High Pressure Transformation of $La_4Cu_3MoO_{12}$ to a Layered Perovskite

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High pressure (HP) can facilitate the synthesis of metastable superconductors because it stabilizes the perovskite structure. In this paper, we describe the HP synthesis of a new copper-rich layered perovskite, $La_4Cu_3MoO_{12}$, which is isotypic with La_2CuSnO_6.[1] When synthesized at ambient pressure (AP), it forms a structure with remarkably low and unusual coordination of the constituents, which after treatment at high pressure and high temperature adopts the new perovskite structure that contains unmixed copper−oxygen planes linked by mixed copper/molybdenum−oxygen planes.

Unlike previous layered perovskites synthesized under pressure,[2] $La_4Cu_3MoO_{12}$ also exists as a polymorphic ambient pressure phase.[3] The complete AP series, $Ln_4Cu_3MoO_{12}$ (Ln = Y, Pr, Nd, Sm−Tm), can be synthesized and will be reported in subsequent papers. The X-ray powder diffraction (XPD) pattern of AP $La_4Cu_3MoO_{12}$ (Figure 1a) is similar to that of $InMO_3$ (M = Mn, Fe, Ga)[4] ($P6_3/mmc$ space group (No.194) $a = 3.95303(5)$ Å, $c = 10.9997(2)$ Å, $V = 148.9$ Å^3, and $Z = {}^1/_2$.[5] The average structure consists of sheets of lanthanum cations between layers of corner-sharing $(Cu/Mo)O_{2+3/3}$ trigonal bipyramids (Figure 2a)). The Cu and Mo cations are distributed on trigonal bipyramidal sites (D_{3h} symmetry) that are oxygen-bridged to three neighboring sites. The two remaining apical oxygen atoms are bonded to the lanthanum cations. However, the XPD data clearly show a superstructure (Figure 1a) which indicates that the structure is a homeotype of $InMO_3$. Electron microscopy and neutron diffraction studies are in progress to confirm the precise structure.

The AP lanthanum phase contains large metal cations, small metal cations, and oxygen anions in a ratio of 1:1:3, the same as perovskite. The low coordination of the Cu, Mo, and La ions of 5, 5, and 6+2, respectively, observed in the AP phase, makes it a prime candidate for a high pressure study because pressure increases the coordination preferences of the constituent ions. When the ambient phase is subjected to 6 GPa and 1200° C for 30 min in a cubic anvil-type HP apparatus and removed from the cell,[6] a new perovskite phase is found which contains unmixed copper oxygen layers. $LnAlO_3$ (Ln = Y, Eu−Er)[7] is a previously reported example of a simple ABO_3 series which transforms under pressure from a hexagonal phase to a perovskite. However, $La_4Cu_3MoO_{12}$ is the first example of a AP → HP transformation for an $A(B'B'')O_3$ type compound. Transformation also occurs with $Pr_4Cu_3MoO_{12}$ and $Nd_4Cu_3MoO_{12}$, and studies are continuing on the other members of the series. On the basis of the Rietveld refinement, the HP lanthanum phase crystallizes in the $P2_1/m$ space group (No. 11) with $a = 8.2354(5)$ Å, $b = 7.7809(4)$ Å, $c = 7.8572(4)$ Å, $\beta = 92.155(2)°$, $V = 503.1$ Å^3, $Z = 2$ (Figure 1b).[5] Differential thermal analysis and XPD reveals that it reverts to the AP phase at around 800° C in air. As described by Anderson et al.,[8] a monoclinic cell of approximately $2a_p \times 2a_p \times 2a_p$, where a_p is the cubic cell parameter of simple perovskite, suggests that the phase is layered. Specifically, the structure consists of alternating layers of corner-sharing $CuO_{6/2}$ octahedra and corner-sharing $(Cu/Mo)O_{6/2}$ octahedra (Figure 2b). In the copper layers, the Cu−O in-plane bond distances range from 1.94(3) Å to 2.11(3) Å, whereas the apical bond distances are 2.26(3) Å and 2.41(3) Å. In the mixed layers, however, the *B*-cations coordinate with longer in-plane (Cu/Mo)−O bond lengths ranging from 2.09(4) Å to 2.17(2) Å, and shorter apical bond lengths of 1.83(3) Å and 1.99(3) Å. These opposite Jahn−Teller distortions cause a mismatch between adjacent layers which forces them to buckle, and as expected, the $(Cu/Mo)O_{6/2}$ layers buckle more than the $CuO_{6/2}$ layers. The average in-plane (Cu/Mo)−O−(Cu/Mo) bond angle is 133(3)° while the average in-plane Cu−O−Cu bond angle is just 162(1)°.

