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Single-Crystal Growth, Alkali Metal Ordering, and Superconductivity in $La_{2-x}M_xCuO_4$ (M = Na, K)

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Single crystals of $La_{2-x}M_xCuO_4$, where M is Na or K, have been prepared by precipitation from molten NaOH at 320 °C or from molten KOH at 450 °C. The composition of several individual crystals as determined by wavelength-dispersive X-ray fluorescence analysis averaged to $La_{1.88}Na_{0.12}CuO_4$ and $La_{1.79}K_{0.21}CuO_4$. Iodometric titrations on polycrystalline samples with identical compositions showed that the formal oxidation states for the Cu atoms are +2.19 and +2.31, respectively. On the basis of the analysis of single-crystal X-ray diffraction data, it has been determined that the alkali metal doped lanthanum copper oxides crystallize in a new structure type that is distinct from the analogous phases containing alkaline earth metal ions. The space group is *P*4/*nmm*, and lattice parameters are $a = 3.766(1)$ Å, $c = 13.216(5)$ Å for the Na-doped material and $a = 3.7708(7)$ Å, $c = 13.321(2)$ Å for the K-doped material. In these phases, the alkali metal ions are ordered in the rock-salt blocks, and the Cu atoms are displaced out of the plane toward the alkali metal ions. Despite this distortion of the CuO_2 planes, both phases exhibit superconductivity, near 26 and 6 K, respectively.

Introduction

The composition of the rock salt-type M–O (e.g., M = La, Sr, Ba) blocks that separate the perovskite-type CuO_2 layers in the high-temperature cuprate superconductors has a direct effect on the superconducting transition temperature, T_c.[1] In particular, there are effects due to substitution of ions with different charges (electronic effects) and different sizes (steric effects). While there have been many studies of the influence of M^{3+} and M^{2+} cations, much less is known about the changes in the structure and the electronic properties that occur upon doping of M^+ cations. Here, we report the synthesis and characterization of single crystals of superconducting $La_{2-x}M_xCuO_4$ (M = Na, K) obtained by precipitation from molten NaOH at 320 °C or from molten KOH at 450 °C. These materials exhibit superconductivity and crystallize in a new structure type that is distinct from the analogous phases containing alkaline earth metal ions.

Materials with substitution of M^+ cations in La_2CuO_4 have been poorly studied due primarily to the difficulties in preparing alkali metal-doped cuprates of known composition. There are several reports of $La_{2-x}M_xCuO_4$ (M = Na, K) synthesized by direct reaction in the solid state at elevated temperatures (between 800 and 1000 °C)[2] with nominal alkali metal content as high as $x = 0.6$.[2c] When the stoichiometries of the products were determined by chemical analysis, the alkali metal content was found to be consistently lower than the starting composition.[2c] This is presumably due to the volatility of the reactant alkali metal salts. The Na-doped materials exhibit superconductivity with $T_c \sim 30$ K.[2a] Reports regarding the K-doped materials include the absence of superconductivity[2a] as well as values for T_c as high as 40 K (with transition widths of 19 K and Meissner fractions of approximately 4%).[2c] Such inconsistencies are most likely caused by the limited control of alkali metal incorporation in solid-state synthesis and the difficulty of precise composition measurements on polycrystalline powders.

Both alkali metal incorporation and crystal growth are significantly enhanced by using molten hydroxides as solvents. The alkali metal-doped $La_{2-x}M_xCuO_4$ materials described here were obtained by dissolving the reactants in hydrated molten NaOH or KOH to form a homogeneous solution and subsequently precipitating the product by removal of water. The solution conditions were controlled to precipitate selectively homogeneous products free of binary impurity phases. This is in contrast to solid-state reaction routes described above which involve mixing solid reactants and heating to cause interdiffusion.

