Al_2O_{42}$ needles were mixed in with the black, tabular $LaMo_5O_8$ crystals. However, in both cases facile mechanical separation based on color and crystal habit was possible. Well faceted crystals were obtained in both cases whose largest dimensions were between 0.5 and 1.0 mm.

Characterization

Powder X-ray diffraction patterns obtained with Cu Kα radiation were used to confirm the purity of the products. Electrical resistivity measurements on selected crystals, typically about $0.1 \times 0.3 \times 0.6$ mm^3, were made by a standard four-probe technique with a conventional liquid helium cryostat in the temperature range of 4–300 K. The orientation of the crystals were confirmed by recording oscillation photographs with a Huber type Weisenberg camera. A two-probe resistivity technique was used to measure the resistivity of the Ca analogue in view of its small size. The crystals were washed with 5% HF solution at ∼ 70 °C for half an hour prior to attaching leads for resistivity measurements. Copper leads were anchored to selected faces of the crystals either with silver paste or ultrasonically soldered indium contacts. The *I–V* profiles were recorded at different temperatures to ensure the ohmic nature of the contacts.

Magnetic susceptibilities over the range 2–300 K were measured on both a VTS 906 and Quantum design SQUID magnetometer.

RESULTS AND DISCUSSION

Structure

All members of the AMo_5O_8 family crystallize with monoclinic symmetry and can be indexed based on the space group $P2_1/c$ (S.G. # = 14). The unit cell parameters of the compounds prepared in this study are presented in Table I. Although no systematic variation of the a and c cell parameters with the size of the A cation is evident, clearly the b unit cell parameter and the monoclinic angle β scale linearly with the ionic radius of the trivalent rare earth cation. The anomalous behavior of Eu suggests that it is most likely in the divalent state.

TABLE I

Unit cell parameters and characteristic electrical properties of
AMo_5O_8 single crystals

A	$a/Å$	$b/Å$	$c/Å$	$\beta/°$	ρRT^a $10^{-3}\ \Omega$ cm	Tc^1 K	Tc^2 K
La	7.578(3)	9.087(3)	9.911(4)	109.05(2)	1.7	175	45
La[1]	7.571(1)	9.088(1)	9.912(1)	109.02(1)	1.9		
La[2]	7.572(1)	9.085(1)	9.916(1)	109.04(1)			
Ce	7.565(3)	9.076(2)	9.910(3)	109.19(2)	1.1	190	30
Pr	7.564(4)	9.049(2)	9.912(4)	109.29(2)	1.1	180	30
Nd	7.561(3)	9.050(2)	9.899(3)	109.45(2)	0.9	175	35
Sm	7.555(3)	9.019(2)	9.916(3)	109.67(2)	1.1	160	35
Eu	7.554(3)	9.168(2)	9.961(3)	109.32(2)	14.4	–	–
Gd	7.559(3)	8.993(1)	9.923(3)	109.81(2)	2.0	135	–
Ca	7.550(5)	9.068(5)	9.983(5)	110.07(4)	–	–	–
Sr	7.558(5)	9.169(5)	9.972(5)	109.26(4)	38.8	–	–
Sr[1]	7.568(2)	9.157(1)	9.973(3)	109.20(2)	37.9		
Sr[2]	7.559(1)	9.157(1)	9.972(2)	109.27(1)			

Unit cell data obtained by single crystal methods, except where noted.
[a] Error is $\pm\ 0.1 \times 10^{-3}$ Ohm cm
[1] Powder diffraction data: sample prepared by electrolysis.
[2] Powder diffraction data: sample prepared by solid state reaction.