In other layered double perovskite structures, the buckling of the cuprate planes is understood to result from the size mismatch between the copper and non-copper *B*-cations.[2] In layered Ln_2CuSnO_6 (Ln = La, Pr, Nd, Sm) for example, Sn^{IV} is markedly larger than Cu^{II} and maintains a near octahedral coordination environment.[1] The size mismatch causes both the $SnO_{6/2}$ and $CuO_{6/2}$ layers to buckle with an average in-plane Sn−O−Sn bond angle of 141(3)° and an average in-plane Cu−O−Cu bond angle of 164(3)°.[1] These angles compare with those of HP $La_4Cu_3MoO_{12}$ even though Mo^{VI} is considerably smaller than Sn^{IV}. The average Cu−O and Cu/Mo−O bond lengths are nearly equal, but the in-plane bond distances of adjacent layers differ because of the different orientations of the Jahn−Teller axes.

The susceptibility data of the HP lanthanum sample reflect the magnetism of the $CuO_{6/2}$ planes without strong interference from the La ions.[9] In Figure 3, two antiferromagnetic transitions are observed at $T_{N1} = 280°$ K and $T_{N2} = 25°$ K.[10] The first is attributed to the 2D antiferromagnetic ordering, similar to that which was observed in Y_2CuO_4,[9] within the cuprate plane and occurs at even higher temperatures than in the layered perovskites, Ln_2CuSnO_6 (Ln = La, Pr, Nd, Sm where 235 K > T_{N1} > 200 K).[2] The second can be assigned to a weak 2D antiferromagnetic ordering within the mixed layers which takes place via super−super Cu−O−Mo−O−Cu exchanges. In the $P2_1/m$ space group, which has been confirmed by electron diffraction, the 2b and the 2d Wyckoff positions are the two crystallographically independent

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(1) Anderson, M. T.; Poeppelmeier, K. R. *Chem. Mater.* **1991**, *3*, 476−482.

(2) Azuma, M.; Kimori, S. and Takano, M. *Chem. Mater.*, accepted.

(3) The ambient pressure $La_4Cu_3MoO_{12}$ phase was prepared by mixing CuO (99.99%), MoO_3 (99.99%), and $LaO_{1.5}$ in stoichiometric ratios. The mixture was then pressed into pellets, fired at 1025° for 4 days with two intermittent grindings, and finally air quenched.

(4) (a) Giaquinta, D. M.; zur Loye, H.-C. *J. Am. Chem. Soc.* **1992**, *114*, 10952−10953. (b) Giaquinta, D. M.; Davis, W..M.; zur Loye, H.-C. *Acta Crystallogr.* **1994**, *C50*, 5−7. (c) Shannon, R. D.; Prewitt, C. T. *J. Inorg. Nucl. Chem.* **1968**, *30*, 1389−1398.

(5) X-ray powder diffraction data for the La compounds were collected every 0.02° for $3° < 2\theta < 120°$ on a Rigaku RINT 2000 diffractometer equipped with monochromator for Cu $K\alpha_1$ radiation. The refinements of both structures were performed using the Rietveld analysis program, FULLPROF (Rodriguez-Carvajal, J., FULLPROF version 3.1, January, 1996; ILL, France), and led to $R_p = 6.60\%$, $R_{wp} = 9.60\%$, $R_{exp} = 6.94\%$, $\chi^2 = 1.91$, $R_{bragg} = 6.63\%$, $R_f = 5.29\%$ for the ambient phase, and $R_p = 3.83\%$, $R_{wp} = 5.55\%$, $R_{exp} = 4.77\%$, $\chi^2 = 1.35$, $R_{bragg} = 8.18\%$, $R_f = 7.31\%$ for the high-pressure phase.

(6) Azuma, M.; Hiroi, Z.; Takano, M.; Bando, Y.; Takeda, Y. *Nature* **1992**, *356*, 775−776.

