The cluster compound In4Ti1.5Mo0.5Mo14O26 containing Mo14 clusters and the new mono- and bi-capped trioctahedral Mo15 and Mo16 clusters: Synthesis, crystal structure, and electrical and magnetic properties.

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Philippe Gall, Thierry Guizouarn, Patrick Gougeon. The cluster compound In4Ti1.5Mo0.5Mo14O26 containing Mo14 clusters and the new mono- and bi-capped trioctahedral Mo15 and Mo16 clusters: Synthesis, crystal structure, and electrical and magnetic properties.. Journal of Solid State Chemistry, 2015, 227, pp.98–103. 10.1016/j.jssc.2015.03.030 . hal-01153431

HAL Id: hal-01153431

https://univ-rennes.hal.science/hal-01153431

Submitted on 4 Nov 2015

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The cluster compound $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ containing Mo_{14} clusters and the new mono- and bi-capped trioctahedral Mo_{15} and Mo_{16} clusters: synthesis, crystal structure, and electrical and magnetic properties.

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Abstract

Single crystals of the new quaternary compound $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ were obtained by solid state reaction. The crystal structure was determined by single-crystal X-ray diffraction. $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ crystallizes in the orthorhombic space group Pbca with unit-cell parameters a = 9.4432(14) Å, b = 11.4828(12) Å, c = 20.299(4) Å and Z = 4. Full-matrix least-squares refinement on F^2 using 3807 independent reflections for 219 refinable parameters resulted in R_1 = 0.0259 and wR_2 = 0.0591. The crystal structure contains in addition to Mo_{14} clusters the first examples of mono- and bi-capped trioctahedral Mo_{14} i.e. Mo_{15} and Mo_{16} clusters. The oxygen framework derives from a stacking along the a direction of close-packed layers with sequence (...ABAC...). The Mo-Mo distances range between 2.6938(5) and 2.8420(6) Å and the Mo-O distances between 1.879(5) and 2.250(3) Å, as usually observed in molybdenum oxide clusters. The indium atoms form In_4^{6+} bent chains with In-In distances of 2.6682(5) and 2.6622(8) Å and the Ti atoms are in highly distorted octahedral sites of oxygen atoms with Ti-O distances ranging between 1.865(4) and 2.161(4) Å. Magnetic susceptibility measurements confirm the presence of Ti^{4+} cations and the absence

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of localized moments on the Mo network. Electrical resistivity measurements on a single crystal of $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ show a semimetallic behavior.

Keywords
Reduced molybdenum oxide, molybdenum clusters, disordered crystal structure, magnetic susceptibility, resistivity measurement.

INTRODUCTION

In solid state chemistry, the octahedral M_6 cluster constitutes the main structural feature of numerous ternary or quaternary chalcogenide, chalcohalide or halide compounds containing transition metals such as Nb, Mo, Ta, W or Re in low oxidation states. Larger clusters which are principally observed with the molybdenum, result either from the uniaxial face- or edge-sharing of Mo_6 octahedra. The former process is observed when the Mo_6 clusters are face-bridged by the ligands such as S, Se and Te and is exemplified by the series of compounds $M_{n-2}Mo_{3n}X_{3n+2}$ (M = Rb, Cs; X = S, Se or Te; n = 3, 4, 5, 6, 7, 8 and 10) containing Mo_9, Mo_{12}, Mo_{15}, Mo_{18}, Mo_{21}, Mo_{24}, Mo_{30} and Mo_{36} clusters [1]. The final stage of this face-sharing condensation is the infinite $|Mo_{6/2}|^1_\infty$ chain found in the quasi-one-dimensional compounds $M_2Mo_6X_6$ (M = Na, K, Rb, Cs; X = S, Se or Te) [2] and $AgMo_6Te_6$ [3]. The edge-sharing condensation of Mo_6 octahedra is observed in the reduced molybdenum oxides where the Mo_6 clusters are edge-bridged by the oxygens. This process leads to columnar bi [4], tri [5], tetra [6] and penta-octahedral [7] oligomers that are observed for example in the series $M_{n-x}Mo_{4n+2}O_{6n+4}$ (n = 2, 3, 4 and 5). The ultimate step of the edge-sharing-condensation process corresponds to the infinite $|Mo_2Mo_{4/2}|^1_\infty$ chain of trans-edge-sharing Mo_6 octahedra that was first observed in $NaMo_4O_6$ [8] and subsequently in the isostructural $M_xMo_4O_6$ (M = K [9], Ba [10], In [11], Sn [12] or Pb) compounds and in the four other structure-types $Sc_{0.75}Zn_{1.25}Mo_4O_7$ [13], $Mn_{1.5}Mo_8O_{11}$ [14], MMo_8O_{10} (M = Li, Zn) [15] and $R_4Mo_4O_{11}$ [16].

