

Ba_{2-x}La_xYCu₃O_{7±δ} perovskite compounds: Crystal chemistry

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We report the crystal chemical properties of solid solutions obtained by substitution of lanthanum for barium in the high- T_c superconductor Ba₂YCu₃O₇. An orthorhombic-to-tetragonal symmetry change occurs at $x=0.4$ in Ba_{2-x}La_xYCu₃O_{7±δ} with the tripled perovskite supercell maintained. Charge compensation is achieved through reduction of the formal copper valence ($\delta=0$) in the orthorhombic phase and by a mixture of excess oxygen accommodation ($\delta>0$) and formal valence reduction in the tetragonal phase. The resistivity increases by several orders of magnitude, even though the average formal copper valence changes very little.

The discovery of high- T_c superconductivity in La-Ba-Cu-O,¹ and later in Y-Ba-Cu-O,^{2,3} has led to intense research into this new class of materials. Ba₂YCu₃O₇, the 90-K bulk superconductor⁴⁻⁷ has of course been of particular interest. The substitution of various rare earths for Y leaves the compound isoelectronic, and generally superconducting.⁸ Recently, there has been literally an avalanche of work on the effect of oxygen stoichiometry on the superconducting T_c in Ba₂YCu₃O_{7-δ}, which of course changes the electron count as well as the oxygen distribution.⁹ In this Rapid Communication we describe the results of a study of the substitution of La³⁺ for Ba²⁺ in Ba_{2-x}La_xYCu₃O_{7±δ} for $0 \leq x \leq 1$, a nonisoelectronic substitution which results in significant changes in the properties of the material although the average formal copper valence is changed very little. The substitution maintains an ABO_{3-x} perovskite stoichiometry. La is of particular interest from a crystal chemical point of view as it has an ionic size (1.18 Å) between that of Ba (1.42 Å) and Y (1.02 Å) and therefore might be expected to disturb the perfect Ba-Y ordering in Ba₂YCu₃O₇. We observe two distinct phases in the Ba_{2-x}La_xYCu₃O_{7±δ} solid solutions, based on the $a \times a \times 3a$ Ba₂YCu₃O₇-type perovskite supercell. For $0.0 \leq x < 0.4$, we find an orthorhombic bulk superconductor; and for $0.4 \leq x \leq 1.0$, a tetragonal non-bulk-superconductor at low La contents, evolving to a semiconductor for $x > 0.6$.

Materials were prepared from mixtures of Ba₂CO₃, La(OH)₃, Y₂O₃, and CuO first slowly heated in air to 950°C and soaked for 1 day, ground, then heated at 980°C for 2 days with intermediate grinding. Polycrystalline pellets were prepared and fired in O₂ for 16 h at 1010°C for $x \leq 0.4$, and 1050°C for $0.4 < x \leq 1.0$. Higher temperatures were necessary for reasonable densification and homogenization of the high lanthana pellets. Samples of all compositions were then annealed for 16 h in O₂ at 600°C and cooled slowly to ambient temperature before removal from the furnace.

Crystallographic unit-cell parameters were determined by least-squares fitting to powder x-ray-diffraction data. Oxygen stoichiometry was determined by measuring the weight loss of reduction of the samples (thermogravimetric analysis) in flowing H₂ gas between ambient tem-

perature and 1000°C. For the compounds of stoichiometry Ba_{1.75}La_{0.25}YCu₃O_x, Ba_{1.5}La_{0.5}YCu₃O_x, and BaLaYCu₃O_x, the range of possible oxygen stoichiometry was explored by annealing the polycrystalline pellets in flowing N₂ gas at elevated temperatures. Temperature-dependent resistivities (ac, 26 Hz) were measured in a 4-probe measurement configuration on bar-shaped samples. Temperature-dependent magnetization was also measured, and will be described elsewhere.

The crystallographic unit-cell parameters for the Ba_{2-x}La_xYCu₃O_{7±δ} series prepared as described are presented in Table I and Fig. 1. For $x \leq 0.2$, the orthorhombic cell of Ba₂YCu₃O₇ is not significantly distorted. For x between 0.2 and 0.4, however, there is a rapid but continuous change to tetragonal symmetry, involving the shortening of the b axis and lengthening of the a axis. The change towards indistinguishability of a and b probably involves depletion of the oxygens from the one-dimensional chains parallel to b and population of the normally vacant oxygen sites between coppers parallel to a until the populations of the two types of sites are equal, on the average, at $x=0.4$. At low La contents in the tetragonal phase, the length of c is very nearly $3a$. For $x \geq 0.7$ we find c to decrease in length quickly with increasing La content. With the exception of very small La doping, the unit-cell volume decreases continuously with increasing x . For $x > 0.7$, we find the presence of Y₂Cu₂O₅ impurity at levels of 0.5–2% as estimated by x-ray diffraction, and measurement of the entropy at its 11-K antiferromagnetic transition. The $x=1$ materials BaLaEuCu₃O_{7±δ} and BaLaGdCu₃O_{7±δ} are much easier to prepare as true single-phase materials. For La contents greater than $x=1$, the major impurity phase is of the La₄BaCu₅O₁₃ type.¹⁰