Hydroxide fluxes have been used successfully to either crystallize[3] or purify a large number of metals and binary metal oxides.[4] By comparison to the solubility of simple binary metal oxides, however, the formation of a ternary transition metal oxide with specific doping levels in the narrow compositional range required for superconductivity is more complex. Previously, we have shown that mixed alkali metal $La_{2-x}(Na,K)_xCuO_4$ can be prepared by precipitation from the molten NaOH/KOH eutectic mixture at temperatures as low as 300 °C,[5] substantially lower than the temperatures typically used to prepare doped lanthanum copper oxides. Similar results were reported recently by Günther *et al.*[6] The present work is the first study of the structure of single crystals of alkali metal-doped $La_{2-x}M_xCuO_4$ (M = Na, K).

Prior to this report, it had been assumed that there are no additional structural effects due to variations in the charges of the dopant ions. Here we show by refinement of single-crystal

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X-ray diffraction data that the alkali metal ions are ordered in the rock-salt blocks, and the Cu atoms in the CuO_2 layers are displaced out of the plane toward the alkali metal ions. A description of the structure and the superconducting properties of these materials is given below.

Experimental Procedures

Synthesis. Single crystals of $La_{2-x}Na_xCuO_4$ and $La_{2-x}K_xCuO_4$ were synthesized by mixing 0.41 g of La_2O_3 and 0.10 g of CuO with 20 g of NaOH or with 20 g of KOH in a silver crucible. These two reaction mixtures were heated in 1 h, with the crucible open to the ambient air, to a final temperature of 320 °C for the reaction in NaOH and to 450 °C for the reaction in KOH. Both reaction mixtures were held for 20 h at the respective final reaction temperature. The reaction was quenched to room temperature by removing the crucible from the furnace, and the hydroxide was removed by dissolution in water. The products consisted of shiny square plates (up to 0.15 mm across a face) dispersed in a deep black powder.

Several additional experiments were performed in order to determine the effects of temperature, reaction time, and partial pressure of water on the crystal growth. For crystal growth in NaOH, three different procedures were tried with conditions identical to those described above except for those of one procedure as follows: the temperature was held at 390 °C instead of 320 °C; the reaction time was increased from 20 to 90 h; and the partial pressure of water was increased from ambient (1–2 Torr) to 60 Torr by flowing compressed air through water and subsequently over the reaction mixture. For crystal growth in KOH, three parameters were changed as follows: the temperature was held at 530 °C instead of 450 °C; the reaction time was increased from 20 to 90 h; and the partial pressure of water was increased from ambient (1–2 Torr) to 60 Torr by flowing compressed air over water and subsequently over the reaction mixture. Additionally, the effects of replacing the silver crucible with nickel and Al_2O_3 were explored.

Characterization. Powder X-ray diffraction data were collected on a Siemens D500 diffractometer with Cu Kα radiation in order to establish phase purity for all samples discussed and to compare the lattice parameters of the single crystals with those of the rest of the sample (polycrystalline powder). Prior to data collection, the samples which consisted of small crystals dispersed in black powder were ground with an agate mortar and pestle. Data were collected in the range $10° \leq 2\theta \leq 90°$ with a step size of 0.05° and count time of 2 s. Average lattice parameters were calculated by using both the General Structure Analysis System (GSAS) Rietveld refinement code written by Larson and Von Dreele[7] and by the addition of Si as an internal standard and fitting the corrected peaks (>20 peaks) with a least-squares refinement. Both the 00*l* and the *hk*0 peaks were expanded to ensure no peak splitting was present, which could arise from inhomogenously doped materials.