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In reduced molybdenum oxides, related clusters to Mo_6 and Mo_{10} were also obtained by capping some faces. For example, the existence of mono- and bi-capped Mo_6 clusters, i.e. Mo_7 and Mo_8, was first mentioned by Leligny et al. in the compound $LaMo_{7.7}O_{14}$ [17] in which both clusters coexist randomly. Subsequently, the Mo_7 and Mo_8 clusters were found in well-ordered structures. The monocapped octahedral Mo_7 unit has been observed up to now either forming infinite chains with bioctahedral Mo_{10} unit or quasi-isolated in the series of compounds $M_4M'_3Mo_{26}O_{48}$ (M = Sr, Eu, Mo'= Al, Ga, Fe) [18]. The bi-capped octahedral Mo_8 cluster was encountered in the two isomeric cis and trans forms in the series of polymorphic compounds RMo_8O_{14} (R = La, Ce, Pr, Nd, Sm) [19]. In addition, the Mo_9 and Mo_{10} clusters formed by capping three or four faces of the octahedral Mo_6 were observed in the modulated compound $EuMo_{7.96}O_{14}$ [20]. More recently, the Mo_{11} and Mo_{12} clusters resulting from the capping of one and two faces of the bioctahedral Mo_{10} cluster were observed in the quaternary reduced molybdenum oxides $M_2Ti_{1.4}Mo_{0.6}Mo_{10}O_{20}$ (M = Sr, Eu) [21]. In the latter compounds, the Mo network is dominated by bioctahedral Mo_{10} clusters, which coexist statiscally with Mo_{11} and Mo_{12} clusters. In this work, we show how the face-capping principle can be extended to trioctahedral Mo_{14} units formed by fusing three Mo_6 clusters with the synthesis, crystal structure, and physical properties of the new compound $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$. This latter compound contains in addition to Mo_{14} clusters the first examples of mono- and bi-capped trioctahedral Mo_{14} clusters i.e. Mo_{15} and Mo_{16} clusters.

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EXPERIMENTAL

Synthesis

$In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ was obtained as single crystals by heating a mixture of In_2O_3, TiO_2, MoO_3 and Mo with the overall composition "In2TiMo4O8" at 1400°C for 96H in a sealed molybdenum crucible. The latter was previously cleaned by heating at about 1500 °C for 15 mn under a dynamic vacuum of about 10^{-5} Torr. The mixture of the starting materials was pressed into a pellet and loaded into a molybdenum crucible which was sealed under a low argon pressure using an arc welding system. The composition of the thus obtained crystals was proved to from single-crystal X-ray diffraction data (see below). Attempts made to prepare a single-phase powder of $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ were unsuccessful (only approximate yields of 15 to 25 % were obtained).

Single Crystal X-ray Study

A black crystal of approximate dimensions 0.196x0.037x0.025 mm^3 was employed in the intensity data collection conducted with a Nonius KappaCCD diffractometer. The COLLECT program package [22] was used to establish the angular scan conditions (ϕ and ω scans) used in the data collection. A total of 317 frames were collected with a frame width of 1.10° and an exposure time of 66 s. Reflection indexing, Lorentz-polarization correction, peak integration, and background determination were performed by using the EvalCCD program [23]. An absorption correction (min/max transmission=0.5744/0.6063) was applied using the description of the crystal faces [24]. Of 54877 reflections collected in the 3.56–36.2 θ range, 5281 were independent (Rint=0.0502). Analysis of the data revealed that the systematic absences (0kl) k = 2n + 1, (h0l) l = 2n + 1, and (hk0) h = 2n + 1 were consistent with the orthorhombic space group Pbca. The initial positions for 7 molybdenum atoms forming a Mo_{14} cluster and some of the oxygen atoms as well as for the indium atom were determined with the direct methods program SIR-97 [25] in the Pbca space group. A subsequent difference Fourier synthesis revealed the remaining oxygen atoms and two peaks at 0.42 Å from each other. As this situation was similar to that encountered in the $M_2Ti_{1.4}Mo_{0.6}Mo_{10}O_{20}$ (M = Sr, Eu) compounds, the peak the closest to the Mo_{14} cluster was assigned to a Mo atom (Mo8) and the peak farthest to a Ti atom. Subsequent refinements of this model included the

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atomic position and anisotropic displacement parameters for all atoms as well as the site occupancy factors for the Mo8 and Ti atoms. The later ones which were first refined freely converged to 0.25(2) and 0.74(3), respectively. Consequently, in the final refinement the sum the site occupancy factors of the Mo8 and Ti atoms was fixed to unity. A calculation of the two Mo8 and Ti probability density functions shows that they do not overlap and that for both atoms the position of the density maximum coincides with the refined position. The final full-matrix least squares refinement on F^2 which was based on a model including the positional and anisotropic displacement parameters for all atoms and site occupancy factors for Ti and Mo8 led to the values of R = 0.0259 and wR = 0.0591 for 3807 reflections with $I > 2\sigma(I)$ and to the stoichiometry $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$. All structure refinements and Fourier syntheses were carried out using SHELXL-97 [26]. Reconstructed reciprocal space sections did not show any superlattice reflexions or diffuse lines that preclude a possible ordering of the different clusters. Crystallographic data and X-ray structural analysis for the $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ compound are summarized in Table 1. The final atomic coordinates, and the equivalent isotropic displacement parameters are gathered in Table S1, and selected interatomic distances are listed in Table S2 in the Supporting information. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD- 428999.