As shown in Figure 1, the trans-edge-shared $Mo_{10}O_{26}$ bi-octahedral clus-
ter found in AMo_5O_8 class of compounds, can be derived by fusing two units
of Mo_6O_{18} fragments (the latter are sometimes referred to as Mo_6O_{12} units
if the 6 corner linked oxygens are not included in the description). Figure 2
shows the inter-cluster connection between the $Mo_{10}O_{26}$ units resulting in
the formation of infinite chains along the monoclinic a axis. The chains then
share additional oxygens to form tunnels in which the large A cations reside.
However, within the chains significant metal-metal interactions between
Mo_{10} clusters exist which are typified by the La compound where one short
inter-cluster Mo-Mo bond of 2.689 Å and two longer distances of 2.911 Å are
found.[9] Two non-bonding inter-cluster Mo-Mo distances of 3.091 Å are also
observed. Within the group of $LnMo_5O_8$ compounds, where Ln = tri-valent
rare earth ion, the shortest inter-cluster separation is observed to decrease
with the decreasing size of the rare earth cation. For example, the inter-clus-
ter separation decreases rather smoothly across the series from 2.690 Å from
La to 2.674 Å for Gd. However, for the divalent cations, i.e., A = Ca, Sr or Eu,
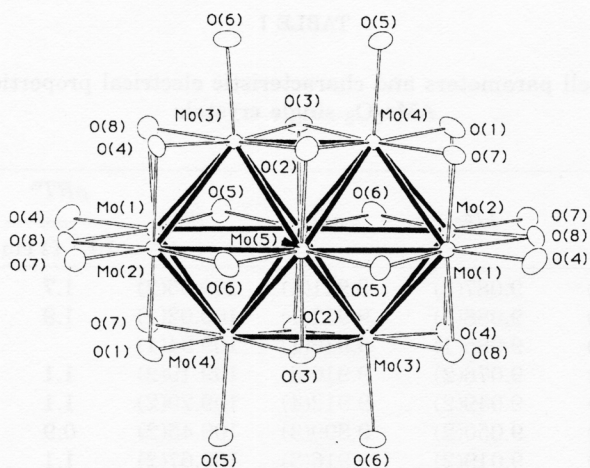one observes a significantly longer inter-cluster separation ~ 2.77 Å.[18] In ad-

Figure 1. Bi-octahedral $Mo_{10}O_{26}$ cluster fragment observed in AMo_5O_8 compounds.
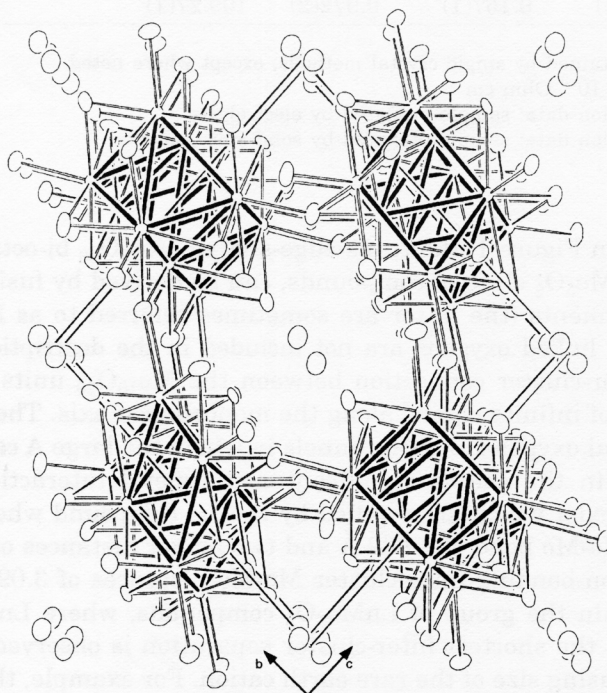

Figure 2. Projection of the crystal structure of AMo_5O_8 along the monoclinic a axis showing the connectivity of bi-octahedral cluster units.

dition, the intra-cluster Mo-Mo distances show a wide distribution of bond distances, ranging from 2.68 to 2.82 Å implying that these clusters are severely distorted. Thus the cluster model shown in Figure 1 is only an ideal representation based on uniform Mo-Mo separation within the cluster. Further, such variations in the metal-metal bonding network could have profound effects on the electrical properties, particularly if delocalized Mo-O π bonding effects are not important.