As La is substituted for Ba in Ba₂YCu₃O₇, charge compensation may occur either by the reduction of the formal copper valence, or by an increased oxygen content, or a combination of both. The oxygen stoichiometry for samples prepared as described is presented in Fig. 2. For the initial La substitutions in the orthorhombic phase, the oxygen content remains near 7.0, and, therefore, the charge compensation is through reduction of formal copper valence. The minimum average formal valence obtained

TABLE I. Lattice parameters, room-temperature resistivities, and magnetic T_c 's for $Ba_{2-x}La_xYCu_3O_{7\pm\delta}$. (Numbers in parenthesis indicate standard deviations.)

Composition x	Lattice parameters (Å)			Volume (Å ³)	ρ (300 K) (mΩ cm)	Magnetic T_c (K)
	a	b	c			
0.00 ^a	3.822(1)	3.891(1)	11.677(2)	173.65	0.7	91
0.05	3.820(1)	3.890(1)	11.675(3)	173.50	3.5	91
0.10	3.827(2)	3.893(2)	11.678(5)	173.96		
0.15	3.825(1)	3.892(1)	11.681(3)	173.89	1.6	88
0.20	3.827(1)	3.890(1)	11.669(4)	173.75		
0.25	3.830(1)	3.889(1)	11.669(3)	173.79	2.6	76
0.30	3.843(1)	3.881(1)	11.644(4)	173.64	5.0	
0.35	3.852(2)	3.873(2)	11.624(6)	173.38	5.3	64
0.40	3.867(1)		11.598(4)	173.46	8.8	
0.50	3.864(1)		11.595(4)	173.12	7.5	
0.60	3.863(1)		11.584(4)	172.88	7.1	
0.70	3.857(2)		11.547(5)	171.78	23.4	
0.80	3.862(2)		11.546(7)	172.21	55.8	
0.90	3.862(1)		11.521(3)	171.83	339	
1.00	3.864(1)		11.501(4)	171.72	1480	

^aData from Ref. 4.

is 2.2. For La contents greater than 0.4, the oxygen content exceeds 7.0, reaching a maximum value of 7.3 at $BaLaYCu_3O_{7.3}$. In this region, charge compensation is achieved by a mixture of mechanisms, with copper reduction increasing in importance with increasing La concentration. The average formal Cu valence changes smoothly

but not monotonically with La concentration, as shown in the figure. At any La concentration, the oxygen content depends on the low-temperature annealing temperature and atmosphere. We have obtained samples of stoichiometry $BaLaYCu_3O_{7.4}$ by annealing for 16 h in O_2 at 500 °C and slow cooling. Figure 3 shows the change in oxygen content as a function of temperature for samples heated in N_2 , comparing the results for selected La substituted materials with that of $Ba_2YCu_3O_7$. All compounds begin to lose oxygen just below 400 °C and decompose above 900 °C. The lanthanum-containing compounds retain the structural oxygen to higher temperature than does $Ba_2YCu_3O_7$. The oxygen absorption/desorption kinetics are considerably slower in the lanthanum-containing materials.

The crystal structures of the tetragonal compounds of the $BaLaYCu_3O_{7\pm\delta}$ type have not yet been determined.

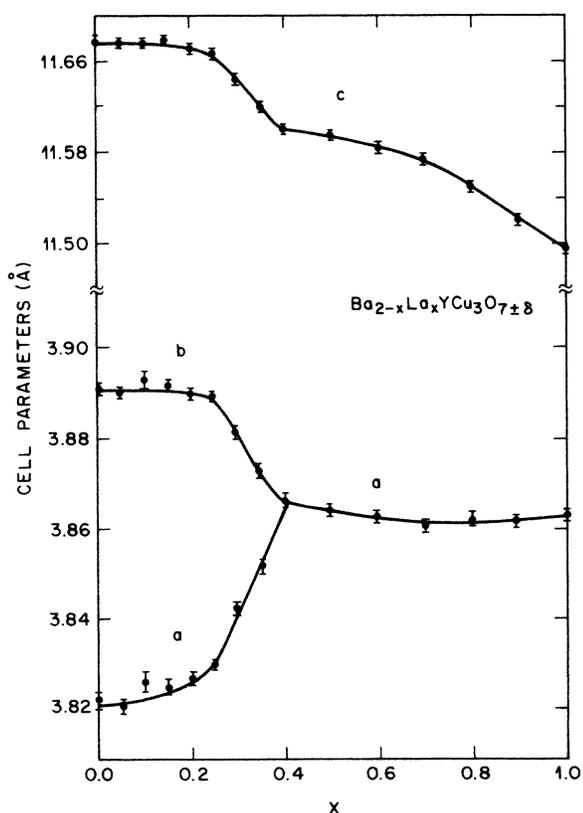


FIG. 1. Crystallographic unit-cell parameters for the $Ba_{2-x}La_xYCu_3O_{7\pm\delta}$ series of compounds prepared with a final anneal of 600 °C in O_2 .