(7) (a) Bertaut, F.; Mareschal, J. *Compt. Rend.* **1963**, *257*, 867−870. (b) Geller, S.; Wood, E. A. *Acta Crystallagr.* **1956**, *9*, 563−568. (c) Geller, S.; Bala, V. B. *Acta Crystallagr.* **1956**, *9*, 1019−1025. (d) Schneider, S. J.; Roth, R. S.; Waring, J. L. *J. Res. Natl. Bur. Stand. (U.S.)* **1961**, *65A*, 345−374.

(8) Anderson, M. T.; Greenwood, K. B.; Taylor, G. A.; Poeppelmeier, K. R. *Prog. Solid State Chem.* **1993**, *22*, 197−233.

(9) Okada, H.; Takano, M.; Takeda, Y. *Phys. Rev. B.* **1990**, *42*, 6813−6816.

(10) Susceptibility measurements for both phases were performed on a Quantum Design MPMS SQUID magnetometer from 5 to 350 K in an external field of 1000 Oe.

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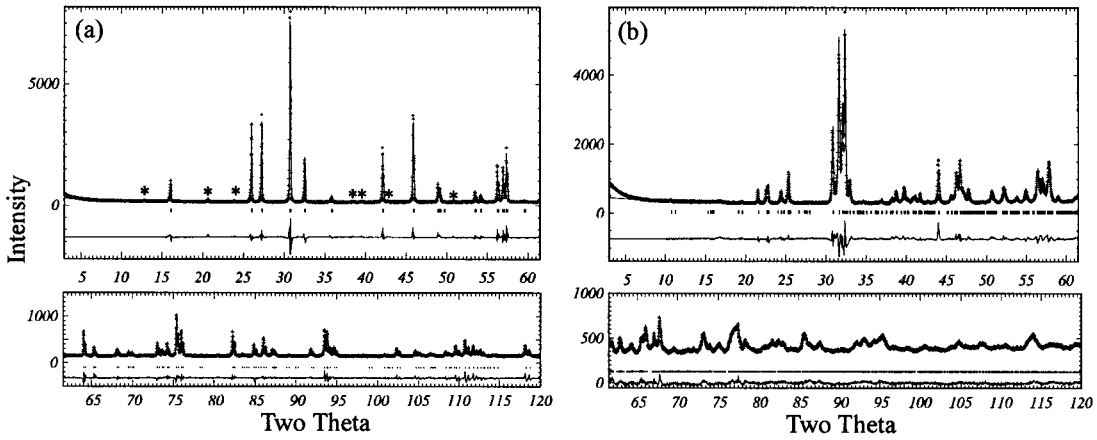

Figure 1. (a) XPD and Rietveld refinement of AP $La_4Cu_3MoO_{12}$. Supercell peaks, indicated with a star, can be described by either a hexagonal or orthorhombic supercell. (b) XPD and Rietveld refinement of HP $La_4Cu_3MoO_{12}$.

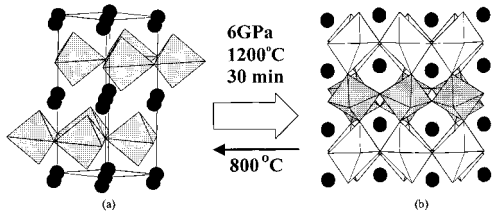

Figure 2. High-pressure transformation of AP $La_4Cu_3MoO_{12}$ to a layered perovskite. $CuO_{6/2}$ polyhedra are white, whereas $(Cu/Mo)O_{6/2}$ and $(Cu/Mo)O_{2+3/3}$ polyhedra are gray. Black circles are lanthanum.

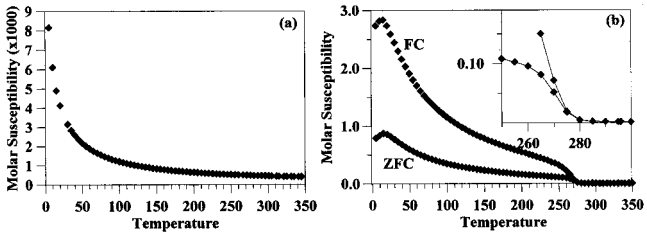

Figure 3. (a) Zero field cooled molar (per copper ion) susceptibility data for AP $La_4Cu_3MoO_{12}$, in contrast with (b) Zero field cooled (ZFC) and field cooled (FC) molar susceptibility data for HP $La_4Cu_3MoO_{12}$.

sites in the mixed plane. These sites are arranged in rows along the *b* axis, owing to the set of mirror planes perpendicular to the *b* axis. According to the Rietveld refinement, the copper and molybdenum cations are arranged randomly rather than in rows for this quenched sample.