Electrical Resistivity

The room-temperature electrical resistivities of $LnMo_5O_8$ compositions (Ln = La-Gd) measured with the current applied parallel the chain of Mo_{10} clusters (*i.e.*, along the crystallographic a axis) are presented in Table I. No significant differences in room temperature (RT) resistivity values exist between samples prepared by solid state and electrolytic methods. The electrical resistivity of the $CaMo_5O_8$ sample was greater than 10^6 Ohm cm and hence no temperature dependence of resistivity was attempted. As can be seen from Table I, the room-temperature resistivity values are dependent on the valence of the lanthanide cations. For the tri-valent cations these values are of the order of ~ 1–2×10^{-3} Ohm cm, however, significantly higher resistivity values are observed when A is a di-valent cation (*i.e.*, A = Ca, Sr and Eu). The temperature dependent electrical resistivities of AMo_5O_8 (A = La, Ce, Pr, Nd, Sm, Gd, Sr and Eu) are presented in Figures 3 a–g. The electrical resistivities are temperature independent or nearly so in the range 180–300 K for all of the tri-valent rare earth ions except for the Gd-analogue. In addition, a cross-over transition from semiconductor to metallic behavior in the temperature region 160–190 K (T_c^1) followed by a broad transition to semi-conducting state below 30–45 K (T_c^2) was observed in all of these compounds except when Ln = Gd. Interestingly, the Gd-analogue showed activated behavior with a broad kink – 110 K which appears to signal a transition to a semi-metallic state. Further, we note that in some of the $GdMo_5O_8$ compositions, a transition to metallic state down to low temperatures was observed in the vicinity of 130–150 K. The differences in the temperature dependent resistivity patterns of $GdMo_5O_8$ compositions may be related to a small amount of non-stoichiometry at the Gd site or to the existence of intergrowths such as $Gd_2Mo_2O_7$ and $Gd_4Mo_{18}O_{32}$, which were often observed as a second phase during the synthesis. Further studies on $GdMo_5O_8$ are currently in progress to determine the origin of the observed differences in the temperature dependent resistivity. Nevertheless, the electrical resistivities of all the $LnMo_5O_8$ compounds above 180 K can be characterized as poor metals or degenerate semiconductors. A qualitative Seebeck coefficient measurement indicated that the primary charge carriers are electrons (n-type).
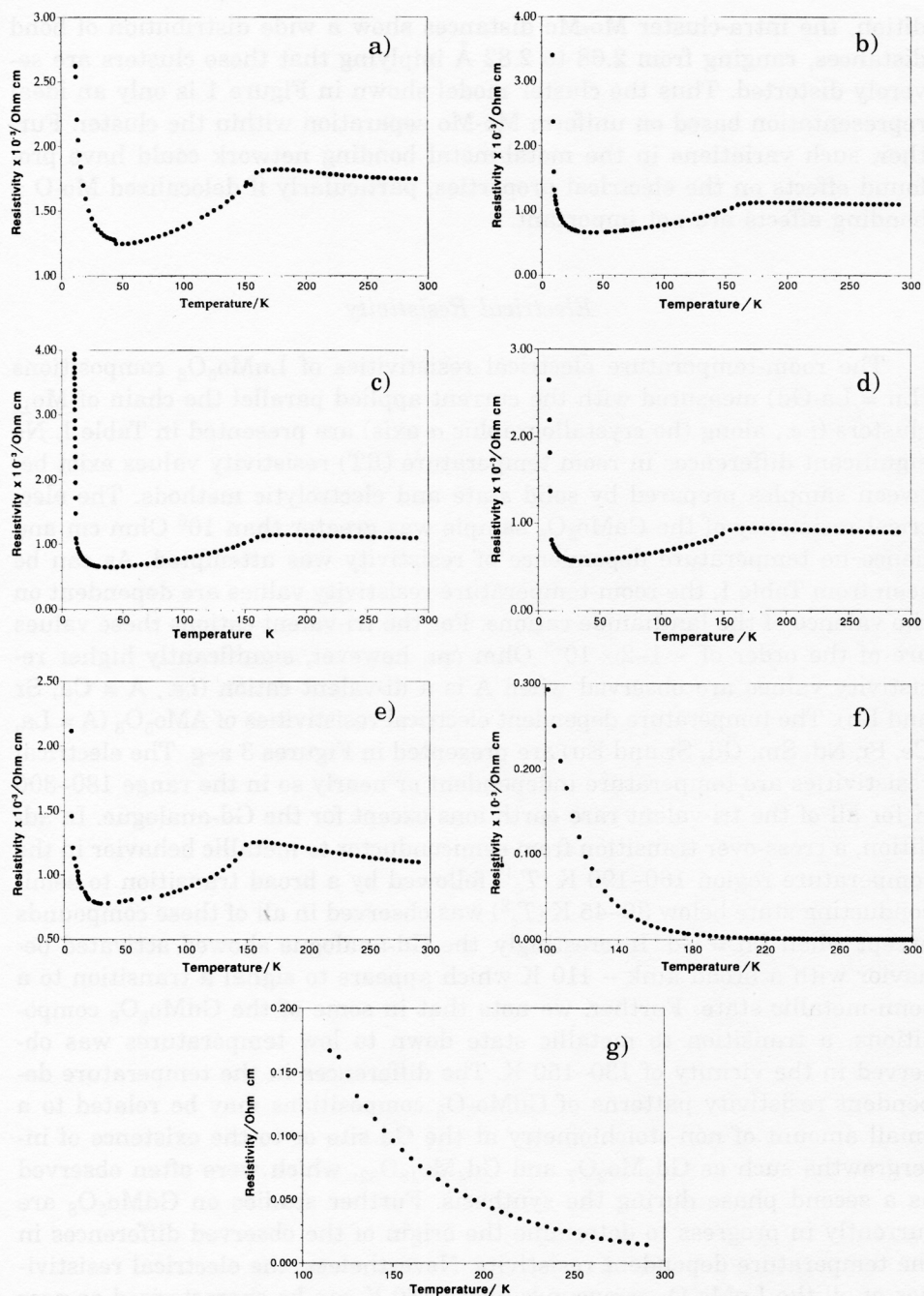
Figure 3. Temperature variation of the electrical resistivity of AMo$_5$O$_8$ crystals: (a) A = La, (b) A = Ce, (c) A = Pr, (d) A = Nd, (e) A = Sm, (f) A = Sr and (g) A = Eu.
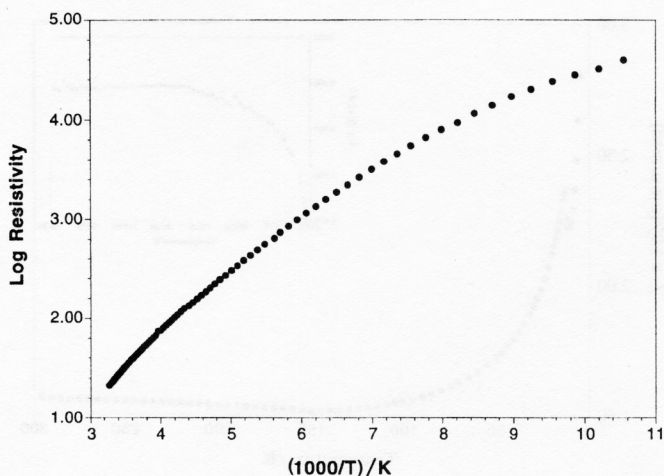
Figure 4. Logarithm of resistivity as a function of inverse temperature (Arrhenius plot) for $SrMo_5O_8$.