Electrical Resistivity Measurements

The study of the temperature dependence of the electrical resistivity was carried out on a single crystal of $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ using a conventional ac four-probe method with a current amplitude of 0.1 mA. Contacts were ultrasonically made with molten indium on the single crystal. The ohmic behavior and the invariance of the phase were checked during the different measurements at low and room temperature.

Magnetic susceptibility measurements.

Susceptibility data were collected on a batch of single crystals (ca. 40 mg) using a Quantum Design SQUID magnetometer between 2 K and 400 K and at an applied field of 0.1 T.

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RESULT AND DISCUSSION

Figure 1 shows the projections of the crystal structures of $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ and $M_2Ti_{1.4}Mo_{0.6}Mo_{10}O_{20}$ (M = Sr, Eu) on the (b, c) plane. From these figures, the structural relationship between the two structure types, which are both described in the space group Pbca, is evident.

The main structural feature of $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ is the presence of trioctahedral edge-sharing Mo_{14}, and mono- and bi-capped Mo_{15} and Mo_{16} clusters which coexist statistically due to the partial occupancy of the capping site Mo8 shown in light blue in Figure 2a. The Fig. 3 shows a perspective view of the crystal structure of $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ along the b axis. As in the $M_2Ti_{1.4}Mo_{0.6}Mo_{10}O_{20}$ compounds, the oxygen framework derives from a stacking along the a direction of close-packed layers with sequence (...ABAC...). Projections of the four layers onto the (100) plane are given in Fig. 4. While the B (y ~ 0.25) and C (y ~ 0.75) layers are entirely occupied by oxygen atoms (Figures 4b and 4d, respectively) and have the composition [O32], in the A layers (y ~ 0.0 and 0.5) one fourth of the oxygen atoms are substituted by the In ions and one eighth are missing in an ordered way (Figures 4a and 4c, respectively). Consequently, the latter layers can be formulated [O20In8□4] where □ stands for the oxygen vacancies. Within the O network, 7/13 of the octahedral interstices are occupied by the Mo1 to Mo7 atoms which form trioctahedral Mo_{14} clusters and one thirteenth statistically by the capping Mo8 and Ti atoms. The trioctahedral Mo_{14} cluster which results from the metal-edge condensation of three octahedral Mo_6-type clusters is similar to those previously observed in the compounds $T1_{1.6}Sn_{1.2}Mo_{14}O_{22}$ [5a and b], $K_3Mo_{14}O_{22}$, $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$, and $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ [5c]. It is also interesting to note that the vacancies in the A layers correspond to the center of the octahedra forming the Mo_{14} clusters. In the latter, the Mo-Mo distances range between 2.6938(5) and 2.8420(6) Å and the Mo-O distances between 1.879(5) and 2.250(3) Å, as usually observed in molybdenum oxide

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clusters. The shortest distances between the Mo_{14} cluster and the capping Mo8 atom agree well with the existence of metallic bonds: 2.798(10) Å for Mo8-Mo1, 2.864(10) Å for Mo8-Mo2 and 2.802(10) Å for Mo8-Mo3 (see Fig. 2a), leading thus to the formation of monocapped and bicapped bioctahedral Mo_{15} and Mo_{16} clusters (Fig. 2b and 2c). The latter clusters which are new to solid-state chemistry coexist thus randomly with the Mo_{14} clusters in $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$. Moreover, it should be noted that the distances between the Mo_{14} clusters and the Ti atoms which are greater than 3.15 Å preclude the presence of heteronuclear clusters such as $Mo_{14}Ti$ or $Mo_{14}Ti_2$ as previously mentioned for the $M_2Ti_{1.4}Mo_{0.6}Mo_{10}O_{20}$ (M = Sr, Eu) compounds. The Ti atoms are surrounded by six oxygen atoms forming a highly distorted octahedron (Figure 6). The Ti-O distances range between 1.865(4) and 2.161(4) Å with a mean value of 2.01 Å closed to the value of 2.00 Å calculated from the sum of the ionic radii of O^{2-} and Ti^{4+} in octahedral coordination according to Shannon and Prewitt [27]. From the Ti-O bond lengths, the valence of the Ti atoms calculated by using the relationship of Brown and Wu [$(s = (dTi\text{-}O /1.806)^{-5.2})$] [28] is +3.7, suggesting a number of oxidation of +4. This confirms the tetravalence of the titanium that was already proved by XPS measurements in $Eu_2Ti_{1.4}Mo_{0.6}Mo_{10}O_{20}$. Another interesting structural feature in $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ is the presence of indium forming an In_4^{6+} bent chain shown in Fig. 5. The two indium distances In1-In2 and In2-In2 are quite comparable, 2.6682(5) and 2.6622(8) Å, respectively. These distances are also of the same order as those observed for the In_5^{7+} chains found in $In_5Mo_{18}O_{28}$ [29] and $In_{11}Mo_{40}O_{62}$ [30] which are comprised between 2.616 and 2.665 Å and for the In_6^{8+} chains in $In_3Mo_{11}O_{17}$ and $In_{11}Mo_{40}O_{62}$ which range from 2.645 to 2.689 Å.

