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Preparation and Properties of $La_{2-x}Bi_xCuO_4$ ($0.1 \geqq x \geqq 0$)

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Samples of $La_{2-x}Bi_xCuO_4$ were prepared by codecomposition of the nitrates in air. Single-phase products were obtained for $x \leqq 0.10$. The substitution of bismuth for lanthanum resulted in an increase in delocalization of holes, as indicated by increased conductivity and a decrease in the Néel temperature. Samples were also annealed in argon at 600°C and their properties compared with the samples as prepared in air. © 1989 Academic Press, Inc.

Introduction

La_2CuO_4 was reported by Longo and Raccah (*1*) to show an orthorhombic distortion of the K_2NiF_4 structure with $a = 5.363$ Å, $b = 5.409$ Å, and $c = 13.17$ Å. La_2CuO_{4-x} undergoes a second-order tetragonal–orthorhombic phase transformation and the temperature at which this transformation occurs is dependent on the value of x (*2*). A plot of the transformation temperature vs anion defect concentration in La_2CuO_{4-x} indicates that for a change of 0.03 in the value of x, the transition temperature is increased by ~75 K. A magnetic susceptibility anomaly also occurs which is due to long-range antiferromagnetic ordering in the sample (*3, 4*); it was shown that the Néel temperature is sensitive to the oxygen vacancy concentration and increases as the anion vacancies are increased.

Fukuda *et al.* (*5*) reported on the substitution of lanthanum by bismuth. For the system $La_{2-x}Bi_xCuO_4$, the orthorhombic structure is maintained for $0.04 > x \geqq 0$. Phases prepared where $x > 0.06$ were not pure but contained unreacted Bi_2O_3. Within the small range of substitution where the orthorhombic structure persists at room temperature, the observed Néel point was found to shift to lower values as the value of x increased.

There appear still to be some uncertainties concerning the magnetic properties of La_2CuO_{4-x} as x approaches zero. Whereas there is agreement concerning the observed increase in T_N as the anion vacancy concentration is increased, the disappearance of observable antiferromagnetic behavior in some of the samples prepared (*2, 6, 7*) has been difficult to reproduce. Furthermore, the preparation of bismuth substituted samples were carried out by direct reaction of the oxides, which is an inferior method when small substitutions are made. Hence

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this system deserves restudy since the effect of bismuth substitution for lanthanum was not clarified.

Experimental

All samples were prepared by dissolving copper metal (5–9's Aesar Chemical Co.), Bi_2O_3, 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, reheated again 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 ($\lambda = 1.5405$ 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.

Reversibility between the orthorhombic and tetragonal structures was shown using a Cahn 113 thermal balance. The sample was purged at room temperature either in a stream of argon or in a stream of oxygen for 2 hr and then the temperature was increased to 600°C at a rate of 60°C/hr and held at that temperature for 12 hr. The flow rate of the gas was 60 sccm/min. The total active oxygen content of the samples was determined by the procedure of Ward and Struthers (*8*). This method allows for the determination of total oxidation of copper, i.e., the amount of formal valence Cu(III) present in the products. 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.

Results and Discussion

Pure La_2CuO_4 was prepared by decomposition of the nitrates followed by an oxygen anneal at 500°C and 600 psi of oxygen. Small anion deficiencies could not be unambiguously determined by direct thermogravimetric analysis which has a limit in accuracy in x of 0.01 for the composition La_2CuO_{4-x}. However, significant shifts in the Néel temperatures confirmed a variation in anion content (*9*).

Polycrystalline samples of the system $La_{2-x}Bi_xCuO_4$ were also prepared by decomposition of the nitrates in air. The limit of substitution of bismuth for lanthanum was established at $x = 0.10$. For an attempted composition of $x = 0.12$, there was evidence for the formation of excess Bi_2O_3 as determined by step counting over the (121) reflection of Bi_2O_3 at a 2θ angle of 27.4°. The compositions of the $La_{2-x}Bi_xCuO_4$ samples were confirmed by iodometric analysis; i.e., the total active oxygen corresponded to a formal oxidation state of Cu(II).