In contrast, the AMo_5O_8 compositions with divalent cations at the A site (A = Sr and Eu) remain semiconducting in the entire temperature range of investigation with no low-temperature anomalies. The thermal activation energy for electrical conduction estimated from the linear portions of the $\log \rho$ vs $1000/T$ plot (Figure 4) is 0.15 eV in the temperature range 200–300 K and 0.06 eV in the range 100–120 K for Sr analogue. The smaller activation energy observed at low temperatures is most likely from extrinsic effects. These results indicate that AMo_5O_8 compounds (A = Sr and Eu) are small band gap semiconductors.

In order to investigate the origin of the electronic anomalies observed in the $LnMo_5O_8$ phases discussed above (Ln = tri-valent rare earth ion), we have carried out careful magnetization measurements as a function of temperature on a batch of randomly oriented crystals, particularly in the vicinity of transition temperatures which essentially confirm the results of earlier investigations.[17] In particular, we did not observe any significant anomalies in the magnetic susceptibilities of these compounds at temperatures corresponding to the transitions observed in the electrical resistivity. In fact this it to be expected because the total change in the electrical resistivity in the entire temperature range of investigation is less than a factor of 10. Thus the changes in the Fermi surface, if any, are expected to be minimal and may not be reflected in the temperature dependent magnetization. Furthermore, the presence of magnetic rare earth ions are expected to dominate the magnetic susceptibility thus making small changes in the molybdenum sub-lattice.
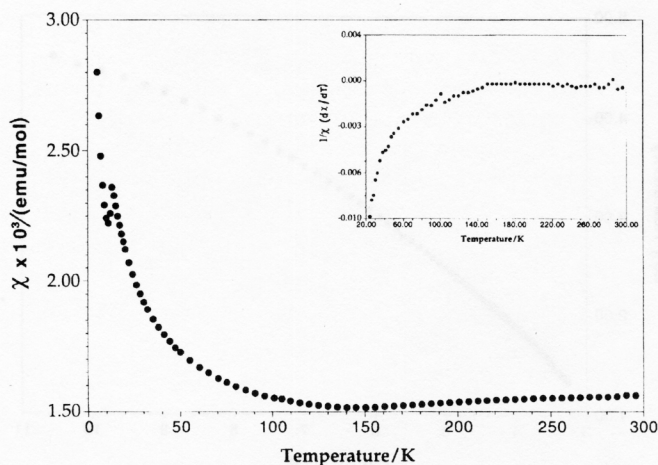
Figure 5. Magnetic susceptibility of $LaMo_5O_8$ as a function of temperature. Inset shows the temperature dependence of $1/\chi$ ($d\chi/dT$).

