High Pressure Transformation of La₄Cu₃MoO₁₂ 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, La₄Cu₃MoO₁₂, which is isotypic with La₂CuSnO₆. 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 unpermixed copper–oxygen planes linked by mixed copper/molybdenum–oxygen planes.

Unlike previous layered perovskites synthesized under pressure, La₄Cu₃MoO₁₂ also exists as a polymorphic ambient pressure phase. The complete AP series, Ln₄Cu₃MoO₁₂ (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 La₄Cu₃MoO₁₂ (Figure 1a) is similar to that of InMO₃ (M = Mn, Fe, Ga)⁴ of AP La₄Cu₃MoO₁₂ (Figure 1a) is similar to that of InMO₃ (M = Mn, Fe, Ga)⁴ (P6/mmc space group (No. 194) a = 3.95303(5) Å, c = 10.9997(2) Å, V = 148.9 Å³, and Z = 1/2). ⁵ The average structure consists of sheets of lanthanum cations between layers of corner-sharing (Cu/ Mo)O₆/2 trigonal bipyramids (Figure 2a). The Cu and Mo cations are distributed on trigonal bipyramidal sites (D₃h symmetry) that are oxygen-bridged to 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 homotype of InMO₃. 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 cations: the high 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. LnAlO₃ (Ln = Y, Eu–Er) is a previously reported example of a simple ABO₃ series which transforms under pressure from a hexagonal phase to a perovskite. However, La₄Cu₃MoO₁₂ is the first example of a AP → HP transformation for an A(B'O₃)₂ type compound. Transformation also occurs with Pr₄Cu₅MoO₁₂ and Nd₄Cu₅MoO₁₂, 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 P2₁/m space group (No. 11) with a = 8.2354(5) Å, b = 7.7809(4) Å, c = 7.8572(4) Å, β = 92.155(2)°, V = 503.1 Å³, 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 2aₚ × 2aₚ × 2aₚ, where aₚ is the cubic cell parameter of simple perovskite, suggests that the phase is layered. Specifically, the structure consists of alternating layers of corner-sharing CuO₆/2 octahedra and corner-sharing (Cu/Mo)O₆/2 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)O₆/2 layers buckle more than the CuO₆/2 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.⁴ In layered Ln₄CuSnO₆ (Ln = La, Pr, Nd, Sm) for example, SnIV is markedly larger than CuII and maintains a near octahedral coordination environment.¹ The size mismatch causes both the SnO₆/2 and CuO₆/2 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 La₄Cu₃MoO₁₂ even though MoV is considerably smaller than SnIV. 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 CuO₆/2 planes without strong interference from the La ions.⁹ In Figure 3, two antiferromagnetic transitions are observed at TN₁ = 280 K and TN₂ = 25 K.¹⁰ The first is attributed to the 2D antiferromagnetic ordering, similar to that which was observed in Y₂CuO₄,⁹ within the cuprate plane and occurs at even higher temperatures than in the layered perovskites, Ln₄CuSnO₆ (Ln = La, Pr, Nd, Sm where 235 K < TN₁ < 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 P2₁/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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(3) The ambient pressure La₄Cu₃MoO₁₂ phase was prepared by mixing CuO (99.99%), MoO₃ (99.99%), and La₂O₃ in stoichiometric ratios. The mixture was then pressed into pellets, fired at 1025°C for 4 days with two intermediate grindings, and finally air quenched.
(5) X-ray powder diffraction data for the La compounds were collected every 0.02° for 3° < 2θ < 120° on a Rigaku RINT 2000 diffractometer equipped with monochromator for Cu Kα radiation. The refinements of both structures were performed using the Rietveld analysis program, FULLPROF (Rodríguez-Carvajal, J.; FULLPROF version 3.1, January, 1996; I.L.L. France), and led to R ϵ = 6.63%, R ϵ = 6.94%, ϵ = 191, R ≈ = 6.3%, R 1 = 5.29% for the ambient phase, and R ϵ = 3.83%, R ϵ = 5.55%, R ≈ = 4.77%, ϵ = 1.35, R ≈ = 8.18%, R 1 = 7.31% for the high-pressure phase.
Cu₃MoO₁₂ (and La₄Cu₃MoO₁₂ based on the assumption that the constituent ions are spherical, of perovskite. La₂CuSnO₆ (iii) series of fully oxygenated perovskites demonstrate that the site symmetry of the lattice. The following pressure, whereas Pr₂CuSnO₆ (Cu/Mo)O₂ polyhedra are white, whereas (Cu/Mo)O₆/2 and (Cu/Mo)O₆/3 polyhedra are gray. Black circles are lanthanum.

Copper is clearly the essential structural and electronic element in layered double perovskites (i.e., the Ln₂CuSnO₆ and Ln₄Cu₃-M VI O₁₂, and Ln₅Cu₄M VII O₁₅. 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 La₄Cu₃MoO₁₂ phases (5 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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Figure 2. High-pressure transformation of AP La₄Cu₃MoO₁₂ to a layered perovskite. CuO₆ polyhedra are white, whereas (Cu/Mo)O₆/2 and (Cu/Mo)O₆/3 polyhedra are gray. Black circles are lanthanum.

Figure 3. (a) Zero field cooled molar (per copper ion) susceptibility data for AP La₄Cu₃MoO₁₂, in contrast with (b) Zero field cooled (ZFC) and field cooled (FC) molar susceptibility data for HP La₄Cu₃MoO₁₂.

MoO₁₂ families) and high-temperature superconductors (HTSCs). In the layered stannates and molybdates, the CuO₂ 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 CuO₂ and CuO₂ units which promote charge delocalization in the plane. Barium substitution for lanthanum in La₅SnCuO₆ to make La₅BaCu₃SnO₁₂ introduces oxygen vacancies and flattens out the cuprate planes. A similar tactic may help to flatten out the cuprate planes in HP La₄Cu₃MoO₁₂ as well. The HP title phase has the advantage of additional CuII 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 Ln₅Cu₃WO₁₂ (Ln = La, Pr, Nd, Gd) does not form under similar ambient or high-pressure conditions.

In conclusion, the new copper-enriched, layered perovskite, La₅Cu₄MoO₁₂, has been synthesized under high pressure from a polymorphic phase. Ln₅CuTiO₄ forms perovskite for Ln = La–Gd but forms a hexagonal phase for Ln = Tb–Lu. 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 Ln₅Cu₄MoO₁₂, Ln₅Cu₃M VI O₁₂, and Ln₅Cu₄M VII O₁₅. 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.

(12) Tolerance factors calculated as follows, t = (rₐ + rₐ)/√2(rₐ + rₐ); rₐ = r(LnIII, 8-coordinate), r₀ = r(Nd, 6-coordinate), and r(CuII) = 0.60 Å. Ionic radii from Shannon, R. D. Acta Crystallogr. 1976, A32, 767–774.