

A New Series of Layered Cuprates (ACuO_{2.5})₂(ATiO₃)_m: Dy₂Ba₂Ca₂Cu₂Ti₄O₁₇, *m* = 4

Kenji D. Otszchi,^{*,†} Kenneth R. Poeppelmeier,[‡]
Paul A. Salvador,[§] Thomas O. Mason,[§] Hong Zhang,[§] and
Laurence D. Marks[§]

Department of Chemistry and the Science and
Technology Center for Superconductivity
Northwestern University, 2145 Sheridan Road
Evanston, Illinois 60208-3113

Department of Material Science and the Science and
Technology Center for Superconductivity
Northwestern University, 2137 Sheridan Road
Evanston, Illinois 60208-3108
Institute for Solid State Physics
University of Tokyo, 7-22-1 Roppongi
Minato-ku, Tokyo 106, Japan

Received June 11, 1996

Extensive research on the high-*T_c* superconductors over the last decade has revealed a large number of layered perovskite-type cuprates with two-dimensional CuO₂ planes. In this short communication we report a new family of layered cuprates, (ACuO_{2.5})₂(ATiO₃)_m, and the *m* = 4 member, Dy₂Ba₂Ca₂Ti₄Cu₂O₁₇. Owing to the tolerance of the perovskite structure for A- (alkaline earth and rare earth) and B-cation (usually transition metals) substitutions, sometimes accompanied by intergrowths of rock salt/fluorite layers, a variety of structurally related families, for example, LnBa₂Cu₃O₇ (Ln = Y, La–Lu), Tl_mBa₂Ca_{n-1}Cu_nO_{m+2n+2}, or Ruddlesden-Popper series, are known.^{1,2,3} The physicochemical properties within related families (as well as contrasts with other families) have proven essential in comprehending structure–property relationships in high-*T_c* cuprates. New families allow the full exploration of these relationships with respect to particular structural features.⁴

We have investigated the structural, electrical, magnetic, and point defect properties of the quadruple-perovskite family Ln₂Ba₂Cu₂M₂O₁₁ (Ln = La–Tb, M = Ti, Sn) as a function of the constituent Ln and M atoms.^{5,6} Superconductivity has not been observed in this system, to date, probably because of both the relatively long in-plane Cu–O distance (≥1.94 Å), which prevents interaction between Cu-3d and O-2p orbitals, and limited doping by alkaline earth substitution for the rare earth constituents. In order to understand the lack of superconductivity in these layered copper titanates, we have focused our attention on related materials with in-plane Cu–O bond distances more amenable to hole-doped superconductivity.

All samples were prepared by solid state reaction of appropriate stoichiometric mixtures of LnO_{1.5} (Ln = La–Lu),

ACO₃ (A = Ca, Sr, and/or Ba), CuO, and TiO₂, all of which are of purity above 99.99%. The LnO_{1.5} precursors were calcined in air at 950–1050 °C before use. The mixtures were first fired at 950 °C for 1–2 days and subsequently sintered at 1025–1100 °C for 2–4 days. Grinding and sintering were repeated in some cases to attain more homogeneous products. Powder X-ray diffraction patterns were collected with a Rigaku diffractometer and Cu Kα radiation for each sample to confirm purity/phases. The oxygen content was obtained by hydrogen reduction in a MacScience TG-DTA assembly or a Dupont Instruments 951 thermogravimetric analyzer. Electron diffraction patterns and high-resolution images were obtained using a Hitachi H9000 microscope. Temperature dependence of the magnetic susceptibility was measured using a Quantum Design MPMS SQUID magnetometer.

Ln₂Ba₂Cu₂Ti₂O₁₁ is known to form for Ln = La–Gd at 1025–1050 °C and for Ln = Tb at 1100 °C in air.⁵ However, for Ln = Tb we could not obtain a single-phase product, as a small amount of Tb₂Cu₂O₅ (2-2-5 green phase) impurity was evident in the diffractograms. For the smaller rare earth elements (Y, Dy–Lu), the nominal compositions resulted in mixtures of 2-2-5 phase and BaTiO₃.