The alkali metal content was estimated by wavelength-dispersive X-ray fluorescence analysis, by using an ARL SEMQ electron beam microprobe. Small crystals (0.1 mm × 0.1 mm) were mounted in epoxy and polished in order to obtain smooth surfaces for quantitative analysis. The intensities of the X-ray emissions from these crystals were compared with those of polished standards: LaB_6 and $AlLa_{3.7}$ were used for La, $NaAlSi_3O_8$ was used for Na, $Na_3(Na_{0.5}K_{0.5})[Al_4Si_4O_{16}]$ was used for Na and K, $(Na_{0.5}K_{0.5})[AlSi_3O_8]$ was used for Na and K, Cu metal was used for Cu, and MgO and NiO were used for O. Background counts for the wavelength regions of interest were determined by measuring the background fluorescence of materials with purities in excess of 99.99%. After correction for the background and interferences, ZAF corrections[8] were applied to the X-ray counts. Up to 10 measurements were taken across the large face of several single crystals; the uniformity of the alkali metal distribution could not be checked through a cross section of a platelet because the crystals were too thin relative to the beam diameter of ~1 μm.

Table 1. Summary of Single-Crystal X-ray Diffraction Data

	$La_{1.78}K_{0.22}CuO_4$	$La_{1.88}Na_{0.12}CuO_4$
color	black	black
size (mm)	0.11 × 0.15 × 0.004	0.12 × 0.13 × 0.004
crystal system	tetragonal	tetragonal
space group	*P*4/*nmm* (No. 129)	*P*4/*nmm*
a (Å)	3.7708(7)	3.766(1)
c (Å)	13.321(2)	13.216(5)
T (°C)	20	20
V (Å^3)	189.4	187.4
Z	2	2
fw	383.40	391.45
calcd density (g/cm^3)	6.688	6.935
μ(Mo) (cm^{-1})	255.26	266.82
diffractometer	Enraf-Nonius CAD4	
radiation (graphite monochromator)	Mo Kα	Mo Kα
no. of data collected	664	652
min, max 2θ (deg)	3.1, 60.0	3.1, 60.0
max *h*,*k*,*l*	5,5,18	5,5,18
data octants	+++, −++	+++, −++
scan method	ω	ω
abs method	analytical[20]	analytical[20]
transm factor range	0.10–0.84	0.16–0.81
no. of unique data ($I > 2.0\sigma(I)$)	168	137
refinement method	full-matrix least-squares on *F*	full-matrix least-squares on *F*
anomalous dispersion	La/K, Cu, O	La/Na, Cu, O
weighting scheme	$\propto[\sigma^2(I) + 0.0009I^2]^{-1/2}$	$\propto[\sigma^2(I) + 0.0009I^2]^{-1/2}$
atoms refined	aniso: La/K, Cu iso: O	aniso: La/Na, Cu iso: O
no. of params varied	19	19
data/parameter ratio	8.84	7.21
R	0.039	0.033
R_w	0.036	0.032
error of fit	1.48	1.35
2nd extn coeff (mm)	0.95(9) × 10^{-4}	0.15(3) × 10^{-4}

Contamination from the Ag crucible was not detected by microprobe. From atomic absorption, the Al_2O_3 and Ni crucibles were found to incorporate into the products in amounts of up to 3% by weight of Al or Ni.

The Cu oxidation state was determined by iodometric titration, according to methods described previously.[9] One Na-doped and one K-doped sample were chosen, each consisting of a mixture of small crystals dispersed in black powder. The lattice parameters and composition of these samples were determined to be essentially identical to those of the single crystals used for the structure determination.

The superconducting properties of all products were measured with either a Quantum Design or SHE SQUID magnetometer by cooling in fields close to 25 G. The field was calibrated with a superconducting tin sphere of known magnetization. Field-cooled susceptibilities were determined and compared to that of an ideal spherical shape with volume susceptibility of $-1/4\pi$.

Structure Determination. Information on the single-crystal X-ray data collection and structural refinement of the single crystals of $La_{2-x}Na_xCuO_4$ and $La_{2-x}K_xCuO_4$ is given in Table 1. Twenty-five intense diffraction maxima were measured and used to obtain the cell parameters and the orientation matrix. For the initial data collection of each compound, the *a* axis of the tetragonal unit cell (*I*4/*mmm* as determined for the alkaline earth metal-doped lanthanum copper oxides) was transformed by $a2^{1/2}$ to give $a = 5.33$ Å in order to allow for the existence of orthorhombic symmetry as found in undoped La_2CuO_4.[10] However, both structures were found to be tetragonal with $a = 3.77$ Å.