An astonishing fact is the very close stoichiometry of the Ti and Mo capping atoms found in the $M_2Ti_{1.4}Mo_{0.6}Mo_{10}O_{20}$ (M = Sr, Eu) compounds and $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ which is not

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understood to date. An intriguing question is also why any variation in the ratio Mo/Ti led to multiphasic products in the case of the $M_2Ti_{1.4}Mo_{0.6}Mo_{10}O_{20}$ (M = Sr, Eu) compounds?

Magnetic Properties. The temperature dependence of the molar magnetic susceptibility of $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ is shown in Figure 6. The susceptibility is nearly temperature-independent in the range 100-300 K with χ_{RT} = 3.4 10-3 emu/mol. This indicates clearly the absence of localized moments on the different Mo clusters as well as on the Ti atoms reflecting their tretravalence as previously observed in the $M_2Ti_{1.4}Mo_{0.6}Mo_{10}O_{20}$ (M = Sr, Eu) series. The low-temperature upturn results probably from small amounts of paramagnetic impurities often present in the starting reactants.

The electrical resistivity of a single-crystal of $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ as a function of the temperature is shown in Figure 7. $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ presents a poorly metallic behavior with a transition to a semiconducting state below 50 K and a room temperature resistivity value of 5 10^{-3} Ωcm. The poor metallic character of this compound probably results from the positional disorder of the clusters as previously observed for the $M_2Ti_{1.4}Mo_{0.6}Mo_{10}O_{20}$ (M = Sr, Eu) compounds.

CONCLUSION

In summary, the novel reduced molybdenum oxide $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ has been synthesized by solid-state reaction at 1400°C for 96h in sealed molybdenum crucibles. Its crystal structure contains in addition to Mo_{14} clusters the first examples of mono- and bi-capped trioctahedral Mo_{14} that is Mo_{15} and Mo_{16} clusters. Magnetic susceptibility measurements confirm the presence of Ti^{4+} cations. Electrical resistivity measurements on a single crystal of $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ show a semimetallic behavior. The existence of Mo_{18} and Mo_{22} clusters in $Ba_3Mo_{18}O_{28}$ [6] and $In_6Mo_{22}O_{34}$ [7], respectively, lets us to envisage that

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the mono and bicapped principle can be extended to the latter two clusters leading thus to Mo_{19}, Mo_{20}, Mo_{23} and Mo_{24} clusters in compounds in which the Mo-Ti-O networks would have the compositions $(Ti_{1.5}Mo_{0.5})Mo_{18}O_{32}$ and $(Ti_{1.5}Mo_{0.5})Mo_{22}O_{38}$, respectively.

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Table 1. X-ray Crystallographic and Experimental data for $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$.

Empirical formula	$In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$
Formula weight	2339.22
Temperature	293(2) K
Wavelength	0.71069 A
Crystal system, space group	orthorhombic, Pbca
Unit cell dimensions	a = 9.4432(14) Å, b = 11.4828(12) Å, c = 20.299(4) Å
Volume	2201.1(6) $Å^3$
Z, Calculated density	4, 7.059 Mg/m^3
Absorption coefficient	12.662 mm^{-1}
F(000)	4186
Crystal size	0.050 x 0.058 x 0.093 mm
Theta range for data collection	3.55 to 31.99 deg.
Limiting indices	-14<=h<=14, -17<=k<=15, -30<=l<=28
Reflections collected / unique	43390 / 3807 [R(int) = 0.0465]
Completeness to theta = 31.99	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3807 / 0 / 219
Goodness-of-fit on F^2	1.140
Final R indices [I>2σ(I)]	R1 = 0.0259, wR2 = 0.0591
R indices (all data)	R1 = 0.0316, wR2 = 0.0620
Extinction coefficient	0.00044(2)
Largest diff. peak and hole	1.829 and -2.241 $e.Å^{-3}$

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FIGURE CAPTIONS

Figure 1. Projections of the crystal structures of (a) $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ and (b) $M_2Ti_{1.4}Mo_{0.6}Mo_{10}O_{20}$ (M = Sr, Eu) compounds on the (b, c) plane.

Figure 2. The (a) Mo_{14}, (b) Mo_{15}, and (c) Mo_{16} clusters with their oxygen and titanium environnements.

Figure 3. Perspective view of the crystal structure of $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ along the *b* axis.