In order to accommodate Dy and reduce the Cu–O separation in the layered perovskite structure, we simultaneously replaced Ba with Sr and Ca, i.e., Dy₂(Ba, Sr, Ca)₂Cu₂Ti₂O_y. However, all samples with nominal compositions other than Dy₂BaCaCu₂Ti₂O_y resulted in mixtures of the 2-2-5 phase and alkaline earth titanates. (For example, Dy₂BaSrCu₂Ti₂O_y = Dy₂Cu₂O₅ + BaTiO₃ + SrTiO₃.) The XRD pattern of Dy₂BaCaCu₂Ti₂O_y, however, showed a main phase, whose diffraction peaks could be indexed as a perovskite other than (Ba, Sr, Ca)TiO₃, and only a small amount of the 2-2-5 phase. In order to isolate the majority phase, we synthesized materials according to the nominal composition (Dy₂BaCaCu₂Ti₂O_y – xDy₂Cu₂O₅), and the main phase was found to be DyBaCaCuTi₂O_y (*x* = 0.5). The oxygen content, as determined by TG measurements, was *y* = 8.52 ± 0.05, which is consistent with divalent Cu²⁺ and trivalent Ti⁴⁺ (*y* = 8.5).

The XRD pattern of DyBaCaCuTi₂O_{8.52±0.05} was quite similar to those of the quadruple perovskites, Ln₂Ba₂Cu₂Ti₂O₁₁, in spite of the different B-cation ratio, Cu/Ti = 0.5 and 1.0, respectively. In order to clarify the ordering of Cu/Ti in the structure, we carried out electron microscopy measurements. Figure 1 shows a high-resolution image of this compound, which exhibits the *c*-axis array of four TiO₆ octahedra separated by two CuO₅ pyramids as depicted in Figure 2e. The chemical formula according to this ordering scheme and the nominal stoichiometry, which is also confirmed by EDX experiment, can be written as Dy₂Ba₂Ca₂Cu₂Ti₄O₁₇.

The lattice constants are calculated as *a* = 3.8442 Å (additional superstructure in the *ab*-plane is expected) and *c* = 23.298 Å, which means a far smaller Cu–O bond distance (≈1.92 Å) than that of quadruple perovskites.⁵ The temperature dependence of magnetic susceptibility exhibits the expected Curie paramagnetic behavior of divalent Cu²⁺ and trivalent Dy³⁺. Detailed Rietveld structural analysis of this new compound is under study.

According to our XRD results, the new sextuple (six perovskite blocks) phase (Ln₂Ba₂Ca₂Cu₂Ti₄O₁₇) forms with Ln = Pr–Dy, but the compositions with Ln = Y, Ho–Lu were mixtures of 2-2-5 phase, BaTiO₃, and CaTiO₃. Since these samples contain very small amounts of CaTiO₃, a certain amount of quadruple perovskite may be present, but it would be difficult to discern with our XRD experiments. The intensities of the diffraction peaks that are due to CaTiO₃, however, are much less than expected for a mixture of Ln₂Ba₂Cu₂Ti₂O₁₁ and CaTiO₃ (1:2 mole ratio), and therefore we conclude that the majority

* To whom correspondence should be addressed.

† University of Tokyo. Present address is Department of Chemistry, Northwestern University.

‡ Department of Chemistry, Northwestern University.

§ Department of Material Science, Northwestern University.

(1) Jorgensen, J. D.; Veal, B. W.; Paulikas, A. P.; Nowicki, L. J.; Crabtree, G. W.; Claus, H.; Kwok, W. K. *Phys. Rev. B* **1990**, *41*, 1863.

(2) (a) Morosin, B.; Ginley, D. S.; Hlava, P. F.; Carr, M. J.; Baughman, R. J.; Schirber, J. E.; Venturini, E. L.; Kwak, J. F. *Physica C* **1988**, *152*, 413. (b) Parkin, S. S. P.; Lee, V. Y.; Nazzari, A. I.; Savoy, R.; Beyers, R.; LaPlaca, S. J. *Phys. Rev. Lett.* **1988**, *61*, 750.

(3) Ruddlesden, S. N.; Popper, P. *Acta Crystallogr.* **1958**, *11*, 54.

(4) Bozovic, I.; Eckstein, J. N. *Superconductivity in Cuprate Superlattices, Physical Properties of High Temperature Superconductors*; Ginsberg, D. M., Ed.; World Scientific: Singapore, 1996; Vol. V.

