

Communications

Close Relations between Doping and Layering in Pure Perovskite

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Low dimensionality has been an inviting concept in the exploration of materials with interesting electrical and magnetic properties. Anisotropy lowers the symmetry and can enhance directional properties. Specifically, perovskite (ABO_3)-related compounds have played an important role because of their versatile layering schemes and tolerance to cation substitution. Consider the pure perovskite series in the A -Cu-Ti-O system, $(ACuO_{2.5})_2(ATiO_3)_{n-2}$.^{1–4} The titanium block stoichiometry, $n-2$, can be incremented to produce discrete phases which are 2-dimensional owing to the layered arrangement of the oxygen vacancies and the c -axis orientation of the CuO_5 Jahn-Teller axis. Many possible choices of A -cations introduce even more freedom to modify the structure. In this communication we develop and evaluate two models (the Random-Defect and the Structure-Dominant models) to describe the relationship between phase changes and doping levels for a fixed A -cation stoichiometry and fractional B -cation ratios.

The general chemical formula of a multifold perovskite can be written as $(ABO_3)_n$ or $A_nB_nO_{3n}$, where n is the perovskite unit cell multiplicity. To start, let two of the B -cations be Cu, the rest Ti, and set the number of oxygen vacancies per unit cell to one (i.e., $A_nCu_2Ti_{n-2}O_{3n-1}$). Restricting the number of vacancies is strategic. Additional oxygen vacancies may occur in the blocking layers, but considering only one vacancy

per unit cell defines the maximum copper oxidation state and delineates the contribution of layering to the doping levels. Now as Cu substitutes for Ti,⁵ $A_nCu_{2+x}Ti_{n-2-x}O_{3n-1}$, the relationship between phase transitions and doping levels can be examined. Fixing the A -cations defines the sum of their oxidation states, represented as $[A_n]$. The average oxidation state of Cu, α , can then be calculated from the equation of charge balance:

$$[A_n] + \alpha(2 + x) + 4(n - 2 - x) = 2(3n - 1)$$

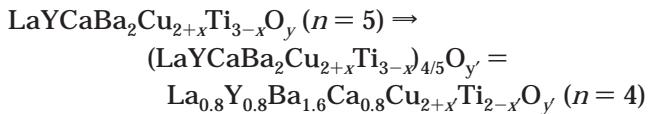
$$\alpha = 4 - ([A_n] + 2 - 2n)/(2 + x) \quad (1)$$

If the n -fold phase exists over the whole Cu-substitution range, eq 1 is sufficient. If the multiplicity changes to n' , however, we should rewrite the chemical formula to reflect the new multiplicity: $(A_nCu_{2+x}Ti_{n-2-x})_{n'/n}O_{3n'-1}$. The average oxidation state of Cu in this phase is

$$\alpha' = 4 - \{[A_n] + 2n(1/n' - 1)\}/(2 + x) \quad (2)$$

Note that there is still only one oxygen vacancy per unit cell.

LaYCaBa₂Cu₂Ti₃O₁₄ is a previously well characterized¹ compound that provides a definitive starting point for the general eqs 1 and 2. A phase change for this reference compound can be understood stoichiometrically by transposing the multiplicity as follows:



where $x' = 4/5x - 0.4$. This method demonstrates how the formula of a quintuple perovskite can be rewritten as that of a quadruple perovskite.

Calculating the average copper valence of $(\text{LaYCaBa}_2\text{Cu}_{2+x}\text{Ti}_{3-x})_{n'/n}O_{3n'-1}$ is straightforward: $n = 5$ and $[A_n] = 12$ so

$$\alpha' = 4 - (2 + 10/n')/(2 + x) \quad (3)$$

Figure 1 shows the theoretical B -cation “doping” lines according to eq 3 for the $n' = 6, 5, 4$, and 3 phases. One phase could exist in the whole x range as represented by the thin dotted line for $n' = 5$ in the figure. However, assuming that Cu prefers the divalent state, the phase “falls” to a lower curve at $x = 0.25$ to restore the average copper oxidation state to two (thick solid line in Figure 1). This structural phase transition increases the relative concentration of oxygen vacancies (theoretically maintained at one per unit cell) by decreasing the multiplicity of the perovskite cell. The phase change

