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Phase Relations in the Composition $(Pb_{1-y}Cu_y)Sr_2(Ln_{1-x}Ca_x)Cu_2O_7$ and the Crystal Structure of $La_{8-x}Sr_xCu_{8-y}O_{20}$

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The compound $(Pb_{0.71}Cu_{0.29})Sr_2(Ln_{1-x}Ca_x)Cu_2O_7$ (1212) has been synthesized as single phase material for La, Pr, Nd, Gd, Er, and Y from the proper starting compositions fired above 950°C. Calcium can be substituted up to $x = 0.5$. When this limit is exceeded the 1212 phase, $SrCuO_2$, and a hexagonal phase are formed. When $x = 1$ only $SrCuO_2$ and the hexagonal phase are formed. The hexagonal phase has the general composition $Sr_{5-x}Pb_{3+x}Cu_yO_{11+z}$. When a mixture corresponding to $PbSr_2Co_{0.5}Cu_{0.5}O_z$ is fired above 960°C a tetragonal phase isostructural with $TlSr_2CuO_5$ (121) forms, but below 960°C the hexagonal phase is formed. A nominal mixture of $PbSr_2CaCu_2$ (1212) fired at 930°C and quenched forms primarily the $SrCuO_2$ phase and some of the hexagonal compound, but slow cooling in the furnace produces a nearly single phase hexagonal product. The crystal structure of a crystal found in a reaction product from a nominal mixture $PbSr_2LaCu_2$ (1212) fired at 1050°C was determined from three-dimensional X-ray diffraction data. Its composition is $(La_{6.16}Sr_{1.84})Cu_{7.66}O_{20}$, $M_r = 1823.6$, tetragonal, $P4/mbm$, $a = 10.7468(8)$ Å, $c = 3.8633(3)$ Å, $V = 446.2(1)$ Å^3, $Z = 1$, $D_x = 6.79$ g cm^{-3}, $\lambda = 0.71069$ Å, $\mu = 288.0$ cm^{-1}, $R = 0.032$, $wR = 0.034$ for 385 observed reflections. The structure is formed by the articulation of Cu octahedra, square pyramids, and square coplanar nets into a three-dimensional framework. La/Sr are in 10-fold coordination to oxygen atoms that are in a perovskite-like arrangement. The octahedral Cu1 site contains 17% vacancies on the basis of the least-squares refinement of the site occupancy. The two apical Cu1–O bond lengths are 1.9317(1) Å, and the four equatorial lengths are 1.978(7) Å. The square Cu2–O bond lengths are 1.9317(1) and 1.869(6) Å, respectively. The square pyramidal Cu3–O bond lengths are 2.364(6) Å to the apex and 1.9322(2) and 1.878(7) Å, respectively, to pairs of the four equatorial oxygen ions. Valence bond calculation and the abence of Jahn–Teller distortion around the octahedrally coordinated Cu1 indicate that it is trivalent. © 1990 Academic Press, Inc.

Introduction

The crystal structure of the superconducting compound $(Tl_{1-x}Bi_x)Sr_2CaCu_2O_7$ (designated 1212) (*1*) is a variant of the now well-known structure of $YBa_2Cu_3O_7$ (123) (*2*). The two CuO_2 square coplanar layers are the common features with Y or Ca between the layers. These layers are sandwiched between CuO_3 chains in 123 and $(Tl, Bi)O_6$ octahedra in 1212. The alkaline earth cations are in interstices formed by oxygen ions in perovskite-related arrangements. While exploring the Pb–Sr–Ca–Y–Cu system near the composition range 1212 a single crystal structure analysis was performed on a nonsuperconducting phase $(Pb_{0.71}Cu_{0.29})Sr_2(Y_{0.73}Ca_{0.27})Cu_2O_7$ (*3*) in which Cu coexists with Pb in the same layer but is displaced from the latter. In a contin-

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uation of this work other lanthanides were substituted for Y and the solid solution range $Ln_{1-x}Ca_x$ was explored. While investigating the La phase $PbSr_2LaCu_2O_x$, a single crystal was found in the reaction product whose composition was shown by EDX (energy dispersive X-ray spectroscopy) to be approximately La + Sr = Cu. A structure determination was carried out that is reported here together with results on the solubility range of Ca–*Ln* in the 1212 structure type.