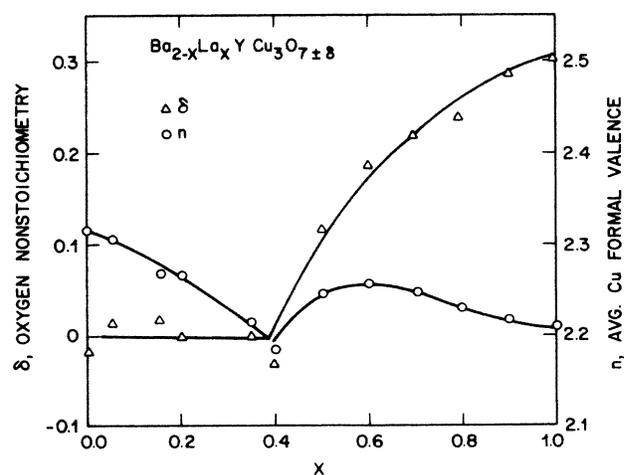


FIG. 2. Oxygen stoichiometry for the $Ba_{2-x}La_xYCu_3O_{7\pm\delta}$ series of compounds prepared with a final anneal of 600 °C in O_2 .

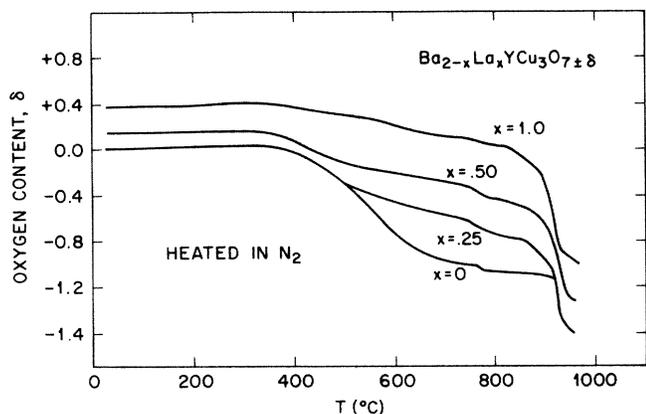


FIG. 3. Change in oxygen stoichiometry with temperature on heating in N₂.

However, to test whether the mixing of ions in the *A* site occurs (there could conceivably be long-range order in the 1:1:1 *A* site at composition BaLaYCu₃O_x with a 3*a* perovskite supercell) the low-temperature specific heat was measured in the Gd-containing analog BaLaGdCu₃O_{7±δ} which also has tetragonal symmetry (*a* = 3.84 Å, *c* = 11.6 Å). The specific heat is compared to that of Ba₂GdCu₃O₇ in Fig. 4. The peak corresponding to the magnetic ordering of the trivalent rare-earth moments has become broadened, indicating a distribution of transition temperatures. This is most likely due to disorder of the rare-earth ions among the available sites. Thus, crystal-chemical mixing of the *A* site ions is likely to be induced by the intermediate size of the La. The Gd compounds are tetragonal for Ba_{2-x}La_xGdCu₃O_{7±δ} from 0.2 ≤ *x* ≤ 1.0. The reduced range of orthorhombic compositions for Gd³⁺, which is only 4% larger than Y³⁺, indicates that there may be factors other than simple *A*-site mixing which determine the crystallographic symmetry. These factors certainly would have to influence the ability of the Cu-O chains to form in the kind of long-range order found in Ba₂YCu₃O₇. The average “tetragonal” symmetry observed in no way implies the absence of Cu-O chains, only

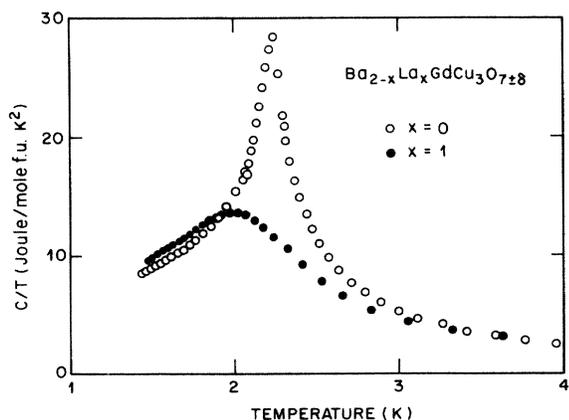


FIG. 4. Low-temperature specific heat of (a) Ba₂GdCu₃O₇ and (b) BaLaGdCu₃O₇.

the absence of long-range ordering of the chains.

