Synthesis, Structure, and Superconductivity of La$_{2-x}$K$_x$CuO$_4$*

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Synthesis, Structure, and Superconductivity of La$_{2-x}$K$_x$CuO$_4$

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Abstract

The structural and superconducting properties of the La$_{2-x}$K$_x$CuO$_4$ system have been studied by neutron and X-ray powder diffraction, $ac$ magnetic susceptibility, and $dc$ electrical resistivity. Superconductivity is observed in both the orthorhombic and tetragonal phases with $x \geq 0.06$ and is absent for $x \leq 0.04$. At room temperature the system undergoes an orthorhombic-to-tetragonal phase transition at approximately $x = 0.07$. Diffraction studies show no evidence of a low temperature tetragonal (LTT) phase at 50 K. Comparison of the structural and superconducting properties with those for earlier reported La$_{2-x}$K$_x$CuO$_4$ compounds indicate that K contents have previously been highly overestimated.
Introduction

There has been considerable interest and effort to explore the substitutional chemistry of La$_2$CuO$_4$ after the discovery of superconductivity in the Ba-substituted La$_2$CuO$_4$ system [I]. Partial substitution of the alkaline earth elements Ca, Sr, and Ba for La results in compounds with superconducting transition temperatures as high as 38 K. The structural characteristics and superconducting properties of these alkaline earth doped systems have been thoroughly investigated and are reasonably well understood. In addition to the alkaline earth metals, the monovalent alkali metals have proven to be suitable candidates for producing the superconducting La$_{2-x}$A$_x$CuO$_4$ (A = Na, K) [2-10] and more recently La$_{2-x}$Rb$_x$CuO$_4$ [11] phases. In contrast to the alkaline earth doped systems, the structures and superconducting behavior, much less the sample composition of the alkali doped materials are not nearly as well defined.

Previous reports of the alkali metal doped compounds are conflicting and generally contradictory with our present knowledge of the structure-property relationships in the La$_2$CuO$_4$ systems. These inconsistencies can be attributed to the very complex synthetic chemistry of the alkali metal doped materials and the inherent difficulties in obtaining an accurate quantitative analysis at such low alkali metal substitution levels. Both conventional solid state techniques and a low temperature hydroxide flux method have been employed to produce powders, and in some cases, single crystals of these materials. The K-susstituted La$_2$CuO$_4$ compounds, that have been synthesized by both methods, illustrate the inconsistencies of the stoichiometries and physical properties between earlier reported samples.

Powder samples of La$_{2-x}$K$_x$CuO$_4$ have been prepared by reacting the binary oxide powders at temperatures generally greater than 800°C. Reports claim that samples in the composition range 0.0 < $x$ < 0.3 can be synthesized, yet they are not superconducting. In fact, superconductivity has only been observed for samples with $x$ ≥ 0.3 and even for
compounds with doping levels as high as \( x = 0.7 \) [9]. In comparison, superconductivity has been observed for the compositions \( 0.07 < x < 0.25 \) with a maximum \( T_c \) occurring at \( x = 0.15 \) in the Sr substituted system [12-14]. Since the monovalent K ion should be twice as effective in doping as \( \text{AE}^{2+} \) (\( \text{AE} = \text{Ca}, \text{Sr}, \text{Ba} \)) by contributing two holes to the CuO\(_2\) sheets per K atom, it is anticipated that for the same number of holes, \( x \) for K should be half that of \( x \) for \( \text{AE} \). This unusually high degree of K incorporation that corresponds to as much as \( x = 1.4 \) in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) suggests that these compounds are well into the overdoped regime and should not exhibit superconductivity. That superconductivity is observed suggests that the reported compositions may not be correct. Volatilization of K from the reaction is likely to occur at temperatures above 800°C, producing samples with considerably lower K contents than the "nominal" or "starting" compositions. In addition these samples may contain structural defects related to the choice of synthesis conditions. Defects in the form of oxygen vacancies may also result at these elevated synthesis temperatures resulting in an oxygen stoichiometry of "4.0 - \( \delta \)". Although these oxygen vacancies will counter the electronic effects of the K substitution, a superconductor with an alkali metal content of \( x = 0.7 \) would require an extraordinarily high value of \( \delta \) to effect the appropriate level of doping. Others have even suggested that a third defect, La vacancies, may be complicating this system [8], although there is no clear evidence to support this claim.