Figure 4. Arrangement of the oxygen and indium atoms within the *ABAC* layers.

Figure 5. The tetrameric cation In_4^{6+} with its oxygen environment.

Figure 6. The temperature dependence of the molar magnetic susceptibility of $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$.

Figure 7. Temperature dependence of the electrical resistivity for $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$.

TABLE CAPTIONS

Table 1. X-ray Crystallographic and Experimental data for $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$.

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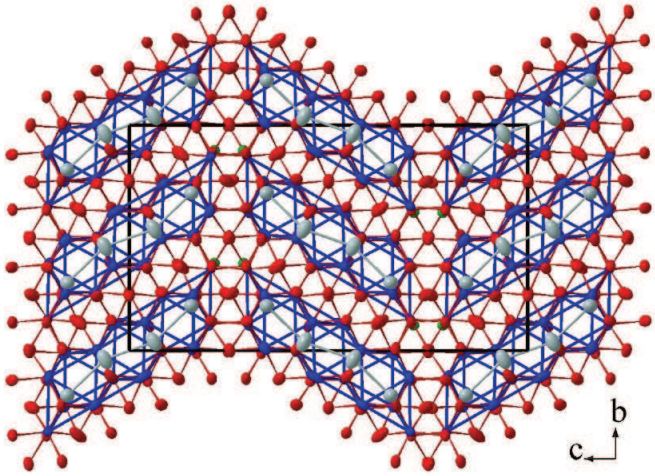
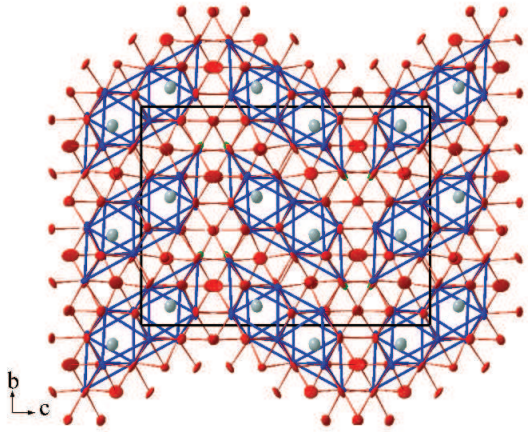


(a)



(b)

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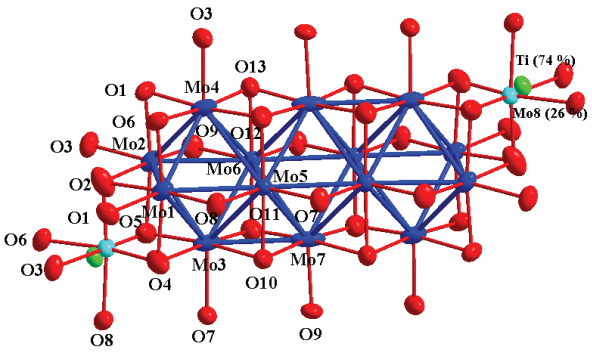
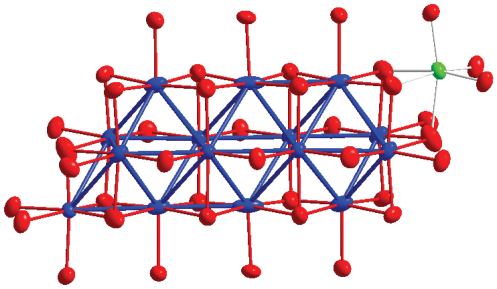


(a)



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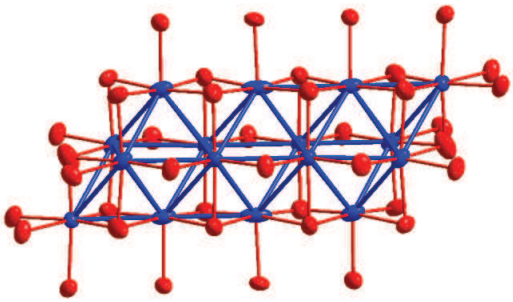
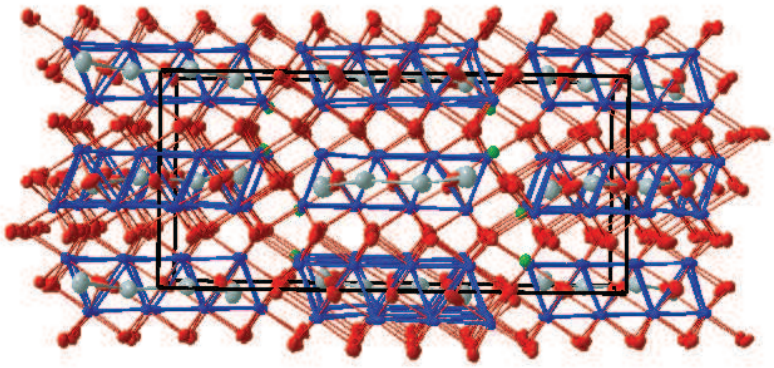


(c)

Figure 2. The (a) Mo_{14}, (b) Mo_{15}, and (c) Mo_{16} clusters with their oxygen and titanium environnements.