Experimental

Reaction mixtures were prepared to yield starting compositions $(Pb_{0.71}Cu_{0.29})Sr_2(Ln_{1-x}Ca_x)Cu_2O_y$. The starting compounds PbO, CuO, Sr_2CuO_3, and rare earth oxides were thoroughly ground, then fired in air in alumina boats at about 960°C and air quenched or furnace cooled. The product was examined by X-ray powder diffraction techniques using Cu*Kα* radiation and an instrument equipped with a diffracted beam monochromator. Lattice constants for the solid solutions were determined by a least-squares refinement of the *d* spacings of the X-ray powder diffraction lines and the results are summarized in Table I. The reaction product from a starting composition $PbSr_2LaCu_2O_z$ that was heated at 1050°C for 12 hr and cooled at 3°C/min contained a crystal in the contact zone between the alumina boat and the reaction product. Weissenberg and precession X-ray diffraction diagrams yielded lattice constants a = 10.76 Å, c = 3.88 Å, and the tetragonal space group *P*4/*mbm*. The lattice constants and space group correspond with those for $La_{8-x}Sr_xCu_8O_{20}$ (*4*). Its crystal structure had been determined by profile fitting of neutron powder diffraction lines. We, therefore, redetermined the structure from single-crystal three-dimensional X-ray diffraction data.

TABLE I

LATTICE CONSTANTS FOR RARE-EARTH SUBSTITUTIONS IN $(Pb_{0.71}Cu_{0.29})Sr_2(Ln_{0.75}Ca_{0.25})Cu_2O_7$

Ln	*a*	*b*	*c*
La	3.857(3)	3.858(2)	11.909(4)
Pr	3.849(1)	3.849(4)	11.916(5)
Nd	3.855(2)	3.854(5)	11.914(5)
Gd	3.836(3)	3.836(3)	11.837(5)
Y	3.819(2)	3.821(4)	11.830(4)
Er	3.816(4)	3.820(4)	11.817(4)

The crystal, 65 × 75 × 240 μm, was mounted on a Krisel automated Picker diffractometer equipped with an incident beam graphite monochromator, $\lambda(\mathrm{Mo}K\alpha) = 0.71069$ Å. The diffractometer angles for 20 reflections ($24° < 2\theta < 28°$) were precisely determined by carefully centering the 8 equivalent reflections for each. A least-squares refinement of the resulting 2θ values yielded the lattice parameters a = 10.7468(8) Å, c = 3.8633(3) Å. Intensity data were collected in the ω-scan mode to 60° 2θ with a scan rate of 4°/min, a scan width $w = 2 + 0.7 \tan \theta$, and 3-sec backgrounds taken at both high and low ω. Four standard reflections (161, 042, 611, 450) were measured every 60 min and their intensities varied randomly ±1%. The 2553 measured reflections, $h \leq 15$, $|k| \leq 15$, $|l| \leq 5$, were corrected for Lorentz, polarization, and absorption (*5*) with $\mu_l = 288\ \mathrm{cm}^{-1}$. The minimum and maximum transmission factors were 0.130 and 0.208. Estimated standard deviations were calculated from counting statistics. Equivalent reflections were averaged to give 401 unique reflections, $R_{\mathrm{int}} = 0.044$. Three hundred and eighty-five reflections were considered observed on the basis that $F \geq 5\ \sigma(F)$.

Refinement of the starting parameters taken from Er-Rakho *et al.* (*4*) with SHELX76 (*6*) using anisotropic temperature factors and allowing for varying Sr oc-

TABLE II

ATOMIC POSITION COORDINATES AND ANISOTROPIC TEMPERATURE COEFFICIENTS ($\times 10^4$) FOR $La_{6.16}Sr_{1.84}Cu_{7.66}O_{20}$[a]

Atom	X	Y	Z	U_{11}, Å^2	U_{22}, Å^2	U_{33}, Å^2	U_{12}, Å^2	U_{eq}, Å^2
Sr, La[b]	2603(1)	4700(1)	1/2	84(4)	95(4)	74(4)	−15(2)	84(2)
Cu1[c]	0	0	0	57(9)	U_{11}	22(13)	0	45(6)
Cu2	0	1/2	0	67(7)	U_{11}	63(11)	28(8)	66(5)
Cu3	2215(1)	$1/2 + x$	0	67(6)	U_{11}	62(9)	15(5)	66(4)
O1	0	0	1/2	138(41)	U_{11}	163(73)	0	146(31)
O2	1/2	0	1/2	304(55)	U_{11}	45(66)	−91(78)	218(34)
O3	2186(7)	$1/2 + x$	1/2	203(33)	U_{11}	28(45)	0(42)	145(22)
O4	3770(6)	$1/2 + x$	0	86(26)	U_{11}	169(49)	−84(35)	114(21)
O5	1574(7)	956(6)	0	131(30)	81(31)	97(32)	−55(24)	103(18)

[a] The anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk)]$. U_{eq} was calculated from $1/3 \sum U_{ii}$. $U_{13} = U_{23} = 0$. Numbers in parentheses are standard deviations.

