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A New Series of Layered Cuprates $(ACuO_{2.5})_2(ATiO_3)_m$: $Dy_2Ba_2Ca_2Cu_2Ti_4O_{17}$, $m = 4$

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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 CuO_2 planes. In this short communication we report a new family of layered cuprates, $(ACuO_{2.5})_2(ATiO_3)_m$, and the $m = 4$ member, $Dy_2Ba_2Ca_2Ti_4Cu_2O_{17}$. 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, $LnBa_2Cu_3O_7$ (Ln = Y, La−Lu), $Tl_mBa_2Ca_{n-1}Cu_nO_{m+2n+2}$, 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 $Ln_2Ba_2Cu_2M_2O_{11}$ (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), ACO_3 (A = Ca, Sr, and/or Ba), CuO, and TiO_2, 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.

$Ln_2Ba_2Cu_2Ti_2O_{11}$ 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 $Tb_2Cu_2O_5$ (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 $BaTiO_3$.

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., $Dy_2(Ba, Sr, Ca)_2Cu_2Ti_2O_y$. However, all samples with nominal compositions other than $Dy_2BaCaCu_2Ti_2O_y$ resulted in mixtures of the 2-2-5 phase and alkaline earth titanates. (For example, $Dy_2BaSrCu_2Ti_2O_y = Dy_2Cu_2O_5 + BaTiO_3 + SrTiO_3$.) The XRD pattern of $Dy_2BaCaCu_2Ti_2O_y$, however, showed a main phase, whose diffraction peaks could be indexed as a perovskite other than (Ba, Sr, Ca)TiO_3, 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 ($Dy_2BaCaCu_2Ti_2O_y - xDy_2Cu_2O_5$), and the main phase was found to be $DyBaCaCuTi_2O_y$ ($x = 0.5$). The oxygen content, as determined by TG measurements, was $y = 8.52 \pm 0.05$, which is consistent with divalent Cu^{2+} and tetravalent Ti^{4+} ($y = 8.5$).

The XRD pattern of $DyBaCaCuTi_2O_{8.52\pm0.05}$ was quite similar to those of the quadruple perovskites, $Ln_2Ba_2Cu_2Ti_2O_{11}$, 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 TiO_6 octahedra separated by two CuO_5 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 $Dy_2Ba_2Ca_2Cu_2Ti_4O_{17}$.

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 Cu^{2+} and trivalent Dy^{3+}. Detailed Rietveld structural analysis of this new compound is under study.

According to our XRD results, the new sextuple (six perovskite blocks) phase ($Ln_2Ba_2Ca_2Cu_2Ti_4O_{17}$) forms with Ln = Pr−Dy, but the compositions with Ln = Y, Ho−Lu were mixtures of 2-2-5 phase, $BaTiO_3$, and $CaTiO_3$. Since these samples contain very small amounts of $CaTiO_3$, 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 $CaTiO_3$, however, are much less than expected for a mixture of $Ln_2Ba_2Cu_2Ti_2O_{11}$ and $CaTiO_3$ (1:2 mole ratio), and therefore we conclude that the majority

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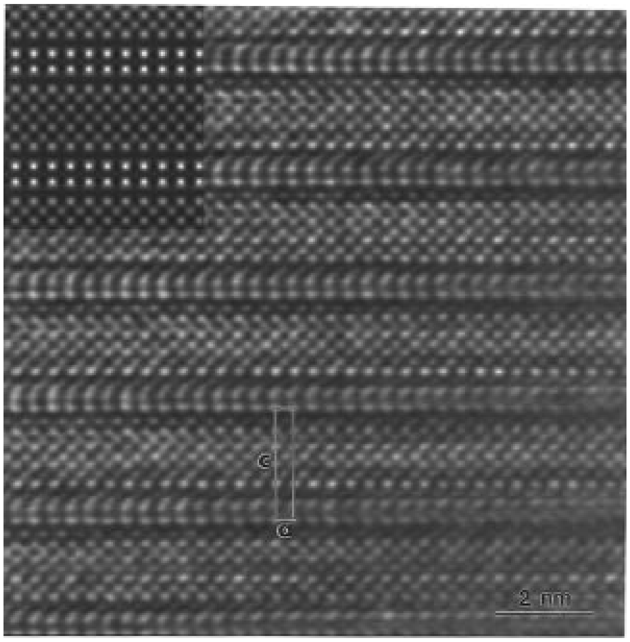

Figure 1. High-resolution electron microscopy image of DyBaCaCuTi$_2$O$_{8.52\pm0.05}$ taken along the [100] direction. A unit cell is outlined, and a simulated EM image is shown in the top left corner.