The cell parameters for $La_{2-x}Bi_xCuO_4$ are given in Table I. It can be seen from Table I

TABLE I

PROPERTIES OF $La_{2-x}Bi_xCuO_4$

Compound	Crystal structure	Lattice parameters (Å) a	b	c	T_N (K)	ρ (77 K) (Ω cm)
x = 0.00	ort	5.357	5.400	13.16	240	1
0.002	ort	5.355	5.401	13.15	200	—
0.005	ort	5.357	5.402	13.16	100	—
0.01	ort	5.357	5.400	13.16	—	—
0.02	ort	5.362	5.397	13.17	—	—
0.04	ort	5.362	5.387	13.17	—	10^{-2}
0.06	ort	5.369	5.381	13.18	—	—
0.08	tet	3.802	—	13.19	—	10^{-2}
0.10	tet	3.802	—	13.20	—	—

and Fig. 1 that for $0.08 > x \geqq 0$ the products crystallize with an orthorhombic structure, and for $x > 0.08$ the phases are tetragonal. Fukuda *et al.* (*5*) have indicated that the phase transition occurs at $x = 0.04$. The difference in the reported compositions at which a phase change occurs may be due to the different preparative methods used. It was formerly established (*10*) that codecomposition of the nitrates is a superior method to the direct combination of oxides. The magnetic susceptibilities of samples prepared in air are given in Fig. 2. For compositions where $0.005 > x \geqq 0$, antiferromagnetic behavior was observed. However, for $x = 0.08$, the susceptibility was almost temperature independent. The susceptibilities of samples prepared where $0.01 < x < 0.08$ were observed to be similar to that obtained for $x = 0.08$.

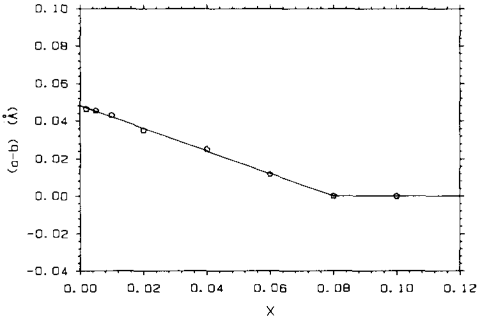

FIG. 1. Magnitude of the orthorhombic distortion (difference between a and b cell edges) as a function of composition for samples of $La_{2-x}Bi_xCuO_4$ as prepared in air.

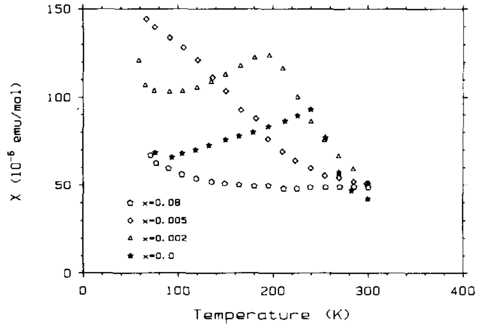

FIG. 2. Variation of magnetic susceptibility with temperature for samples of $La_{2-x}Bi_xCuO_4$ as prepared in air.

Resistivity measurements of the samples prepared in air are shown in Fig. 3. It is apparent that the resistivity decreases with increasing bismuth content. It is evident from both the magnetic and electrical measurements that there is an increase in delocalization of carriers in the system as bismuth is substituted for lanthanum. All of

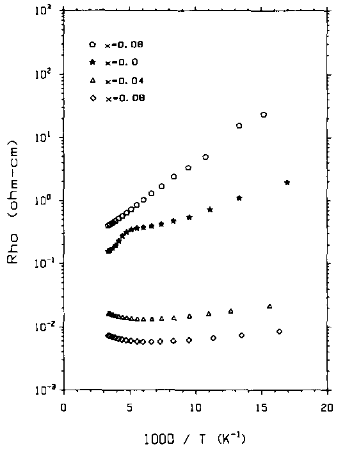

FIG. 3. Comparison of the magnitude and temperature dependence of the resistivities of several compositions of $La_{2-x}Bi_xCuO_4$ as prepared in air, together with a sample of $La_{1.92}Bi_{.08}CuO_{3.96}$ which was annealed in argon.

