JOURNAL OF SOLID STATE CHEMISTRY 80, 201–205 (1989)

Preparation and Properties of $La_{2-x}A_xCuO_{4-y}$, Where A = Pb, Cd

C.-M. NIU

Department of Chemistry, Brown University,
Providence, Rhode Island 02912

C.-H. KIM

Department of Chemistry, Chongju University,
Chongiu-shi, South Korea

AND R. KERSHAW, K. DWIGHT, AND A. WOLD*

Department of Chemistry, Brown University,
Providence, Rhode Island 02912

Received December 12, 1988

The substitution of lead and cadmium for lanthanum in La_2CuO_4 was studied and the limits of solubility were established. Single-phase compositions were characterized and their physical properties were correlated with the substitution of bismuth and are interpreted on the basis of a model proposed by Goodenough. © 1989 Academic Press, Inc.

Introduction

In a previous study (*1*), it was shown that small substitutions of bismuth for lanthanum resulted in an increase in the delocalization of carriers as the bismuth content was increased. All of the samples showed *p*-type conductivity. This was found to be consistent with a model proposed by Goodenough (*2, 3*) in which antiferromagnetic behavior gives rise to correlation splitting of the σ^* band. The σ^* upband is essentially empty, but the observed *p*-type character of $La_{2-x}Bi_xCuO_4$ samples where $x > 0.08$ is consistent with some hole occupancy of the π^* band.

In an effort to further elucidate the role of A-site substitution on the electronic properties of La_2CuO_4, a study was undertaken to prepare samples in which both lead and cadmium were substituted for A-site lanthanum. There appears to be no report concerning the substitution of cadmium, but Guker *et al.* (*4*) indicated that even at a concentration of 5 at.% of lead substitution, a pure phase was not formed and the sample showed an activated conductivity. Since their preparations were attempted by direct combination of oxides or carbonates between 1000 and 1100°C, it is not surprising that pure products were not obtained. The purpose of this study was, therefore, to apply the method of double decomposition of mixed metal nitrates to prepare single-phase compounds with the compositions $La_{2-x}A_xCuO_4$ (A = Pb, Cd) and to charac-

---

* To whom all correspondence should be addressed.

0022-4596/89 $3.00

terize their electronic and magnetic properties.

Experimental

All samples were prepared by dissolving copper metal (5-9's Aesar Chemical Co.), $PbCO_3$ (reagent grade, Mallinckrodt) or Cd (5-9's Cominco), and La_2O_3 (4-9's Aesar Chemical Co.) in 1 : 1 dilute nitric acid. The solution was evaporated on a hot plate to dryness, then placed in a furnace and heated to 500°C for 24 hr in order to decompose the nitrates. The product was reground and reheated again for 24 hr at 800°C. After a final grinding, the product was heated for 24 hr at 950°C and allowed to slow cool in air to room temperature. In order to prepare samples which are oxygen deficient, the products were heated in a predried argon atmosphere (flow rate of 50 sccm/min) at 600°C.

Characterization of Samples

X-ray powder diffraction patterns were obtained with a Philips–Norelco diffractometer using monochromatic high-intensity $CuK\alpha_1$ radiation (λ = 1.5405 Å). For the qualitative identification of the phases present, the patterns were taken from $12° < 2\theta < 72°$ with a scan rate of 1° 2θ/min and a chart speed of 30 in./hr. The scan rate used to obtain X-ray patterns for precision cell constant determination was 0.25° 2θ/min with a chart speed of 30 in./hr. Cell parameters were determined by a least-squares refinement of the reflections using a computer program which corrects for the systematic errors of the measurement. The total active oxygen content of the samples was determined by the procedure of Ward and Struthers (5). This method allows for the determination of total oxidation of copper, i.e., the amount of formal valence Cu(III) present in the products. Thermogravimetric analysis indicated no loss of copper, lead, or cadmium up to the temperature of preparation. Therefore, the compositions of the prepared samples corresponded to the stoichiometries given. Magnetic susceptibility measurements were carried out using a Faraday balance from 77 to 300 K with a field strength of 10.4 kOe. Field dependency measurements were carried out at 77 and 300 K. The van der Pauw method was used to measure the electrical resistivity. Contacts were made by ultrasonically soldering indium directly onto sintered pellets and their ohmic behavior was established by measuring the current–voltage characteristics. Qualitative Seebeck measurements were also made to characterize the carrier type of the samples.