[b] The fractional occupancy of La at this eight-fold site is 0.77(2).

[c] The fractional occupancy of Cu at the two-fold site is 0.83(1).

cupancy on the La site converged to $R = 0.056$. An examination of F_o vs F_c for strong, low index, reflections led to the inclusion of an isotropic extinction correction in the next refinement for which R dropped to 0.038. At this point it was noted that the thermal parameters for Cu1 were quite high indicating the possibility of less than full Cu occupancy at that site. Final refinement with 38 parameters using anisotropic temperature factors for all atoms, fractional occupancy of Sr on the La site, with the condition that $x_{Sr} + x_{La} = 1$, partial Cu1 occupancy, and an isotropic extinction correction, $F = F(1 - 1.5 \times 10^{-7} F^2/\sin\theta)$, $w = 6.7/[\sigma^2(F) + 0.0004 F^2]$, converged to $R = 0.032$, $wR = 0.034$, $S = 1.67$, $|\Delta/\sigma|_{max} = 0$ for the observed reflections; $R = 0.0350$, $wR = 0.0362$ for all 401 reflections. The largest peak in the final difference map, located at $z = 0$, was about 2.5 eÅ^{-3}. The scattering factors used were for neutral atoms corrected for real and imaginary parts of dispersion taken from the *International Tables for X-ray Crystallography* (*7*). Final atomic parameters are listed in Table II; a table of observed and calculated structure factor amplitudes as well as $\sigma(F)$ has been deposited.[1]

Discussion

A. Phase Relationships and Solid Solubility in 1212 Pb–Sr–Ln–Ca–Cu

The X-ray powder diffraction patterns for the compositions shown in Table I indicated that the products were single phase 1212 structures within the limits of detectability of the technique. The changes in lattice constants scale with rare-earth ion, as expected. A four-probe electrical resis-

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[1] See NAPS document No. 04750 for 4 pages of supplementary material. Order from ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy. $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material, $1.50 for postage of any microfiche orders.

tance measurement between room temperature and 20 K shows that these materials are semiconductors with a rapid rise in resistance below 100 K. The loss of O_2 was investigated by TGA. Desorption begins at about 500°C and is 0.3 wt% when the temperature reaches 810°C. Assuming an initial oxygen content of 7 this weight loss corresponds to a 6.88 oxygen composition in the formula at 810°C. Cooling the sample in air in the apparatus shows that the weight change is reversible. When the Ca concentration exceeds 0.5, X-ray diffraction lines from another phase or phases, in addition to those from 1212, are seen in the pattern. The X-ray diffraction pattern of a compound with nominal composition $(Pb_{0.71}Cu_{0.29})Sr_2(Y_{0.25}Ca_{0.75})Cu_2O_7$ shows the presence of the 1212 phase, a phase isostructural with $SrCuO_2$ (*8*) (hereafter designated as *M–B* phase), and lines from a hexagonal phase. When only Ca is present, i.e., nominal composition $(Pb_{0.71}Cu_{0.29})Sr_2CaCu_2O_7$, only the *M–B* and hexagonal phases are observed.

The hexagonal phase had also been seen previously in reaction products formed from Sr–Pb–Cu mixtures (*9*). The product from an initial mixture of 4Sr : 3Pb : 1Cu showed a diffraction pattern whose lines could all be ascribed to the hexagonal phase. This hexagonal phase was also observed when a mixture with nominal composition $PbSr_2Co_{0.5}Cu_{0.5}$ was fired below 960°C (*9*). When fired above 960°C it formed a tetragonal phase isostructural with $TlSr_2CuO_5$ (121) (*9–11*). It was observed that the phases produced from a nominal mixture $PbSr_2CaCu_2$ fired at 930°C and quenched into liquid N_2 were *M–B* and hexagonal, but furnace cooling resulted in a nearly single phase hexagonal product. A DTA curve of a sample in which the hexagonal phase was nearly single phase shows a strong endotherm at about 900°C. Quenching from above this temperature results primarily in the *M–B* phase while the hexagonal phase is stable below 900°C. EDX spectra and the single-phase preparation from 4Sr : 3Pb : 1Cu showed that this phase is low in Cu. The crystal structure of this compound has been determined and will be reported elsewhere (*12*). The hexagonal lattice constants are $a = 10.0$ Å, $c = 3.5$ Å, $P\bar{6}2m$ with a composition near $Sr_5Pb_3Cu_{0.6}O_{11}$.