Even in the case of $LaMo_5O_8$, where no magnetic contribution from the rare earth sub-lattice is expected, a plot of the magnetic susceptibility as a function of temperature (Figure 5) did not show significant anomalies at temperatures in the vicinity of the resistive transitions (~ 150 K). The susceptibility of $LaMo_5O_8$, however, decreases slightly with temperature in the range 300–150 K which is clearly seen when $1/\chi(d\chi/dT)$ as function of temperature is plotted (see inset of Figure 5). The small variations in the magnetic susceptibility with temperature rule out the presence of localized spins on the molybdenum sub-lattice. The phenomenon of decreasing susceptibility with temperature is often attributed to the onset of short-range anti-ferromagnetic correlations. Below 150 K, the susceptibility increases with a small kink ~ 13 K which is observed only in crystals prepared by high temperature solid state reactions. Crystals prepared by electrolytic methods however, did not show this anomalous kink. Although the origin of this kink is not clear yet, it appears likely that it may be related to the defects commonly observed in crystals prepared at high temperatures or a phase transition.

A study of the crystal structure of $LaMo_5O_8$ at 125 K, *i.e.*, below T_c^1, has been carried out recently and showed no significant differences with respect to either structure or bond distances as compared to the room temperature structure.[19] We therefore conclude that the anomalies in the electrical resistivity cannot be attributed to structural changes.

In summary we have successfully synthesized good quality single crystals of several AMo_5O_8 compositions by electrolytic and high temperature solid state reactions and examined their structure, electrical and magnetic properties. Anomalous temperature dependent electrical resistivities were

observed for the AMo_5O_8 compositions with the trivalent rare earth ions, A = La-Sm, Gd while those with A = Ca, Sr, Eu are semiconducting at all temperatures. The higher conductivities observed in the former appear to be consistent with a shorter inter-cluster separation distances while the semi-conductivity in the latter may be related to relatively longer inter-cluster separations. No detectable changes in the magnetic susceptibility or crystal structure were observed to accompany the resistive transitions. These results suggest that the electronic correlations in this class of compounds are quite complex and further studies, in particular detailed electronic band structure calculations would be useful.

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SAŽETAK

Rast kristala i neobična transportna svojstva nekih reduciranih oksida molibdena s bioktaedarskim klusterima Mo10

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Tehnikom rasta iz elektrolitne taline soli pri visokoj temperaturi pripravljeni su monokristali AMo_5O_8(A = Ca, Sr, La-Gd) pogodni za mjerenje električne provodnosti. U strukturi tih spojeva izrazita je prisutnost bioktaedarskih klustera molibdenovih atoma međusobno spojenih paralelno monoklinskoj osi α, tvoreći beskonačne lance. Mjerenjem električke otpornosti u ovisnosti o temperaturi AMo_5O_8 (A = La, Ce, Pr, Nd, Sm) pokazuje anomalne prijelaze metal-poluvodič blizu 180 i 30 K. Otpornosti europijeva i gadolinijeva analoga razlikuju se po tome što je prvi poluvodič, a drugi pokazuje slabu anomalnost kod ~ 110 K. Analozi kalcija i stroncija također su poluvodiči u rasponu (20 – 30) K. Električna provodnost tih faza usko je povezana s međuklusterskom udaljenošću i brojem elektrona u metalnom klusteru. Magnetska susceptibilnost tih spojeva ne pokazuje anomalije na temperaturama koje odgovaraju prijelazima opaženima pri mjerenju električne otpornosti. Magnetska susceptibilnost spoja $LaMo_5O_8$ pokazuje mali pad na grafu $1/\chi$ ($d\chi/dT$) prema T kod ~ 150 K.