TABLE I

PROPERTIES OF $La_{2-x}Pb_xCuO_{4-x/2+\delta}$ AS PREPARED AT 950°C

Compound	Lattice parameter (Å)					ρ (77 K)
(x)	a	b	c	δ	T_N (K)	(Ω cm)
0.00	5.357(2)	5.400(2)	13.16(1)		240	1
0.002	5.355(2)	5.402(2)	13.15(1)		230	
0.01	5.358(2)	5.403(2)	13.16(1)		185	10^{-1}
0.02	5.353(2)	5.397(2)	13.16(1)			
0.05	5.353(2)	5.396(2)	13.16(1)	0.01		
0.10	5.351(2)	5.380(2)	13.18(1)	0.02		
0.15	3.354(2)	5.378(2)	13.20(1)	0.03		10^{-2}
0.20	5.355(2)	5.380(2)	13.21(1)	0.03		10^{-2}

TABLE II

PROPERTIES OF $La_{2-x}Pb_xCuO_{4-x/2+\delta}$ ANNEALED IN ARGON AT 600°C

Compound	Lattice parameter (Å)					ρ (77 K)
(x)	a	b	c	δ	T_N (K)	(Ω cm)
0.00	5.356(2)	5.406(2)	13.15(1)		300	
0.002	5.355(2)	5.404(2)	13.14(1)		280	
0.01	5.355(2)	5.403(2)	13.15(1)		200	1
0.02	5.354(2)	5.399(2)	13.16(1)		105	
0.05	5.357(2)	5.400(2)	13.16(1)		90	
0.10	5.352(2)	5.382(2)	13.19(1)	0.02		
0.15	3.355(2)	5.379(2)	13.20(1)	0.02		10^{-2}
0.20	5.354(2)	5.377(2)	13.20(1)	0.03		10^{-2}

Results and Discussion

Polycrystalline samples of the systems $La_{2-x}Pb_xCuO_{4-x/2+\delta}$ and $La_{2-x}Cd_xCuO_{4-x/2}$ were prepared by decomposition of the appropriate nitrates in air. The limit of substitution of lead for lanthanum was established at x = 0.15. For the composition where x = 0.24, there was evidence for the presence of excess PbO as determined from X-ray diffraction patterns using a scan rate of 0.25° 2θ/min with a chart speed of 30 in./hr. For cadmium substitution the limit was established at $0.05 > x > 0.02$. CdO appeared in X-ray patterns of the composition x = 0.05.

The lattice parameters for members of the lead-substituted series are given in Table I and Table II. It is readily seen that for x = 0.2, the a and b parameters approach each other. However, at this composition, the structure is still orthorhombic. It was shown (*1*) that for bismuth substitutions at $x > 0.08$, the products were tetragonal. It is apparent that lead does not affect the orthorhombic to tetragonal transition as markedly as bismuth. The degree of substitution of cadmium for lanthanum is too small to change the cell parameters.

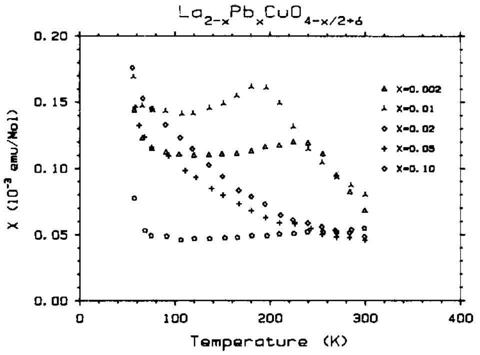

FIG. 1. Magnetic susceptibility as a function of temperature for members of the system $La_{2-x}Pb_xCuO_{4-x/2+\delta}$ as prepared in air.

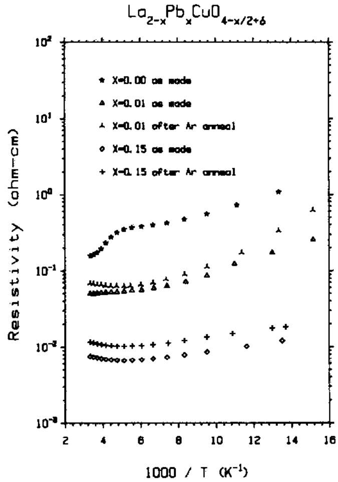

FIG. 2. Temperature dependence of the resistivity of members of the system $La_{2-x}Pb_xCuO_{4-x/2+\delta}$.

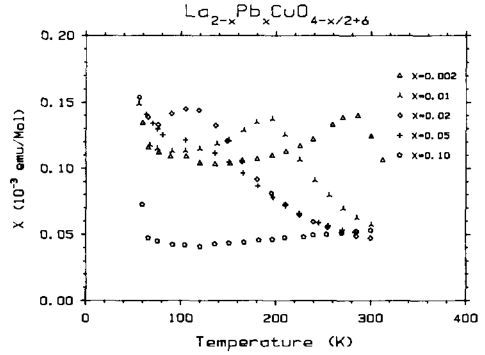

FIG. 3. Magnetic susceptibility as a function of temperature for members of the system $La_{2-x}Pb_xCuO_{4-x/2+\delta}$ annealed in argon.