Single crystals of \( \text{La}_{2-x}\text{K}_x\text{CuO}_4 \) have been prepared by the recently described molten KOH flux method [2, 5, 11]. Superconducting crystals of compositions \( x = 0.07, 0.08, 0.20, \) and 0.20 have been described that have \( T_{c(\text{onset})} \)'s of 20, 21, 41, and 6 K, respectively. The lattice parameters, compositions, and \( T_{c(\text{onset})} \)'s of these compounds vary widely and do not exhibit the systematic behavior of \( T_c \) vs. \( x \) that is commonly found in other high-\( T_c \) copper oxide systems. Owing to the problems in determining accurate alkali metal contents coupled with the possibility of oxygen vacancies, it is
difficult to draw comparisons in the La$_{2-x}$K$_x$CuO$_4$ system. Clearly, a consistent synthesis procedure followed by a careful analysis of crystallographic and physical property data is necessary to understand any structure-superconductivity relationships or systematic structural behavior in La$_{2-x}$K$_x$CuO$_4$.

Here, we describe the synthesis, quantitative analysis, superconducting behavior, and structural analysis of La$_{2-x}$K$_x$CuO$_4$ (0.0 $\leq x \leq$ 0.16). We demonstrate that the La$_{2-x}$K$_x$CuO$_4$ system compares well with the Sr substituted system, and that several previous reports highly overestimate the K content. The onset of superconductivity with increasing $x$ is at $x = 0.06$ and the system undergoes an orthorhombic-to-tetragonal phase transition at $x = 0.07$.

**Synthesis and Characterization**

In a dry nitrogen atmosphere powders of KO$_2$, La$_2$O$_3$, and CuO were combined in stoichiometric ratios and intimately mixed. Care was taken throughout the various stages of synthesis to minimize alkali metal loss from the synthesis reaction by containing the powders and choosing a relatively low synthesis temperature. The powders were pressed into pellets and wrapped in gold foil before placing them in alumina tubes. The pellets were heated at 750°C for three days in a flowing oxygen atmosphere. Although oxygen vacancy formation, if occurring at all, should be slight at this low synthesis temperature, post synthesis treatment was performed to minimize such defects. Sample annealing was performed in flowing oxygen with an initial temperature of 475°C and cooling at 3.5°C/hr to 150°C.

Quantitative analysis of the powders with the Oxford Link ISIS EDS (Energy Dispersive Spectroscopy) unit (equipped with a thin window detector) on a Hitachi S-2700 scanning electron microscope confirmed the presence of all four elements in the powders. There were no trace impurities detected by EDS. The alkali metal contents
were determined from an average of at least four spectra. Figure 1 shows the potassium content in $\text{La}_{2-x}\text{K}_x\text{CuO}_4$ for the post-firing "sample compositions" versus the pre-firing "starting" compositions. Despite the care taken during the synthesis procedure to avoid potassium volatilization, some degree of potassium loss is unavoidable. From a least-squares fit of the data $x_{\text{sample composition}} = 0.4 \times x_{\text{starting composition}}$. Throughout the discussion in this paper the $x$ values refer to the post-synthesis "sample composition".

Sample homogeneity was checked by powder X-ray diffraction on a Rigaku Powder X-ray diffractometer. The ac susceptibility measurements were made between 4.5 and 50 K in a 1 Gauss field at 100 Hz with a Lake Shore Cryotronics Susceptometer. The variable temperature resistivity measurements were performed using the standard four-probe technique.