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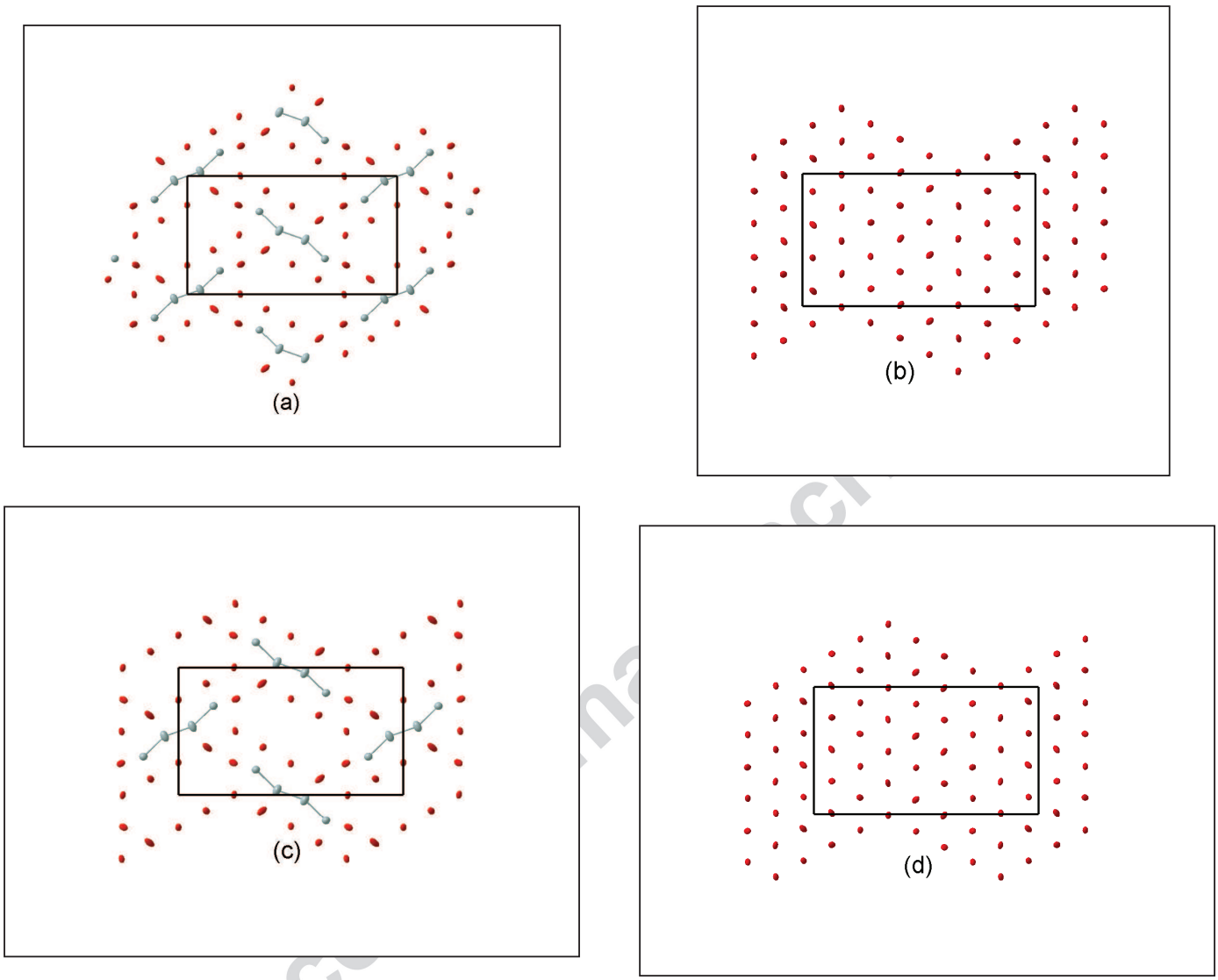

Figure 4. Arrangement of the oxygen and indium atoms within the *ABAC* layers.

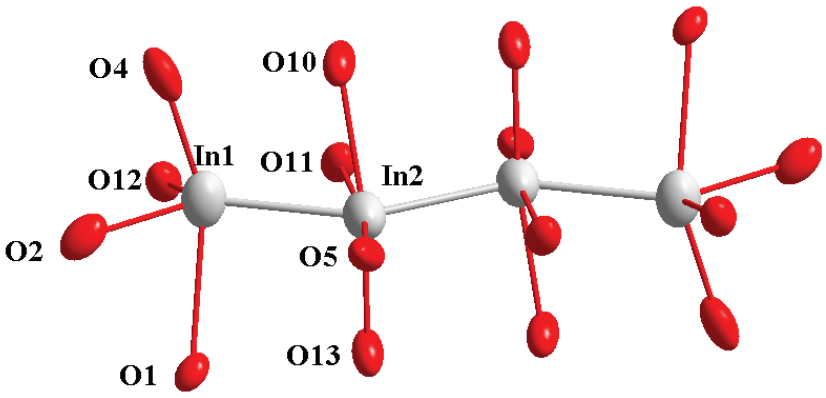

Figure 5. The tetrameric cation In_4^{6+} with its oxygen environment.