B. $(La_{6.16}Sr_{1.84})Cu_{7.66}O_{20}$

The crystal structure is shown in Fig. 1. The three crystallographically independent Cu atoms are respectively, in octahedral (Cu1), square coplanar (Cu2), and square pyramidal (Cu3) coordination. The polyhedra articulate by corner sharing into a three-dimensional framework in which La/Sr are in perovskite-like interstices formed by 10 oxygen atoms and two oxygen vacancies. The oxygen vacancy is responsible for the square pyramidal coordination around Cu3.

Two oxygen atoms in the square coplanar configuration around Cu2 connect to other Cu2 units by corner sharing to form an infinite chain parallel to *c*. The corner sharing of a third oxygen forms the connective link to the square pyramidal Cu3 units. The Cu2–O–Cu3 direction is parallel to [110]. The Cu3 square pyramidal units extend as an infinite column by corner sharing parallel to *c*. The Cu1 octahedra share apical oxygens to form an infinite column parallel to *c* and connect to Cu3 pyramids by corner sharing of the four equatorial oxygen atoms. The zig-zag line of atoms Cu1–O–Cu3–O–Cu1 is also parallel to [110]. The missing oxygen atoms would provide an octahedral environment around each Cu and form the perovskite structure.

The positional parameters listed in Table II agree with those reported by Er–Rahko, *et al.* (*4*). These authors postulate an oxygen deficiency in the structure shown as $O_{20-\varepsilon}$ although they emphasize that the occupancy factors for all oxygen sites refined

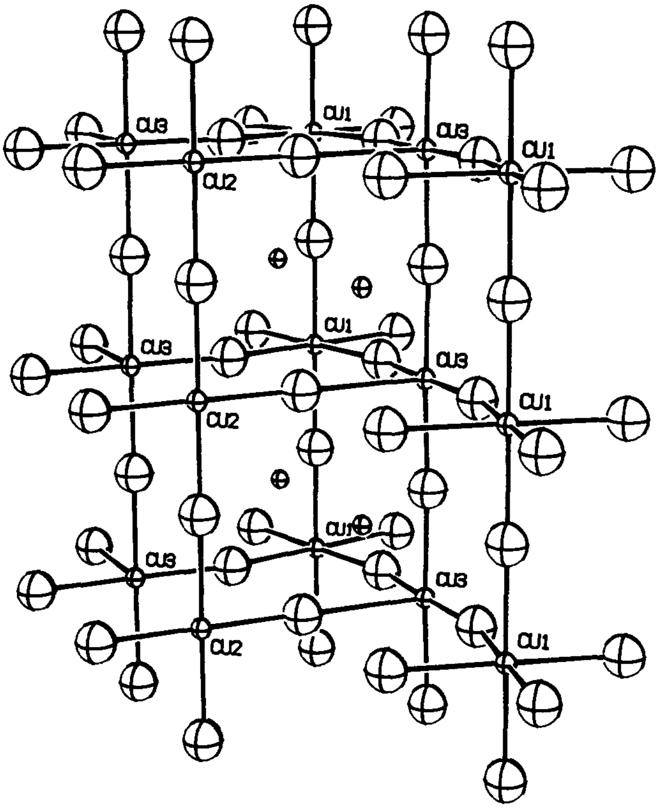

FIG. 1. The c axis is vertical and two repeats are shown. The direction from Cu1 at the lower right to Cu1 at the lower center is the $[\bar{1}10]$. The small unlabeled sphere is La/Sr; the large spheres are oxygen. The spheres have arbitrary radii.