Weak reflections were observed that violated the body-centering of the 3.8 × 13 Å unit cell. These reflections were not observed in powder X-ray diffraction patterns or in long-exposure (18 h) precession photographs. The data averaged very well in 4/*mmm* symmetry, and the extinctions were consistent with the space group *P*4/*nmm*. Subsequently, the data collection was repeated more slowly in order to measure more accurately the weak reflections. For the K-containing material, the number of weak, non-body-centered reflections with $I > 2\sigma(I)$ was 62 out

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Table 2. Positional[a] and Isotropic Thermal Parameters[b] for $La_{1.78}K_{0.22}CuO_4$ and $La_{1.88}Na_{0.12}CuO_4$[c]

atom	site	*x*	*y*	*z*	*B* (Å^2)
La(1)	2c	0.250	0.250	0.88919(6)	0.63(4)
				0.8889(1)	0.63(7)
La/M(1)	2c	0.250	0.250	0.60858(6)	0.63(5)
				0.6090(1)	0.82(8)
Cu(1)	2c	–0.250	–0.250	0.7492(1)	0.59(7)
				0.7487(3)	0.67(7)
O(1)	4f	–0.250	0.250	0.7521(5)	1.3(1)
				0.7513(8)	0.8(1)
O(2)	2c	0.250	0.250	0.4305(8)	1.2(2)
				0.4348(14)	1.5(4)
O(3)	2c	0.250	0.250	0.0677(12)	2.6(4)
				0.0666(17)	2.2(5)

[a] Space group *P*4/*nmm*. [b] Metal atoms were refined anisotropically; B_{equiv} is given here. [c] First line is for the K-containing compound; second line, for the Na-containing compound.

Table 3. Anisotropic Thermal Parameters[a] ($\times 10^3$) for the Metal Atoms of $La_{1.78}K_{0.22}CuO_4$ and $La_{1.88}Na_{0.12}CuO_4$[b]

atom	U_{11}	U_{22}	U_{33}
La(1)	8.2(5)	8.2	7.6(6)
	7.6(10)	7.6	8.6(7)
La/M(1)	10.4(6)	10.4	3.2(7)
	9.9(12)	9.9	11.5(8)
Cu(1)	5.6(8)	5.6	11.4(10)
	4.7(7)	4.7	16.0(10)

[a] $\exp[-19.739(U_{11}h^2a^{*2} + ... + 2(U_{12}hka^*b^* + ...))]$. $U_{12} = U_{13} = U_{23} = 0.0$. [b] First line is for the K-containing compound; second line, for the Na-containing compound.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for $La_{1.78}K_{0.22}CuO_4$ and $La_{1.88}Na_{0.12}CuO_4$

		$La_{1.78}K_{0.22}CuO_4$	$La_{1.88}Na_{0.12}CuO_4$
Cu(1)–O(1)	×4	1.8858(4)	1.8833(6)
Cu(1)–O(2)	×1	2.393(11)	2.425(19)
Cu(1)–O(3)	×1	2.438(17)	2.440(23)
La(1)–O(1)	×4	2.626(5)	2.618(8)
La(1)–O(3)	×4	2.727(3)	2.727(5)
La(1)–O(3)	×1	2.379(17)	2.349(22)
La(1)–O(av)		2.643	2.637
La/M(1)–O(1)	×4	2.685(5)	2.662(8)
La/M(1)–O(2)	×4	2.717(2)	2.725(4)
La/M(1)–O(2)	×1	2.373(11)	2.302(19)
La/M–O(av)		2.665	2.650
O(1)–Cu(1)–O(1)	×2	177.7(5)	177.9(8)
O(1)–Cu(1)–O(1)	×4	89.98(1)	89.98(2)
O(1)–Cu(1)–O(2)	×4	91.2(2)	91.0(4)
O(1)–Cu(1)–O(3)	×4	88.8(2)	89.0(4)