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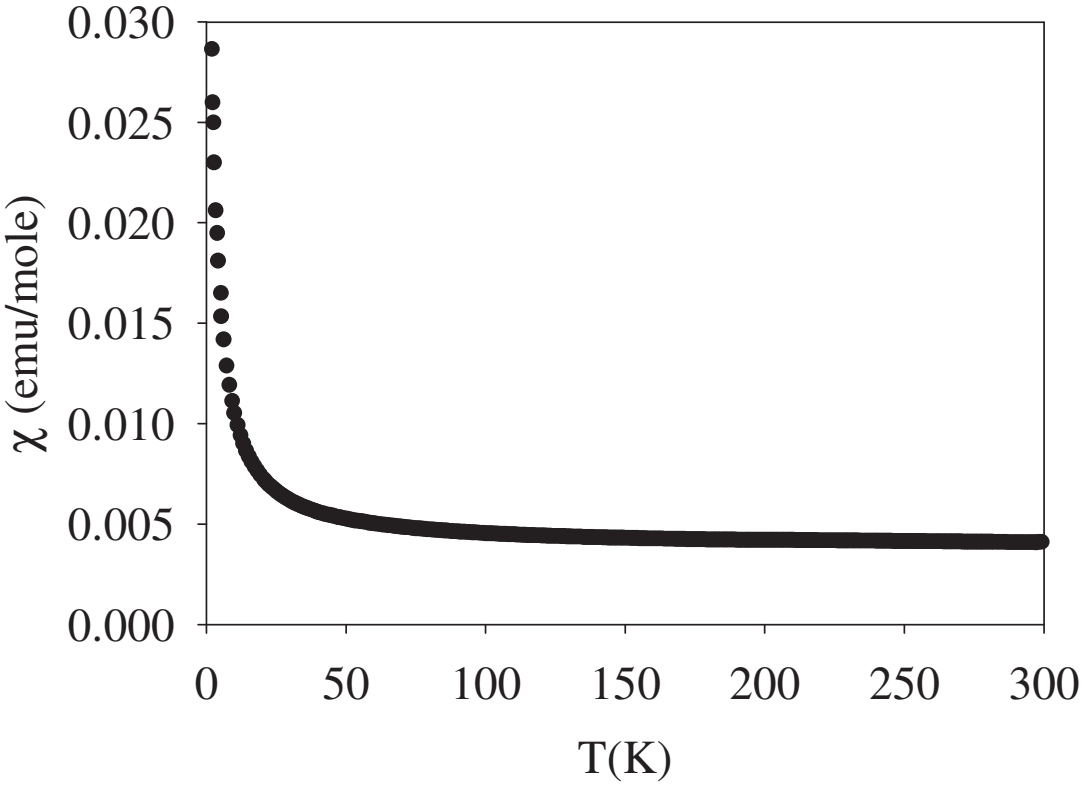

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Figure 6. The temperature dependence of the molar magnetic susceptibility of $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$.