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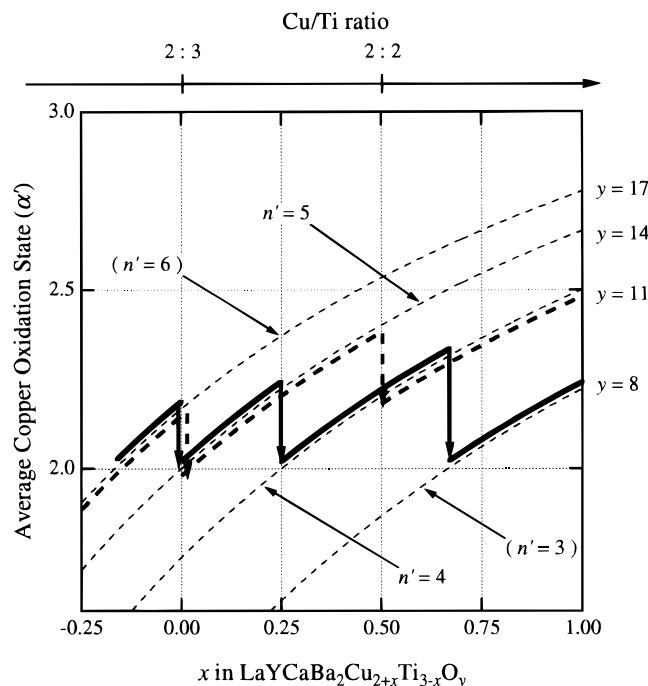


Figure 1. Thin dotted lines are the average oxidation state of Cu, α' , versus the amount of doped Cu, x in $\text{LaYCaBa}_{2+x}\text{Cu}_{3-x}\text{O}_y$, for the $n' = 3-6$ phases. Thick solid and dotted curves show the ideal phase change according to the Random-Defect model and the Structure-Dominant model, respectively.

does not depend on the distribution of *A*-cations or the arrangement/layering of *B*-cations.

This Random-Defect model predicts a transition from the $n' = 5$ (quintuple) phase to the $n' = 4$ (quadruple) phase at $x = 0.25$. As modeled, the oxygen vacancies are disordered within the lattice but likely located between Cu cations rather than Ti.⁶ A transition at $x = 0.25$ results in less than two coppers per oxygen vacancy ($\text{La}_{0.8}\text{Y}_{0.8}\text{Ca}_{0.8}\text{Ba}_{1.6}\text{Cu}_{1.8}\text{Ti}_{2.2}\text{O}_{11}$) so the oxygen vacancies must partially cluster and some Cu must be square planar.

A second possibility is the Structure-Dominant model that arranges the oxygen vacancies in planes. This arrangement requires two square pyramidal coppers per unit cell to coordinate around the oxygen vacancy and consequently defines a lowest possible Cu concentration for each phase: $x = 0.0$ for the $n' = 5$ phase and $x = 0.5$ for the $n' = 4$ phase, for example. At these points, the Cu/Ti ratios are 2/3 and 2/2, corresponding to archetypal quintuple and quadruple perovskites (as shown on the top of Figure 1), respectively. The thick dotted line in Figure 1 illustrates the phase changes according to the Structure-Dominant model. The $n' = 5$ phase can be doped to $x = 0.5$ in comparison with $x = 0.25$ for the Random-Defect model. It is also important to note that the $x = 0.5$ sample is doped with Ca ($\alpha' > 2.0$) even as a quadruple perovskite according to the second model. This result is because the decrease in the average oxidation state of copper that accompanies the phase change will not occur before $x = 0.5$ if the structure is layered.

To test these models, $\text{LaYCaBa}_{2+x}\text{Cu}_{3-x}\text{O}_y$ samples were prepared by conventional solid-state reaction at

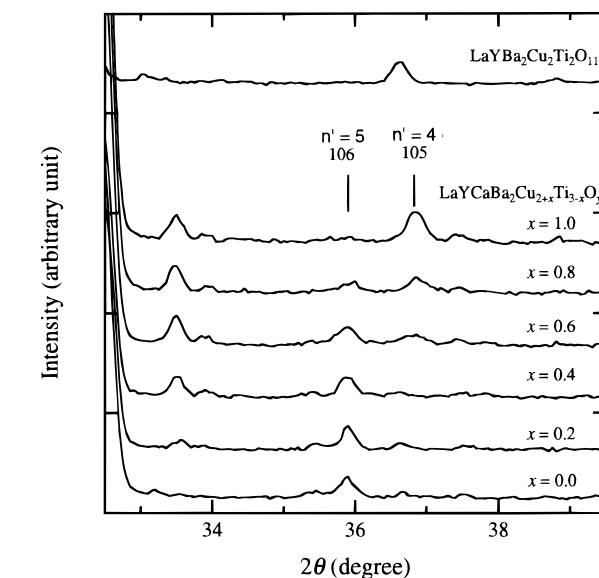


Figure 2. PXD patterns for $\text{LaYCaBa}_{2+x}\text{Cu}_{3-x}\text{O}_y$ samples ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0). One for the quadruple perovskite, $\text{LaYBa}_2\text{Cu}_2\text{Ti}_2\text{O}_{11}$, is also shown at the top for comparison. The peak positions corresponding to the 106 ($n' = 5$) and 105 ($n' = 4$) reflections are shown by vertical lines. The former decreases in intensity with Cu substitution, while the latter increases. The other small peak around 33.5° , which increases with x , is due to $\text{Y}_2\text{Cu}_2\text{O}_5$.