Table 5. Variations in Synthetic Conditions

hydroxide	*T* (°C)	time (h)	*P*(H_2O)	products
NaOH	320	20	ambient	$La_{2-x}Na_xCuO_4$
NaOH	320	20	60 Torr	no precipitate
NaOH	320	90	ambient	$La(OH)_3 + CuO$
NaOH	390	20	ambient	$La_{2-x}Na_xCuO_4$
KOH	450	20	ambient	$La_{2-x}K_xCuO_4$
KOH	450	20	60 Torr	no precipitate
KOH	450	90	ambient	$La(OH)_3 + CuO$
KOH	530	20	ambient	$La_{2-x}K_xCuO_4$

of a total of 168 (39 out of 143 reflections greater than 3σ). For the Na-containing material, there were 32 out of 137 (see Table 2). All data were treated for Lorentz and polarization effects and corrected for absorption.

Initial atomic positions were calculated by shifting the coordinates of the body-centered K_2NiF_4 structure to the *P*4/*nmm* symmetry. In the space group *P*4/*nmm*, the La atoms occupy two crystallographically independent sites rather than one, and the *z* coordinates for the Cu atoms and the in-plane O atoms are not constrained as they are in the space group *I*4/*mmm*. Also, the two apical oxygen atoms, weakly bonded to copper, are independent of one another.

Full-matrix least-squares refinements were performed with anisotropic thermal parameters for the metal atoms. Site occupancies were refined for the two independent La sites. For both the Na and K materials, one La site refined to full occupancy while the other refined to a value indicating partial occupancy. The values of the correlation matrix elements for the scale factor, site occupancy, and thermal parameters for the La/Na(1) site were less than 0.51 and for the La/K(1) site less than 0.53. This result is consistent with occupancy of the latter site by all of the Na or K ions incorporated into the structure. The amount of alkali metal on the site was estimated by refining the site multiplier as a function of the ratio of the lanthanum and alkali metal scattering factor curves, assuming full occupancy of these metal atom sites. The stoichiometries obtained were $La_{1.78(1)}K_{0.22(1)}CuO_4$ and $La_{1.88(1)}Na_{0.12(1)}CuO_4$, in excellent agreement with the microprobe results as discussed below. Positional and thermal parameters are given in Tables 2 and 3. A selection of interatomic distances and angles is given in Table 4. Observed and calculated structure factors are available upon request.

Results and Discussion

Synthesis. The temperature, reaction time, and partial pressure of water were varied in order to gain a better understanding of the melt conditions necessary for crystal growth. A summary of the results of these experiments is given in Table 5. For both NaOH and KOH, CuO and La_2O_3 dissolve to form clear, blue solutions as the hydroxides melt near 320 and 420 °C, respectively. After 20 h, a deep black powder and shiny crystals are observed in each generally clear melt. Precipitation of the product was first observed in 3–10 h. Over the following 10 h, the crystal size tended to increase as small crystallites redissolved and the larger ones grew.

We presume that dissolution of CuO and La_2O_3 occurs due to the presence of a sufficient quantity of water. Because of the hygroscopic nature of NaOH and KOH, they typically contain 1 and 14 wt % water, respectively, from exposure to the atmosphere.[4]

The solubility of water is known to decrease with increasing temperature.[11] At the temperatures used for crystal growth, a sufficient quantity of water is removed, thereby increasing the O^{2-} activity sufficiently to cause precipitation of the product. When a partial pressure of water of 60 Torr is flowed over the melt, precipitation is prevented at the temperatures used to obtain the crystals reported here as shown in Table 5. These observations are consistent with other studies that have shown that the solubility of metal oxides in molten hydroxide depends on the concentration of water.[12]

Longer periods of time were tried in an attempt to increase the size of the crystals. However, as indicated in Table 5, CuO and $La(OH)_3$ were isolated after 90 h with only a small amount of $La_{2-x}M_xCuO_4$. This suggests that, under the conditions used, either $La_{2-x}M_xCuO_4$ is a kinetic product or the melt changes sufficiently over time to cause decomposition of $La_{2-x}M_xCuO_4$.