(5) (a) Anderson, M. T.; Poeppelmeier, K. R.; Zhang, J.-P.; Fan, H.-J.; Marks, L. D. *Chem. Mater.* **1992**, *4*, 1305. (b) Palacin, M. R.; Fuertes, A.; Casañ-Pastor, N.; Gómez-Romero, P. *J. Solid State Chem.* **1995**, *119*, 224. (c) Gormezano, A.; Weller, M. T. *Physica C* **1994**, *235–240*, 999.

(6) (a) Greenwood, K. B.; Sarjeant, G. M.; Poeppelmeier, K. R.; Salvador, P. A.; Mason, T. O.; Dabrowski, B.; Rogacki, K.; Chen, Z. *Chem. Mater.* **1995**, *7*, 1355. (b) Salvador, P. A.; Shen, L.; Mason, T. O.; Greenwood, K. B.; Poeppelmeier, K. R. *J. Solid State Chem.* **1995**, *119*, 80.

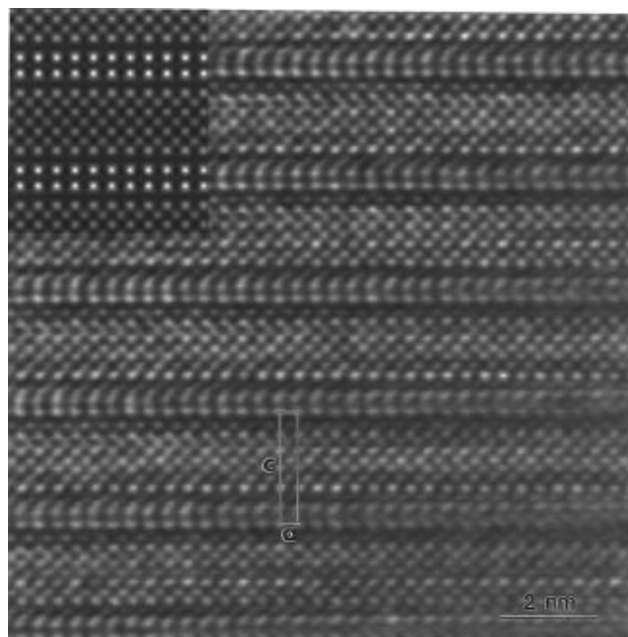


Figure 1. High-resolution electron microscopy image of DyBaCa-CuTi₂O_{8.52±0.05} taken along the [100] direction. A unit cell is outlined, and a simulated EM image is shown in the top left corner.

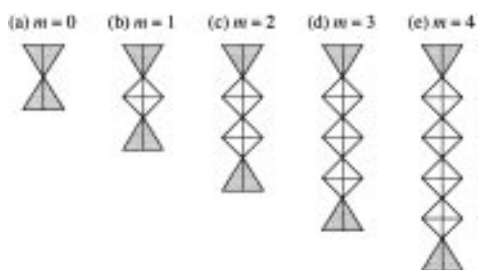


Figure 2. Schematic representations of the structures of the new *c*-axis-aligned series (ACuO_{2.5})₂(ATiO₃)_{*m*}, (a) *m* = 0, (b) *m* = 1, (c) *m* = 2; Ln₂Ba₂Cu₂Ti₂O₁₁ (quadruple perovskite), (d) *m* = 3 and (e) *m* = 4; Ln₂Ba₂Ca₂Cu₂Ti₄O₁₇ (sextuple perovskite). Shaded triangles and open squares with cross stand for CuO₅ pyramids and TiO₆ octahedra, respectively.

of the sample is the Ln₂Ba₂Ca₂Cu₂Ti₄O₁₇ phase, as supported by the HR-TEM images.

As described above, there is a striking similarity between the structures of the quadruple perovskite Ln₂Ba₂Cu₂Ti₂O₁₁ (Figure 2c) and the sextuple perovskite Ln₂Ba₂Ca₂Cu₂Ti₄O₁₇ (Figure 2e). If we focus on the two kinds of two-dimensional layers, the TiO₆ perovskite layer and the CuO₅ oxygen deficient layer, each formula can be rewritten as Ln₂Ba₂Cu₂Ti₂O₁₁ = A₄Cu₂Ti₂O₁₁ or (ACuO_{2.5})₂(ATiO₃)₂ and Ln₂Ba₂Ca₂Cu₂Ti₄O₁₇ = A₆Cu₂Ti₄O₁₇ or (ACuO_{2.5})₂(ATiO₃)₄, when the difference of the A-cations is ignored. Therefore a general formula for this family of layered perovskites is (ACuO_{2.5})₂(ATiO₃)_{*m*}, and we have identified the first compound with *m* = 4.