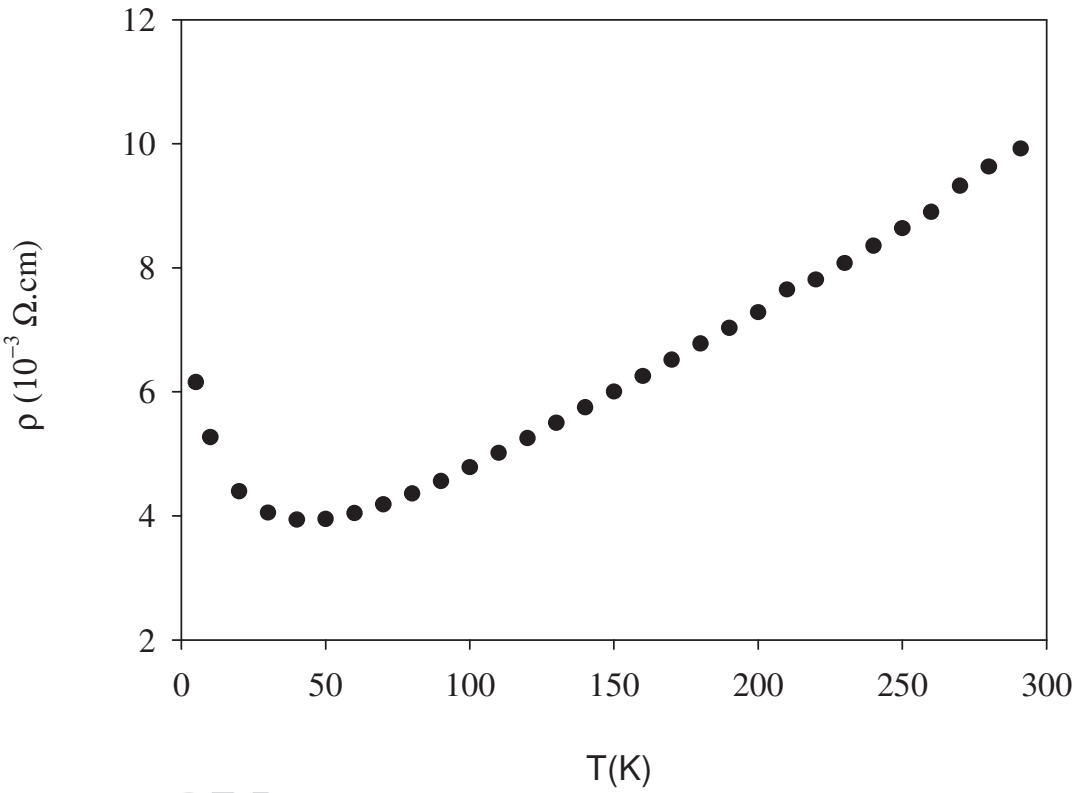
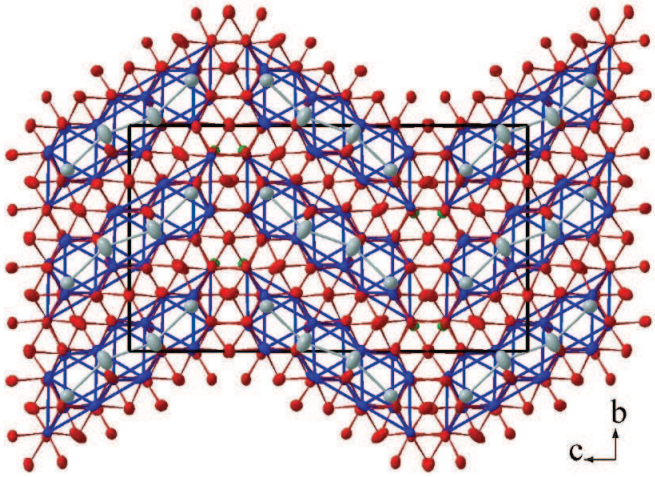


Figure 7. Temperature dependence of the electrical resistivity for $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$.

Synopsis

The novel reduced molybdenum oxide $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ has been synthesized by solid-state reaction at 1400°C for 96h in sealed molybdenum crucibles. Its crystal structure contains in addition to Mo_{14} clusters the first examples of mono- and bi-capped trioctahedral Mo_{14} i.e. is the Mo_{15} and Mo_{16} clusters. Magnetic susceptibility measurements confirm the presence of Ti^{4+} cations and the absence of localized moments on the Mo network. Electrical resistivity measurements on a single crystal of $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ show a semimetallic behavior.



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The cluster compound $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ containing Mo_{14} clusters and the new mono- and bi-capped trioctahedral Mo_{15} and Mo_{16} clusters: synthesis, crystal structure, and electrical and magnetic properties.

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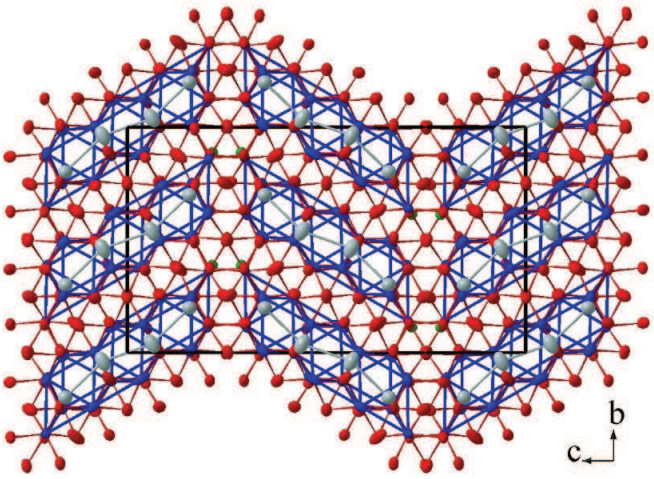
We present here the synthesis, the crystal structure, and the electrical and magnetic properties of the new compound $In_4Ti_{1.5}Mo_{0.5}Mo_{14}O_{26}$ in which Mo_{14} clusters coexist statistically with mono- and bi-capped trioctahedral Mo_{14} that is Mo_{15} and Mo_{16} clusters.



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Highlights

. Single crystals of In4Ti1.5Mo0.5Mo14O26 were obtained by solid state reaction.

. The crystal structure contains Mo14, Mo15 and Mo16 clusters.

. The indium atoms form $In4^{6+}$ bent chains.

. Poorly metallic behavior.

. Absence of localized moments on the Mo network as well as on the Ti atoms.

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