The product $La_{2-x}M_xCuO_4$ contains some Cu^{3+} proportional to the doping level (for small *x*). This suggests that some of the Cu^{2+} is oxidized to Cu^{3+} in solution. The most likely oxidants are peroxide and superoxide. These have complex equilibria in molten hydroxides that differ depending on which alkali metal hydroxide is used. Since peroxide and superoxide do not exist under conditions where the concentration of water is high,[4] this may be another reason that $La_{2-x}M_xCuO_4$ cannot be prepared under hydrated conditions.

The crystals investigated here were prepared at 320 and 450 °C from NaOH and KOH, respectively. Lower temperatures

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Table 6. Comparison of Lattice Parameters

sample	composition	*a* (Å)	*c* (Å)
single crystal	$La_{1.88}Na_{0.12}CuO_4$	3.766(1)	13.216(5)
polycrystalline	$La_{1.88}Na_{0.12}CuO_4$	3.771(1)	13.215(2)
single crystal	$La_{1.79}K_{0.21}CuO_4$	3.7708(7)	13.322(2)
polycrystalline	$La_{1.79}K_{0.21}CuO_4$	3.773(1)	13.323(3)

were not used because these temperatures are near the melting points of these hydroxides. Higher temperatures (up to 390 and 530 °C for NaOH and KOH, respectively) also lead to the crystallization of doped lanthanum copper oxides as shown in Table 5. However, for $La_{2-x}Na_xCuO_4$, the Meissner fraction was significantly lower for samples isolated at higher temperatures. For $La_{2-x}K_xCuO_4$, the transition temperatures were 6 and 20 K for the samples prepared at 450 and 530 °C, respectively. The dependence of the superconducting properties, as well as changes in composition with synthesis temperature, will be reported elsewhere.

Another critical parameter for the synthetic method reported here is the choice of crucible. While crucibles made of Al_2O_3, Ni, or Ag are reasonably stable to the molten hydroxide, we have found that small amounts of Al^{3+} and Ni^{2+} which dissolve in the melt are incorporated into the material (presumably on the Cu site). Therefore, it is difficult to distinguish the effects of Al^{3+} and Ni^{2+} doping (which tend to depress the onset of superconductivity) from alkali metal doping on T_c. Although Günther *et al.* used Al_2O_3 crucibles,[6] they did not report an analysis for Al in their products. We found Ag crucibles to be particularly inert. While Ag metal is found occasionally in the powder X-ray diffraction patterns, elemental analysis of the crystals indicates Ag is not incorporated into the bulk.

Characterization. The compositions of small crystals were determined to be $x = 0.12(6)$ for $La_{2-x}Na_xCuO_4$ and $x = 0.21(2)$ for $La_{2-x}K_xCuO_4$ from the microprobe data. Since several crystals were analyzed and the alkali metal content did not vary within the error reported in 5–10 measurements across each crystal, we conclude that the products are reasonably homogeneous. On the basis of the similarity of the lattice parameters (shown in Table 6), the compositions of the single crystals are identical to those of the bulk powders.