While the *m* = 2 and *m* = 4 phases are known for the copper titanates, related phases are known for *m* = 0 and 1. The structure of the *m* = 0 member (Figure 2a), A₂Cu₂O₅, is

illustrated by YBaCuFeO₅⁷ and is related to infinite layer structure.⁸ Interestingly ABO_{2.5} structures with only copper in the B-site adopt the three-dimensional CaMnO_{2.5} structure.⁹ The *m* = 1 structure (Figure 2b), which is related to the YBa₂Cu₃O_y structure, can be obtained in the Cu/Ta, Cu/Nb,¹⁰ and Cu/Ru¹¹ systems. Several synthesis attempts using Cu/Ti have been reported,^{5,6} but A₃Cu₂TiO₈ has not been obtained as a single phase. The combination of divalent Cu²⁺ and tetravalent Ti⁴⁺ requires the large divalent ion (such as Ba²⁺) to fill the large A-site cavity between CuO₅ and TiO₆ polyhedra,^{6a} thus competing chemical effects render it difficult to obtain the *m* = 1 phase with the tetravalent Ti⁴⁺ ion. Notably, there are also currently no examples for the *m* = 3 phase (Figure 2d), and we are pursuing the incorporation of two Ba²⁺ ions adjacent to the cuprate layers to facilitate its direct synthesis compared to the *m* = 1 phase.

Our interests have been in the electronic and structural features which stabilize two-dimensional (layered) structures in pure perovskite systems. In the intergrowth phases such as the Ruddlesden–Popper series, SrO(SrTiO₃)_{*m*}, the structural force for layering is the SrO rock salt layer. By comparison of the formulas, (ACuO_{2.5})₂(ATiO₃)_{*m*}, and AO(ABO₃)_{*m*}, the electronic/structural characteristic which leads to the former series can be found in the ACuO_{2.5} oxygen deficient layers, or more precisely the *c*-direction alignment of the Jahn–Teller axis of the Cu²⁺O₅ pyramids. The Jahn–Teller distortion by itself, however, is not sufficient to overcome competing forces in all cases. This is why only a few examples are known of layered perovskites, yet there are many examples of the intergrowth systems. In the (ACuO_{2.5})₂(ATiO₃)_{*m*} family, the “Jahn–Teller” stabilization and an ordering of the Ba²⁺ ions into the A-sites between Cu²⁺O₅ and Ti⁴⁺O₆ polyhedra combine together to stabilize the two-dimensional (layered) structures. If we can obtain the entire *c*-axis-aligned pure perovskite family, (ACuO_{2.5})₂(ATiO₃)_{*m*} (*m* = 0–4), we can investigate the physical properties of the CuO₂ layer with changing thickness of the block layer (TiO₆). Attempts to hole-dope Dy₂Ba₂Ca₂Cu₂Ti₄O₁₇ by aliovalent impurities and/or oxygen defects are currently underway. It is of interest to compare the high-temperature transport/defect behavior with that of the other layered cuprates.

Acknowledgment. Authors are grateful to Prof. Y. Ueda, Dr. A. Hayashi, and Mr. M. Isobe (University of Tokyo) for their support. One of us (K.O.) is partly supported by Research Fellowship of the Japan Society for the Promotion of the Science for Young Scientists. This work was supported by the National Science Foundation (Award No. DMR-9120000) through the Science and Technology Center for Superconductivity and also made use of the Central Facilities, supported by the National Science Foundation, at the Materials Research Center of Northwestern University (Award No. DMR-9120521).

JA961967Z

(7) Er-Rakho, L.; Michel, C.; LaCorre, P.; Raveau, B. *J. Solid State Chem.* **1988**, *73*, 531.

(8) Takano, M.; Azuma, M.; Hiroi, Z.; Bando, Y.; Takeda, Y. *Physica C* **1991**, *176*, 441.

(9) Poeppelmeier, K. R.; Leonowicz, M. E.; Longo, J. M. *J. Solid State Chem.* **1982**, *44*, 89.

(10) Rey, M.-J.; Dehaut, P.; Joubert, J.; Hewat, A. H. *Physica C* **1990**, *167*, 162.

(11) Bauernfeind, L.; Widder, W.; Braun, H. F. *Physica C* **1995**, *254*, 151.