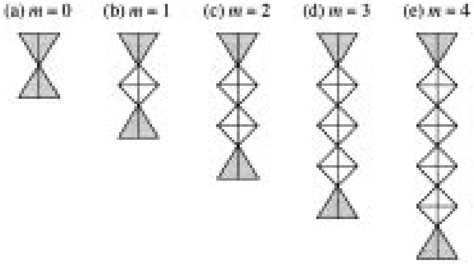

Figure 2. Schematic representations of the structures of the new *c*-axis-aligned series $(ACuO_{2.5})_2(ATiO_3)_m$, (a) $m = 0$, (b) $m = 1$, (c) $m = 2$; $Ln_2Ba_2Cu_2Ti_2O_{11}$ (quadruple perovskite), (d) $m = 3$ and (e) $m = 4$; $Ln_2Ba_2Ca_2Cu_2Ti_4O_{17}$ (sextuple perovskite). Shaded triangles and open squares with cross stand for CuO_5 pyramids and TiO_6 octahedra, respectively.

of the sample is the $Ln_2Ba_2Ca_2Cu_2Ti_4O_{17}$ phase, as supported by the HR-TEM images.

As described above, there is a striking similarity between the structures of the quadruple perovskite $Ln_2Ba_2Cu_2Ti_2O_{11}$ (Figure 2c) and the sextuple perovskite $Ln_2Ba_2Ca_2Cu_2Ti_4O_{17}$ (Figure 2e). If we focus on the two kinds of two-dimensional layers, the TiO_6 perovskite layer and the CuO_5 oxygen deficient layer, each formula can be rewritten as $Ln_2Ba_2Cu_2Ti_2O_{11} = A_4Cu_2Ti_2O_{11}$ or $(ACuO_{2.5})_2(ATiO_3)_2$ and $Ln_2Ba_2Ca_2Cu_2Ti_4O_{17} = A_6Cu_2Ti_4O_{17}$ or $(ACuO_{2.5})_2(ATiO_3)_4$, when the difference of the A-cations is ignored. Therefore a general formula for this family of layered perovskites is $(ACuO_{2.5})_2(ATiO_3)_m$, 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), $A_2Cu_2O_5$, is illustrated by $YBaCuFeO_5$[7] 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 $YBa_2Cu_3O_y$ structure, can be obtained in the Cu/Ta, Cu/Nb,[10] and Cu/Ru[11] systems. Several synthesis attempts using Cu/Ti have been reported,[5,6] but $A_3Cu_2TiO_8$ has not been obtained as a single phase. The combination of divalent Cu^{2+} and tetravalent Ti^{4+} requires the large divalent ion (such as Ba^{2+}) to fill the large A-site cavity between CuO_5 and TiO_6 polyhedra;[6a] thus competing chemical effects render it difficult to obtain the $m = 1$ phase with the tetravalent Ti^{4+} ion. Notably, there are also currently no examples for the $m = 3$ phase (Figure 2d), and we are pursuing the incorporation of two Ba^{2+} 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, $SrO(SrTiO_3)_m$, the structural force for layering is the SrO rock salt layer. By comparison of the formulas, $(ACuO_{2.5})_2(ATiO_3)_m$, and $AO(ABO_3)_m$, 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 $Cu^{2+}O_5$ 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 $(ACuO_{2.5})_2(ATiO_3)_m$ family, the "Jahn−Teller" stabilization and an ordering of the Ba^{2+} ions into the A-sites between $Cu^{2+}O_5$ and $Ti^{4+}O_6$ polyhedra combine together to stabilize the two-dimensional (layered) structures. If we can obtain the entire *c*-axis-aligned pure perovskite family, $(ACuO_{2.5})_2(ATiO_3)_m$ ($m = 0-4$), we can investigate the physical properties of the CuO_2 layer with changing thickness of the block layer (TiO_6). Attempts to hole-dope $Dy_2Ba_2Ca_2Cu_2Ti_4O_{17}$ 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.

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