to unity. We did not detect any oxygen deficiency in our structure determination in agreement with the result of their much more oxygen-sensitive neutron diffraction work. However, it was evident from the temperature factors of Cu1 that its site occupancy might be less than 1. A least-squares refinement in which this parameter was varied showed that 17% of the Cu1 sites are vacant. The average valence of Cu if the site is fully occupied would be +2.23 while it is +2.33 in this composition, corresponding to an approximate ratio of $2Cu^{2+} : 1Cu^{3+}$. It is interesting to speculate that the octahedral Cu1 site contains the trivalent Cu and the vacancy concentration reduces the $Cu^{+2} : Cu^{+3}$ ratio from about 3 : 1 to 2 : 1, similar to the average oxidation state found in $YBa_2Cu_3O_7$. To test this hypothesis bond valences were calculated around each Cu atom using the expression $S = \exp[(r_0 - r)/B]$, where $r_0 = 1.679$, $B = 0.37$, and r is the Cu–O bond length (*13*). The oxidation state of Cu is then equal to the sum of S, the valence of the bond between the cation, and the coordinating oxygen ion. These values for Cu1, Cu2, and Cu3 are, respectively, 2.79, 2.21, and 2.33. The sum of the cation valence using the values calculated for the three crystallographically independent Cu atoms is 40.4, in agreement with the requirement of −40 from the 20 oxygen ions. The value 2.79 for Cu1 lends credence to the supposition that

TABLE III

SIGNIFICANT BOND DISTANCES IN Å AND ANGLES IN DEGREES FOR $La_{6.16}Sr_{1.84}Cu_{7.66}O_{20}$

La,Sr–O1	2.5961(6)		
–O2	2.8159(6)		
–O3	2.708(8)		
–O3	2.712(8)		
–2O4	2.628(4)		
–2O5	2.517(4)		
–2O5	2.829(5)		
Cu1–2O1	1.9317(1)		
–4O5	1.978(7)		
Cu2–2O2	1.9317(1)		
–2O4	1.869(6)		
Cu3–2O3	2.9322(2)	O3–Cu3–O5	90.0(2)
–O4	2.364(6)	O3–Cu3–O5	91.1(3)
–2O5	1.878(7)	O3–Cu3–O4	91.3(2)

Note. Standard deviations are in parentheses.

it is the primary site for trivalent Cu. Further support for trivalent Cu1 is provided by the absence of a Jahn–Teller distortion.

The possibility that Al^{3+} is present in the Cu1 site can not be excluded since the crystal grew in the contact zone between the alumina boat and the reaction product. Standardless energy dispersive X-ray spectroscopic (EDS) analysis shows the presence of a very small amount of aluminum. With this assumption the Cu deficiency can be interpreted as due to a statistical site occupancy of approximately 0.7 Cu and 0.3 Al. The stoichiometry of this phase becomes then $La_{6.16}Sr_{1.84}(Cu_{7.4}Al_{0.6})O_{20}$. To maintain charge balance some trivalent Cu may be present as well in the octahedral site.

Er-Rakho *et al.* (*4*) present lattice constants for three compositions $La_{8-x}Sr_x$ and three values of ε, the oxygen deficiency. The *c* axis dimension reported here agrees very well with the value reported by those authors for $La_{6.08}Sr_{1.92}Cu_8O_{19.68}$ but *a* for the latter is 10.825(4) Å while in this work it is 10.7468(8) Å, well outside experimental error. We ascribe this difference to the Cu vacancies and the question whether the latter is influenced by the thermal history of the specimen remains to be answered.

The atomic coordinates and bond lengths shown in Tables II and III are in essential agreement with the previously published values. The octahedral Cu1–O1 apical distances agree very well but our Cu1–O5 are about 0.06 Å shorter. This would be consistent with a more trivalent oxidation state of the cation.

Conclusion

The limit of Ca replacement in the phase $(Pb_{0.71}Cu_{0.29})Sr_2(Y_{1-x}Ca_x)Cu_2O_7$ (1212) is 0.5. When this limit is exceeded two additional phases are observed. One is $SrCuO_2$ (*8*) and the other one is a new hexagonal structure with general composition $Sr_{5-x}Pb_{3+x}Cu_yO_z$. The replacement of Y by other lanthanides changes the lattice constants of the 1212 phase as expected. When the 1212 composition with $y = 0$, $x = 1$ and La was prepared a crystal with the general composition $(La_{8-x}Sr_x)Cu_{8-y}O_{20}$ was found. Its crystal structure was determined and it agrees in general with a previous determination based on neutron powder diffraction data. The octahedral Cu site contains 17% vacancies. No oxygen vacancies were found in this structure.

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