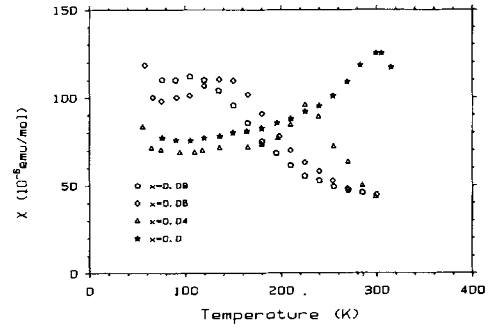

FIG. 4. Variation of magnetic susceptibility with temperature for samples of $La_{2-x}Bi_xCuO_{4-y}$ which were annealed in argon.

the samples prepared in air showed p-type conductivity. This is consistent with a model proposed by Goodenough (*11, 12*) in which antiferromagnetic behavior gives rise to correlation splitting of the σ^* band. Such samples are orthorhombic and show higher resistivities than the more metallic tetragonal compositions. Furthermore, the σ^* up-band is essentially empty but the observed p-type character of samples where $0.08 < x$ is consistent with some hole occupancy of the π^* band.

The properties of $La_{2-x}Bi_xCuO_{4-\delta}$ samples, prepared by annealing the above compositions in argon at 600°C, are listed in Table II. It can be seen that all of these samples crystallize with an orthorhombic structure and (from Fig. 4) show long-range antiferromagnetic ordering. For the composition $x = 0.08$, direct thermogravimetric analysis gave a composition of $La_{1.92}Bi_{.08}CuO_{3.96}$. When this sample is heated in oxygen, a weight gain is obtained (Fig. 5) which corresponds to an oxidation to the composition $La_{1.92}Bi_{.08}CuO_4$. This was confirmed by results from iodometric analysis. The oxidized sample is tetragonal, has a lower resistivity (Fig. 3), and there is no longer an observed Néel point. For the argon annealed samples, the phase crystallizes as an orthorhombic structure, there exists a Néel point, and the sample shows relatively high resistivity (Table II). These observations are consistent with an increase in localization, a splitting of the σ^* band, and most of

TABLE II

PROPERTIES OF $La_{2-x}Bi_xCuO_{4-\delta}$ ANNEALED IN Ar AT 600°C

Compound	Crystal structure	Lattice parameters (Å) a	b	c	T_N (K)	ρ (77 K) (Ω cm)
$x = 0.00$	ort	5.356	5.406	13.15	300	—
0.02	ort	5.360	5.407	13.15	255	—
0.04	ort	5.359	5.404	13.15	225	—
0.06	ort	5.362	5.402	13.16	135	—
0.08	ort	5.369	5.402	13.16	105	30

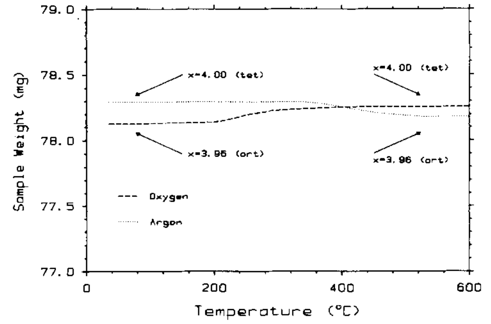

FIG. 5. Changes in weight associated with the tetragonal-to-orthorhombic transformation of a sample of $La_{1.92}Bi_{.08}CuO_4$ heated in argon and its reverse orthorhombic-to-tetragonal transformation when reheated in oxygen.

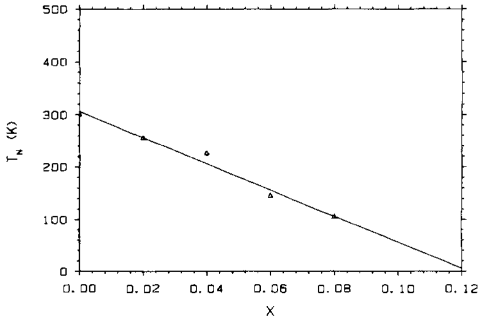

FIG. 6. Variation of Néel temperature with composition for samples of $La_{2-x}Bi_xCuO_4$ which were annealed in argon.

the hole concentration located in the σ^* upband. The observed Néel points, for the argon annealed samples containing increased bismuth content, are plotted in Fig. 6. The observed linear decreases in the Néel point with increased bismuth content is consistent with an increase in the degree of electron delocalization in the system.

Samples of $La_{2-x}Bi_xCuO_4$ were also annealed under 2000 psi oxygen at 500°C. The total metal-to-oxygen content did not vary from 3 : 4. This is consistent with the nature of the orthorhombic La_2CuO_4 structure which cannot tolerate an excess of oxygen (*9*).

Acknowledgments

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