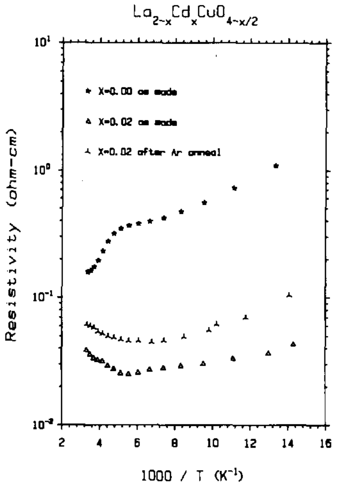

FIG. 5. Temperature dependence of the resistivity of members of the system $La_{2-x}Cd_xCuO_{4-x/2}$

The magnetic susceptibility vs temperature measurements were made on members of the series $La_{2-x}Pb_xCuO_{4-x/2+\delta}$ where $0.002 < x < 0.2$. The results of these measurements are summarized in Tables I and II and Figs. 1 and 3. As the lead content is increased, there is a marked decrease in the observed Néel point and, at $x \geq 0.1$, Pauli paramagnetic behavior is observed. The resistivities of the as-prepared samples are plotted vs $1000/T$ in Fig. 2. It can readily be seen that the resistivity decreases with increasing lead substitution and the lead-substituted samples show metallic behavior. Both the magnetic and electrical measurements indicate that, as observed with the bismuth-substituted system (*1*), there is an increase in delocalization of carriers with increased lead substitution. The observed *p*-type character of these materials indicates some hole occupancy of the π^* band. The σ^* band is split and the σ^* upband is essentially empty. When the samples were annealed in argon, an observable increase in the resistivity as well as an increase in the Néel temperature were obtained (Table 2, Figs. 2 and 3) for samples where $x < 0.1$.

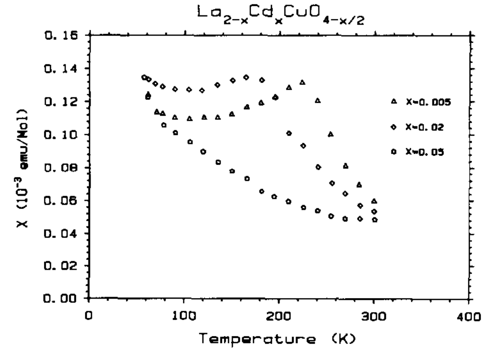

FIG. 4. Magnetic susceptibility as a function of temperature for members $La_{2-x}Cd_xCuO_{4-x/2}$ as prepared in air.

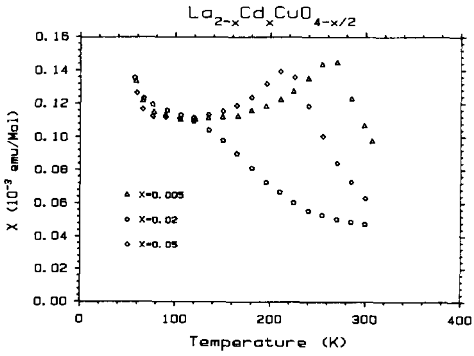

FIG. 6. Magnetic susceptibility as a function of temperature for members of the system $La_{2-x}Cd_xCuO_{4-x/2}$ as annealed in argon.

For samples where $x \geq 0.1$, metallic behavior is still observed. All of the argon-annealed samples retained an orthorhombic structure. Attempts to analyze the active oxygen content of all the samples prepared (by iodometric analysis) gave compositions which were close to $La_{2-x}Pb_xCuO_{4-x/2}$. However, several of the samples with a lead content greater than 0.1 did show a detectible increase in active oxygen, i.e., $La_{2-x}Pb_xCuO_{4-x/2+\delta}$ where $\delta \approx 0.02$.

Samples of $La_{2-x}Cd_xCuO_{4-y}$ where $0.005 < x \leq 0.05$ were also prepared by decomposition of mixed nitrates. Since the amount of cadmium which was substituted for lanthanum was small, it was not possible to analyze for the value of y which appeared to approach that of $x/2$. The susceptibility and resistivity data of the products are given in Figs. 4 and 5. It can be seen that the Néel point is no longer observable when there is greater than 2.5 at.% cadmium substitution for lanthanum. All samples showed p-type metallic behavior with a decrease in the resistivity as cadmium is introduced into the sample. Annealing the products in argon increases the resistivity and also the observed Néel temperatures (Figs. 5 and 6). These observations are also consistent with the Goodenough model (*2, 3*). It therefore appears that the substitution of Bi, Pb, and Cd all increase the degree of electron delocalization in La_2CuO_4, and that annealing of the samples in argon results in an increase in localization and splitting of the σ^* band with most of the hole concentration located in the σ^* upband.

Acknowledgments

This research was partially supported by the Office of Naval Research and by the Eastman Kodak Company, Rochester, New York.

References

1. C.-M. Niu, J. DiCarlo, K. Dwight, and W. Wold, *J. Solid State Chem.*, in press.

2. J. B. Goodenough, *J. Mater. Education* **9**(6), 619 (1987).

3. J. B. Goodenough, A. Manthiram, Y. Dai, and A. Campion, "Superconductor Science and Technology," IOP Pub., Bristol, in press.

4. D. U. Gucker, R. A. Hein, S. H. Lawrence, M. S. Osofsky, D. J. Schrodt, L. E. Toth, and S. A. Wolf, *Phys. Rev. B* **35**, 5350 (1987).

5. R. Ward and J. D. Struthers, *J. Amer. Chem. Soc.* **59**, 1849 (1937).