The Goldschmidt tolerance factor[11,12] (*t*), which is calculated based on the assumption that the constituent ions are spherical, predicts that the perovskite structure forms for $0.80 < t < 1.00$.[13] For copper to incorporate into the perovskite structure, the local site symmetry of the d^9 Jahn−Teller Cu^{II} ion must be compatible with the translational symmetry of the lattice. The following series of fully oxygenated perovskites demonstrate that the presence of octahedrally coordinated Cu^{II} frustrates the formation of perovskite. La_2CuSnO_6 ($t = 0.89$) forms perovskite at ambient pressure, whereas Pr_2CuSnO_6 ($t = 0.88$) and Nd_2CuSnO_6 ($t = 0.87$) form perovskite only under pressure.[1] The analogous copper molybdate series has 50% more copper than the stannates, and $La_4Cu_3MoO_{12}$ ($t = 0.91$), $Pr_4Cu_3MoO_{12}$ ($t = 0.90$), and $Nd_4Cu_3MoO_{12}$ ($t = 0.89$) all form perovskite only under pressure.

Copper is clearly the essential structural and electronic element in layered double perovskites (i.e., the Ln_2CuSnO_6 and $Ln_4Cu_3MoO_{12}$ families) and high-temperature superconductors (HTSCs). In the layered stannates and molybdates, the $CuO_{6/2}$ octahedra distort and organize into layers at the expense of *B*-cation entropy. These Cu−O planes possess the connectivity of known HTSCs but they buckle heavily. Almost all HTSCs possess nearly flat cuprate planes consisting of oxygen deficient $CuO_{5/2}$ and $CuO_{4/2}$ units which promote charge delocalization in the plane. Barium substitution for lanthanum in La_2SnCuO_6 to make $La_2Ba_2Cu_2Sn_2O_{11}$ introduces oxygen vacancies and flattens out the cuprate planes.[14] A similar tactic may help to flatten out the cuprate planes in HP $La_4Cu_3MoO_{12}$ as well. The HP title phase has the advantage of additional Cu^{II} in the blocking layers to facilitate charge transfer between the Cu−O planes. It is clear that molybdenum contributes uniquely to the nature of these phases as well because $Ln_4Cu_3WO_{12}$ (Ln = La, Pr, Nd, Gd) does not form under similar ambient or high-pressure conditions.

In conclusion, the new copper-enriched, layered perovskite, $La_4Cu_3MoO_{12}$, has been synthesized under high pressure from a polymorphic phase. Ln_2CuTiO_6 forms perovskite for Ln = La−Gd but forms a hexagonal phase for Ln = Tb−Lu.[8] On the basis of the present work, we suggest that members of the latter hexagonal series would be good candidates for high-pressure transformation into perovskite structures with cuprate planes. Also, other high valent *B*-cations could be utilized as well to make more Cu-rich perovskite-type compounds such as $Ln_3Cu_2M^{V}O_9$, $Ln_4Cu_3M^{VI}O_{12}$, and $Ln_5Cu_4M^{VII}O_{15}$. Most importantly, modification of the *A*-cation constituency to include mixed aliovalent and heterovalent species should further stabilize Cu-rich perovskite structures and create oxygen vacancies or introduce hole-charge carriers.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positions, bond lengths, and selected bond angles based on the Rietveld refinement for both the AP and HP $La_4Cu_3MoO_{12}$ phases (5 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(11) Goldschmidt, V. M. *Mater. −Nutrv. K.* **1926**, *2*, 117.

(12) Tolerance factors calculated as follows, $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$; $r_A = r(Ln^{III}$, 8-coordinate), $r_O = 1.35$ Å, $r_B = r_{avg}(B^{II,IV,VI}$, 6-coordinate), and $r(Cu^{II}) = 0.60$ Å. Ionic radii from Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751−767.

(13) Giaquinta, D. M.; zur Loye, H.-C. *Chem. Mater.* **1994**, *6*, 365−372.

(14) Anderson, M. T., Poeppelmeier, K. R., Zhang, J.-P., Fan, H.-J., Marks, L. D. *Chem. Mater.* **1993**, *4*, 1305−1313.