1050° as described in previous reports.⁴ Results obtained by powder X-ray diffraction (PXD), transmission electron microscopy (TEM), and susceptibility measurements suggest the higher Cu concentration for the phase change. Figure 2 shows the observed PXD profiles for the $x = 0.0, 0.2, 0.4, 0.6, 0.8$, and 1.0 samples in the range of 32.5 to 39.5° . Within this range, two characteristic peaks are observed. The first around 36° arises from the 106 reflection planes of the $n' = 5$ phase, and the other at 37° is the 105 reflection of the $n' = 4$ phase. The PXD spectra of the $x = 0.0, 0.2$, and 0.4 samples are dominated by the 106 reflection, indicating that the quintuple perovskite structure persists to substantial Cu substitution levels. In contrast, the 105 reflection dominates the $x = 1.0$ sample indicating a transition from the quintuple perovskite to the quadruple structure. The intermediate compositions ($x = 0.6, 0.8$) show both peaks so they are biphasic. An impurity peak at 33.5° can be assigned to $\text{Y}_2\text{Cu}_2\text{O}_5$ and is neglected in the analysis because its intensity is $<3\%$ of that of the main peak of the perovskites.

Electron microscopy experiments on the $x = 0.0, 0.2, 0.6, 0.8$, and 1.0 samples confirm the phase change behavior. The diffraction along [100] zone axis of the $x = 0.0$ and 0.2 samples shows only five layer patterns, which is consistent with the PXD results. Likewise, the $x = 1.0$ sample exhibits a four-layer pattern consistent with a quadruple structure. The $x = 0.6$ sample clearly shows stacking faults between quadruple and quintuple perovskite structures (Figure 3), while the $x = 0.8$ sample has discrete domains of each phase. The PXD data support these observations. The increasing peak width of the 106 reflection with increasing x correlates with the breakdown of long-range structure.

These experiments confirm the Structure-Dominant model with $\text{CuO}_{5/2}$ planes between blocking layers. However, it is reasonable to expect that considerable

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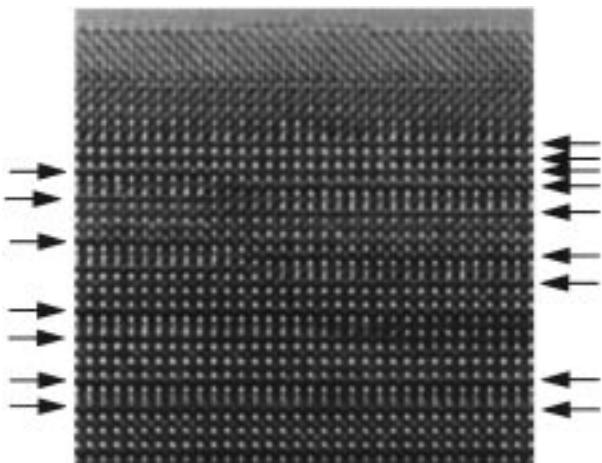


Figure 3. TEM image of $\text{LaYCaBa}_2\text{Cu}_{2.6}\text{Ti}_{2.4}\text{O}_y$ ($x = 0.6$). Arrows mark the layer of oxygen vacancies and A -cations (evidenced by dark lines) between the copper oxygen planes. Notice the stacking faults between quintuple and quadruple phases.

oxygen vacancies occur in the blocking layers as the fraction of copper that substitutes for titanium increases.⁷ In fact, thermogravimetric analysis (TGA) of this particular system reveals that the copper valence is not $> 2.02(1)$ when prepared in air. Susceptibility measurements ($x = 0.0, 0.2, 0.6$, and 1.0) were performed from 5 to 300 K in an external field of 1 T and all samples exhibit paramagnetic behavior. Nevertheless, the interdependence of doping and layering exists and can be exploited if more fully oxygenated materials can be synthesized.

In conclusion, we have observed a phase change in the A –Cu–Ti–O system, $\text{LaYCaBa}_2\text{Cu}_{2+x}\text{Ti}_{3-x}\text{O}_y$,

from the quintuple structure to the quadruple one by changing only the B -cation ratio. In these phases, the A -cation ratios are fixed at $\text{La}/\text{Y}/\text{Ca}/\text{Ba} = 1/1/1/2$, and even though this system contains six kinds of cations, x is the only variable. This example is the first of a “fixed A -cation” phase change on the “Perovskite Line” and may allow for superconductors, poor metals, and semiconductors all in one system at distinct Cu/Ti ratios.

We have defended a model that supports a critical relationship between doping and layering that is completely compatible with thin-film techniques. Although doping is frustrated by ionic compensation, optimizing A -cation combinations or changing the synthesis conditions may improve the attainable doping levels.

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Supporting Information Available: Plot of X-ray powder diffraction data (20 to 60° 2θ) for all samples. Plot of susceptibility data (5 to 300 K) for $x = 0.0, 0.2, 0.6$, and 1.0 (2 pages). Ordering information is given on any current masthead page.

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