The normalized electrical resistivities ($\rho(T)/\rho(300 \text{ K})$) of the $\text{La}_{2-x}\text{K}_x\text{CuO}_4$ series of powders is shown in Figure 2. For the $x = 0.04$ sample, semiconducting behavior is observed. Superconductivity is observed in both the tetragonal and orthorhombic phases with K concentrations of $0.06 \leq x \leq 0.14$. However, only a slight increase in the resistive transition temperature with increasing K concentration is found. Resistive transition onset temperatures varied from 15 K for $x = 0.08$ to 21 K for $x = 0.14$. The temperature dependent susceptibility data agree well with the resistivity results. The onset of superconductivity occurs in the same temperature range of approximately 15 to 20 K. The shielding fractions were estimated from the powder susceptibility at 4.5 K using a density of 6.9 g/cm$^3$. The superconducting samples exhibited relatively low shielding fractions between 2 and 5 percent. The actual superconducting phase fraction may be somewhat larger if density corrections due to sample porosity were considered.
Neutron Powder Diffraction

Neutron powder diffraction data were collected at room temperature using the special environment powder diffractometer at Argonne National Laboratory's Intense Pulsed Neutron Source (IPNS) \[15\]. For the $x = 0.08$ sample diffraction data were collected at several temperatures from 50 to 340 K. The samples were contained in thin-walled, 0.25 inch diameter vanadium containers.

The powder diffraction data were analyzed with the Rietveld technique using the IPNS time-of-flight Rietveld code \[16\]. Only data from the high-resolution back-scattering detector banks ($2\theta = 145^\circ$) were used in the refinements. The scattering lengths used for La, K, Cu, and O were 0.827, 0.367, 0.772, and 0.581. The data were fit with either the orthorhombic Bmab space group that is isomorphic to space group Cmca or the tetragonal F4/mmm space group that is isomorphic to I4/mmm. The refined structural parameters for the samples are provided in Table I.

All samples were determined to contain La$_{2-x}$K$_x$CuO$_4$ as the major phase with some of the compositions containing the unreacted CuO and La$_2$O$_3$ phases. The Rietveld refinements included the La$_{2-x}$K$_x$CuO$_4$, CuO, and La$_2$O$_3$ phases. Only the scale factors of the CuO and La$_2$O$_3$ phases were refined and the cell and atomic positional parameters were taken from the literature. The occupancy of the La/K site in La$_2$. $x$K$_x$CuO$_4$ was fixed at the composition determined by analysis of the EDS data. The molar phase fractions of the three phases were determined from the refinement. Figure 2 shows the Rietveld refinement profile for La$_{1.92}$K$_{0.08}$CuO$_4$ as a representative sample.

For the smaller values of $x$ ($x = 0.02$ and 0.04) the molar phase fraction of the La$_{2-x}$K$_x$CuO$_4$ phases is as low as 50%, while the samples with $x \geq 0.06$ are more completely reacted with the major phase fraction over 90%. This increase in the La$_2$. $x$K$_x$CuO$_4$ phase that is associated with the larger amounts of KO$_2$ clearly may result from the mineralizing effect of the deliquescent peroxide or hydroxide on the reaction. The
KO₂ or KOH enhances the reactivity of the constituent binary oxide powders by promoting particle migration and diffusion.

The structural phase diagram of La₂₋ₓKₓCuO₄ (up to x = 0.16) contains two crystallographic phases at room temperature: for 0 ≤ x ≤ 0.06, the so-called low-temperature orthorhombic (LTO) phase that has Bmab space group symmetry exists; for 0.08 ≤ x ≤ 0.16, the high-temperature tetragonal (HTT) phase with F4/mmm space group symmetry is found. According to the standard settings the LTO and HTT phases have Cmca and I4/mmm symmetry, respectively. The nonstandard space groups were chosen to provide a clearer comparison between the two phases: \( c_{\text{ext}} = c_{\text{ortho}} \); \( a_{\text{F4/mmm}} = (a_{\text{ortho}} + b_{\text{ortho}})/2 \); \( a_{\text{I4/mmm}} = a_{\text{F4/mmm}}/\sqrt{2} \).