The general behavior of the resistivity in the series is shown in Fig. 5. For *x* less than 0.6 the behavior of $\rho(T)$ is metallic, and superconducting transitions are observed. For *x* greater than 0.7, semiconducting behavior is observed, with increasing resistivity and activation energy with increasing *x*. The room-temperature resistivities increase by about 10³ between Ba₂YCu₃O₇ and BaLaYCu₃O_{7.3} (Table I), with the most substantial increase occurring in the tetragonal phase for *x* ≥ 0.7.

In the orthorhombic phase, the bulk *T_c*, measured magnetically, decreases smoothly from 91 to 64 K as the lanthanum concentration increases to the orthorhombic phase limit at *x* = 0.4 (see Table I). In the tetragonal phase at low La contents, a superconducting *T_c* can be measured magnetically, however the diamagnetism is only 5% of that expected, indicating that the material as prepared is not a bulk superconductor. Ba_{1.5}La_{0.5}YCu₃O_{7±δ}, the tetragonal composition which shows the sharpest resistive *T_c* and best flux exclusion, is one member of a solid solution studied earlier by Er-Rakho, Michel, Provost, and Raveau,¹¹ namely Ba₃La_{3-x}Y_xCu₆O_y. We therefore prepared materials in this solid solution at Δ*x*' = 0.25 intervals from *x*' = 0 to *x*' = 2.0 and tested their superconducting properties magnetically to see whether the true bulk tetragonal superconductor existed somewhere along that line in composition. The fraction of ideal diamagnetism increased from a low value of 1% to a high of 5% as *x* increased, with maximum value at *x*' = 2, the original member of our Ba_{2-x}La_xYCu₃O₇ (*x* = 0.5) solid solution series. We also submitted the Ba_{1.5}La_{0.5}YCu₃O_{7.1} prepared under normal synthetic conditions to a heating in Ar gas for 16 h at 600°C. The result was a complete loss of superconductivity, with a decrease of oxygen content to Ba_{1.5}La_{0.5}YCu₃O_{6.8}. This suggests that superconductivity in the tetragonal phase may be due to an inhomogeneous oxygen distribution near or greater than

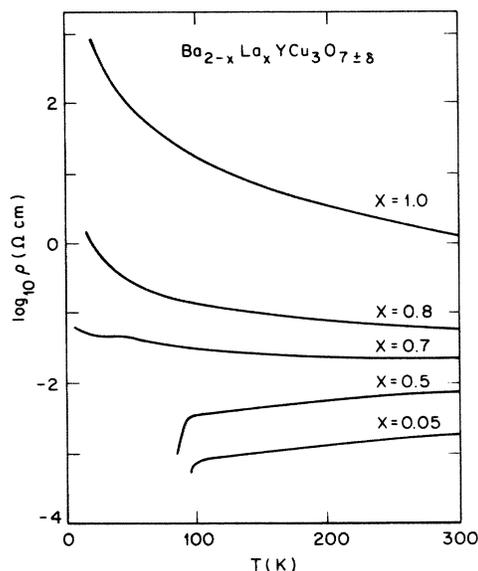


FIG. 5. Temperature-dependent resistivities for selected compositions in the Ba_{2-x}La_xYCu₃O_{7±δ} series.

oxygen contents of 7.0.

In conclusion, we have shown that La can be substituted for Ba in Ba_{2-x}La_xYCu₃O_{7±δ} while maintaining a perovskite stoichiometry, up to $x = 1$. Charge compensation is achieved by reduction of the average formal copper valence in the orthorhombic Ba₂YCu₃O₇-type phase ($x < 0.4$) and by a mixture of reduction and excess oxygen accommodation in the tetragonal phase ($0.4 \leq x \leq 1$). Specific-heat measurements on BaLaGd-

Cu₃O_{7±δ} suggest at least partial mixing of the large *A* ions among the available large atom sites in the $a \times a \times 3a$ perovskite cell, induced by the intermediate size of La. We have also successfully prepared the $x = 1$ end members BaLaRCu₃O_{7±δ} in single-phase polycrystalline form for $R = \text{Eu}$ and Gd ; and were not successful for $R = \text{Sc}$, Lu , La , Pr , Yb , and Bi , suggesting that the BaLaYCu₃O_{7±δ}-type phase may exist over an intermediate range of rare-earth radii.

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