The results of the iodometric titrations showed that the formal oxidation states for the Cu atoms are +2.19 and +2.31 in the Na- and K-doped materials, respectively. These oxidation states are higher than the value of +2.15 which is observed for the Sr- and Ba-doped materials with the optimum value for T_c.[13,14] The errors in the x values obtained by microprobe analysis indicate, assuming stoichiometric oxygen, Cu-oxidation-state ranges of 2.12–2.36 and 2.38–2.46 for the Na- and K-doped materials, respectively. The higher values predicted on the basis of microprobe analysis suggest that the K-doped materials are slightly deficient in oxygen. Oxygen nonstoichiometry is also observed for the alkaline earth metal-doped materials with $x > 0.35$, corresponding to a similar Cu oxidation state of 2.35.[14] It is notable that the K-doped samples have substantially higher doping levels. This may be a consequence of the fact that superoxides and peroxides are more stable in KOH than in NaOH.[4]

Structure Description. On the basis of the analysis of the X-ray diffraction data, we conclude that $La_{1.88}Na_{0.12}CuO_4$ and $La_{1.79}K_{0.21}CuO_4$ both exhibit cation ordering, a structural feature that is new to the cuprate superconductors. The ordering is due to the segregation of the M^+ (M = Na, K) cations into every other La–O double layer along the *c* axis as shown in Figure 1. Several crystals were examined with a range of doping level, and all were found to exhibit ordering. Within the La^{3+}/M^+–O double layers, the alkali metal ions appear uniformly distributed.

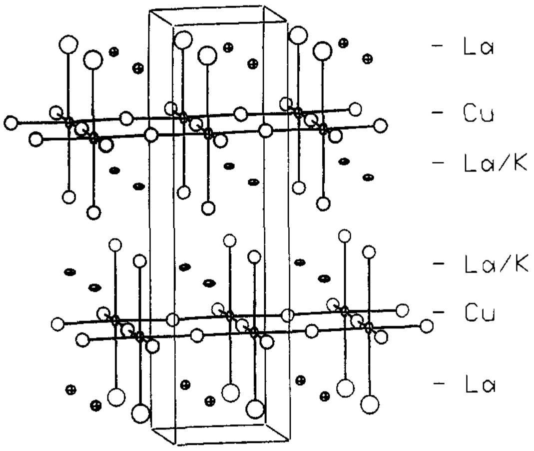

Figure 1. ORTEP representation[21] of the structure of $La_{2-x}M_xCuO_4$ (M = Na, K) approximately perpendicular to the *c* direction of the tetragonal unit cell. The large open circles are the O atoms, and the small open circles are the Cu atoms. The La–O layers and the La/M–O layers are labeled.

Frequently the ordering of cations occurs when the charge of the two cations differs by more than one unit. Two examples with the perovskite structure type are $Pb_2(ScTa)O_6$, where Sc^{2+} and Ta^{5+} are ordered,[15] or similarly La_2CuSnO_6, where Sn(IV) and Cu(II) form alternating layers.[16] An example with the K_2NiF_4 structure is $La_2Li_{0.5}Au_{0.5}O_4$, which has Li^+ and Au^{3+} ordering.[17] Rather than undergoing complete segregation where the cations are present in a 1:1 ratio as in the previous examples, the alkali metal-doped lanthanum copper oxides alternate between doped and undoped rock-salt layers. Thus in $La_{2-x}Na_xCuO_4$ every other double layer is doped with an alkali metal with a sequence of $[La–O]_2–CuO_2–[(La/Na)–O]_2–CuO_2$ alternating layers. This is in contrast to the alkaline earth metal-doped lanthanum copper oxides such as $La_{2-x}Ba_xCuO_4$, where Ba randomly substitutes for La.[13c]

The presence of these larger, lower valent ions is reflected in the longer average La/M–O bond lengths (2.67 Å for M = K and 2.65 Å for M = Na) when compared to the average La–O bond lengths (2.64 Å for both compounds) (see Table 4). This trend is expected from the sizes of the atoms, where the ionic radii for K^+, Na^+, and La^{3+} in nine-coordination with oxygen are 1.55, 1.24, and 1.22 Å, respectively.[18] Both the La–O and La/M–O double layers are sandwiched between sheets of O(1) atoms from the CuO_2 layers. The separation between the sheets containing the O(1) atoms along the *c* axis is greater for the La/M–O double layer because the M cations push these oxygen layers further apart. When compared to that of the La–O double layer, the separation is ~0.11 Å longer for M = K and ~0.07 Å longer for M = Na.