A polyhedral representation of the LTO and HTT phases is shown in Figure 4. In the HTT phase the coordination geometry about the Cu atoms is a tetragonally elongated octahedron of \( D_{4h} \) symmetry; the La/K sites have \( C_{4v} \) symmetry and are nine-coordinate. As shown in Figure 4(b) the structure comprises layers of distorted corner-sharing octahedra that are shifted with respect to adjacent layers by the face-centering symmetry operation. The La/K atoms are in a rock salt arrangement with apical oxygen atoms of the CuO₆ octahedra. Although closely related to the HTT structure, the LTO structure has some very significant distortions that are associated with the orthorhombic strain. In the orthorhombic structure, the O(1) atoms are not in the same plane as the Cu atoms and the O(2) atoms are no longer constrained to be directly above the Cu atoms. This results in the "tilting" of the octahedra as depicted in Figure 4(a). Although difficult to see in Figure 4(a), the in-plane O(1)-Cu-O(1) or "scissor" angle departs from 90° as the difference between \( a_{\text{ortho}} \) and \( b_{\text{ortho}} \) increases.
Results and Discussion

Lattice parameters in the La$_{2-x}$K$_x$CuO$_4$ system as a function of $x$ are shown in Figures 5 and 6. The lattice parameters dependence on doping exhibits a significant variation in the range of $0.0 \leq x \leq 0.08$ with essentially no systematic variation beyond 0.08. This behavior suggests that the solubility limit of K for La has been reached at $x = 0.08$, a relatively low level in comparison to other K-substituted La$_2$CuO$_4$ systems. For instance, a previously reported compound has lattice parameters of $a = 5.33$ and $c = 13.32$ Å[2,3] indicating a considerably larger degree of K substitution (cf. $a_{\text{min}} = 5.35$ and $c_{\text{max}} = 13.22$ Å in our system). This low solubility limit is consistent with the thermodynamics of the reaction conditions. The 750°C reaction temperature is significantly lower than the typical $>1000°C$ temperature used for the majority of the substituted La$_2$CuO$_4$ phases, where substitution continues to occur beyond $x = 0.25$. Although diffraction studies indicate that a solubility limit has been reached, EDS measurements indicate that for $x > 0.08$ that the K content of the sample is still increasing. This could be a result of residual K-containing impurities, the most obvious being amorphous KOH. This solubility limit in La$_{2-x}$K$_x$CuO$_4$ could potentially be extended by employing high pressure synthesis and/or higher reaction temperatures combined with excess amounts of KO$_2$ to compensate for the increased volatilization of K. However, under these conditions, defects may be difficult to avoid as it has been shown that the alkali metal substituted systems have a great propensity for oxygen vacancy formation.

Based on comparisons with the La$_{2-x}$Sr$_x$CuO$_4$ system, we conclude that the K content is overestimated by approximately 15 to 30 percent. The decrease of the $a$ axis length and increase of the $c$ axis length is consistent with the incorporation of K into the La$_2$CuO$_4$ lattice. The contraction of the Cu-O(1) bond upon substitution of a lower valence ion for La provides an indication of the degree of oxidation of the CuO$_2$ planes and a measure of the doping level. The Cu-O(1) distances of 1.894(1), 1.893(1), and
1.891(1) Å found in compositions of \( x = 0.04, 0.06, \) and 0.08 occur at doping levels of approximately 0.085, 0.090, and 0.125 in the \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) system [14]. For the same degree of oxidation, this would correspond to compositions of \( x = 0.042, 0.045, \) and 0.062 in the \( \text{La}_{2-x}\text{K}_x\text{CuO}_4 \) system. These values are slightly lower than the composition we determined by EDS measurements. However, it has been demonstrated that the substitution of a larger cation on the La site not only expands the \( c \) axis but also increases the \( a \) axis length [17]. Substitution of La by the larger cation \( \text{K}^+ (r_{\text{K}^+} = 1.55 \text{ Å}) \) compared to \( \text{Sr}^{2+} (r_{\text{Sr}^{2+}} = 1.27 \text{ Å}) \) would result in somewhat longer Cu-O(1) distances for the same degree of oxidation. Therefore, in comparing the Cu-O(1) distances of the two systems while taking into account the size effect, the actual amount of K is slightly less than our reported values.

The \( a,b \) lattice parameter dependence as shown in Figure 5 indicates that the room temperature orthorhombic-to-tetragonal phase transition occurs between \( x = 0.06 \) and 0.08. The orthorhombic strain and the square of the tilt angle vs. \( x \) are shown in Figures 7 and 8, respectively. It is clear from the linear dependence in the orthorhombic region that the two parameters follow mean-field theory, as observed in other alkaline-earth substituted systems [14]. The orthorhombic strain and \( \Theta^2 \) behavior provide two independent routes to determining the doping level at the phase transition. The \( x_{\text{phase transition}} \) values, determined by extrapolation of the data in the orthorhombic region are 0.067(3) and 0.075(2), respectively. In the \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) system, \( x_{\text{phase transition}} \) at room temperature occurs at 0.113(4) and corresponds to 0.113 holes per \( \text{CuO}_2 \) sheet. When comparing the values of \( x_{\text{phase transition}} \) in the K- and Sr-doped systems, it is clear that the reported amount of K is 15 to 25 percent larger than anticipated.

Lattice parameters as a function of temperature for the \( \text{La}_{1.92}\text{K}_{0.08}\text{CuO}_4 \) composition are shown in Figure 9. Although 50 K may not be sufficiently low to observe the low temperature (LTT) phase, analysis of the diffraction data reveals that
there is no evidence of the LTT phase at 50 or 100 K in the $x = 0.08$ sample. The transition from orthorhombic (LTO) to tetragonal (LTT) symmetry with increasing temperature occurs at approximately 230 K. For the $La_{2-x}Sr_xCuO_4$ system, this transition temperature occurs at $x = 0.14$ and would correspond to $x = 0.07$ for $La_{2-x}K_xCuO_4$. It has been shown for the alkaline earth substituted systems [18, that the substitution of a larger cation shifts this transition to even lower values of $x$. Thus, the amount of K in the $La_{1.92}K_{0.08}CuO_4$ sample judged by comparison of the phase transition temperature is probably overestimated.

Overall, the reported $x$ values in $La_{2-x}K_xCuO_4$, as judged by the comparisons of the two independently determined $x_{phase\ transition}$ values and the Cu-O(1) bond lengths with those found in the $La_{2-x}Sr_xCuO_4$ system, are overestimated by EDS measurements by approximately 15 - 30%. Based on these structural correlations, we conclude that the value of $x$ in our $La_{1.92}K_{0.08}CuO_4$ composition is actually between 0.055 and 0.07.

Conclusions

The careful and consistent synthetic procedure we described is essential for producing samples with a minimum number of oxygen vacancies to facilitate the investigation of any systematic behavior in these systems. From our study we observe that this alkali metal doped system behaves much like the alkaline earth doped systems:

i. Superconductivity is suppressed at the lower levels of K incorporation. Considering that these K levels are 30 percent too large, the region $0.0 \leq x \leq 0.028$ (cf. $0.0 \leq x \leq 0.06$ in the $La_{2-x}Sr_xCuO_4$ system) remains nonsuperconducting.

ii. The onset of superconductivity with increasing $x$ occurs at at similar hole concentrations.

iii. Superconductivity is found in both the orthorhombic and tetragonal phases.
Because we reached a solubility limit at $x = 0.08$, the overdoped region was not accessed in this study. We believe that optimum doping has not yet been attained, as evidenced by reaching the solubility limit without decreasing the values of $T_c$. This investigation demonstrates that the hole concentrations are not nearly as high as previously reported and actually correspond fairly well to values in the alkaline earth doped systems.

Acknowledgments

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References


TABLE I. Refined structural parameters from neutron powder diffraction data at room temperature for La₂₋ₓKₓCuO₄ samples. The non-standard space groups Bmab (isomorphic to the standard space group Cmca) and F4/mmm (isomorphic to the standard space group I4/mmm) were used for the orthorhombic and tetragonal phases, respectively. The atomic positions are La/K [0,y,z], Cu[0,0,0], O(1) [1/4,1/4,z], O(2) [0,y,z]. The La/K site was set to full occupancy with the K content fixed at the determined sample composition. Numbers in parentheses are statistical errors of the last significant digit.