Another new structural feature is an apparent distortion of the CuO_2 layers with the Cu atom displaced out of the plane toward the La/M–O double layers. This small distortion is similar to that found in $YBa_2Cu_3O_7$ but has not been observed before in the $La_{2-x}M_xCuO_4$ phases. All four in-plane Cu–O bond distances remain the same (1.886 and 1.883 Å for M = K and Na, respectively). However, the distortion results in two different apical Cu–O bond lengths (see Table 4). Although these bond lengths are well within two standard deviation units of being equal, this subtle distortion appears to be real for several reasons.

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First, for both the Na and K materials, constraining the Cu and in-plane O atoms to lie in the same plane gave statistically worse agreement factors. Also, when the CuO_2 sheets were inverted to make Cu atoms lie closer to the La–O double layers, the refinements shifted the atoms back to their original positions. Of course, the strongest argument for the existence of a distortion is that the two apical O atoms reside in different structural and electronic environments, one in the La–O double layers and the other in the La/M–O double layers.

Superconducting Properties. For $La_{1.88}Na_{0.12}CuO_4$, the susceptibility decreases to diamagnetic values below 26 K to a value of -3.72×10^{-3} emu/g at 5 K, which corresponds to a Meissner effect of 29%. The onset of superconductivity near 30 K has been reported previously for Na-doped materials, but higher doping levels were claimed.[2a,c] For $La_{1.79}K_{0.21}CuO_4$, the susceptibility decreases below 6 K to a value of -9.50×10^{-4} emu/g at 2 K, which corresponds to a Meissner effect of 7%. The onset temperature for superconductivity near 6 K is substantially lower than the onset temperature of 40 K reported previously.[6,2a] Our preliminary results indicate that T_c does increase to about 20 K if the doping level is decreased.

The superconducting transition temperature is depressed for Na-doping compared with Sr-doping. It is reasonable to compare these two dopant ions because $La_{1.85}Sr_{0.15}CuO_4$ and $La_{1.88}Na_{0.12}CuO_4$ both have similar lattice parameters and similar formal oxidation states for Cu; i.e., the electronic and steric effects are similar. However, the T_c of 39 K[13a] for the Sr-doped material is significantly higher than that of 26 K for the Na-doped material. This suggests that it is not only the size of the dopant ions and the number of holes in the CuO_2 layers that influence T_c but also changes in the electronic properties due to differences in structure upon alkali metal doping.

It is surprising that superconductivity is observed for $La_{1.79}K_{0.21}CuO_4$, given the large amount of doping and the high formal oxidation state for Cu. In contrast, superconductivity is not observed for Sr- and Ba-doped samples with comparable Cu oxidation states.[13] Therefore, while the maximum T_c is lower for the alkali metal-doped materials compared with the alkaline earth metal-doped materials, the range in Cu oxidation states over which superconductivity is observed appears to be broader for the alkali metal-doped materials.

Conclusions

It appears that small changes in the structure such as the subtle distortions in the CuO_2 layers due to the ordering of the alkali metal cations in every other La–O double layer can cause large changes in T_c. Since the new structure type for the alkali metal-doped materials was not evident from analysis of powder X-ray and neutron diffraction data,[2] it is clear that the growth of single crystals is extremely important in elucidating structure–property relationships in the cuprate superconductors. The method we have reported here that utilizes molten hydroxides as solvents yields single crystals of suitable quality for single-crystal X-ray diffraction. This is a versatile crystal growth method; by optimizing the synthetic conditions (e.g., time, temperature, choice of alkali metal hydroxides, etc.), it should be possible to grow larger crystals and crystals with different doping levels, and in addition, other classes of copper oxides can be crystallized.[19]

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