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<td>c (Å)</td>
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% Molar Phase Fraction:

| La₂₋ₓKₓCuO₄ | 100 | 49.9(8) | 72(1) | 97(1) | 97(2) | 90(2) | 98(1) | 96(1) | 88(2) |
| CuO | 0 | 19.2(8) | 11(1) | 3(1) | 3(2) | 7(2) | 2(1) | 4(1) | 12(2) |
| La₂O₃ | 0 | 30.9(8) | 17(1) | 0 | 0 | 3(2) | 0 | 0 | 0 |

R_wp % | 6.002 | 4.935 | 6.027 | 5.673 | 5.000 | 5.320 | 6.622 | 7.052 | 6.163 |

Figure Captions

Figure 1. Potassium content in La$_{2-x}$K$_x$CuO$_4$ for the final sample composition versus the pre-synthesis starting composition.

Figure 2. Normalized resistivity $\rho(T)/\rho(300)$ for La$_{2-x}$K$_x$CuO$_4$ samples. ($\blacksquare$ $x = 0.04$; $\square$ $x = 0.06$; $\bigcirc$ $x = 0.08$; $\bigtriangleup$ $x = 0.10$; $\times$ $x = 0.12$; $\Delta$ $x = 0.14$)

Figure 3. Rietveld refinement profile of neutron powder diffraction data for the tetragonal La$_{1.92}$K$_{0.08}$CuO$_4$ sample. The plus (+) signs are the raw time-of-flight diffraction data. The solid line is the calculated profile. The tick marks below the profile indicate the position of the allowed Bragg peaks for the La$_{2-x}$K$_x$CuO$_4$, CuO, and La$_2$O$_3$ phases from top to bottom, respectively. The background was fit as part of the refinement, but has been subtracted before plotting. A difference curve (observed minus calculated) is plotted at the bottom.

Figure 4. Polyhedral representations of the LTO (left) and HTT (right) La$_{2-x}$K$_x$CuO$_4$ phases. According to our convention, the two structures have Bmab and P4/mmm space-group symmetry, respectively. The Cu atoms are at the center of the octahedra; the O(2) and O(1) atoms are at the apices and corner-sharing vertices of the octahedra, respectively. The large spheres are the disordered La/K atoms. The $b$ axis extends from left to right and the $c$ axis extends from top to bottom.

Figure 5. The $a$ and $b$ lattice parameters versus $x$ for the La$_{2-x}$K$_x$CuO$_4$ phases.

Figure 6. The $c$ lattice parameters versus $x$ for the La$_{2-x}$K$_x$CuO$_4$ phases.

Figure 7. Orthorhombic strain $(2(b-a)/(b+a))$ versus $x$ in La$_{2-x}$K$_x$CuO$_4$.

Figure 8. The square of the tilt angle ($\theta_1$) versus $x$. $\theta_1$ is defined as $\tan^{-1}(y[O(2)] \times b/z[O(2)] \times c))$. 

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Figure 9. The $a$ and $b$ lattice parameters versus temperature for La$_{1.92}$K$_{0.08}$CuO$_4$. The lines are guides to the eye.
$x$ in $\text{La}_{2-x} K_x \text{CuO}_4$ (sample composition)

Figure 1

$x$ in $\text{La}_{2-x} K_x \text{CuO}_4$ (starting composition)
Figure 2

Temperature (K)

\[ \rho(T)/\rho(300) \]
Figure 4

(a)

La/K

O(1)

O(2)

(b)

La/K

O(1)

O(2)
Figure 5

Graph showing the relation between x in La$_{2-x}$K$_x$CuO$_4$ (starting composition) and the a, b lattice parameter (Å). The graph includes data points for sample composition, with a clear trend observed.
Figure 6

$x$ in La$_2-x$K$_x$CuO$_4$ (sample composition) vs. c Lattice Parameter (Å)

$x$ in La$_2-x$K$_x$CuO$_4$ (starting composition)
Figure 7

$2(b-a)/(b+a)$

$x$ in $\text{La}_{2-x}\text{KCuO}_4$ (sample composition) vs. $x$ in $\text{La}_{2-x}\text{KCuO}_4$ (starting composition)
Figure 8

\[ \Theta_1^2 (\text{deg}^2) \]

\[ x \text{ in La}_2 \text{K}_{1-x} \text{CuO}_4 \] (sample composition)

\[ x \text{ in La}_2 \text{K}_{1-x} \text{CuO}_4 \] (starting composition)
Figure 9

Temperature (K)

Lattice Parameter (Å)