Superconducting properties of $La_{2-x}Bi_xCuO_{4+\delta}$: Suppression of the phase separation observed for $La_2CuO_{4+\delta}$

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(Received 13 September 1991)

Superconducting properties of a solid solution, $La_{2-x}Bi_xCuO_{4+\delta}$ ($0 \le x \le 0.2$), treated at high oxygen pressures were studied by dc magnetic-susceptibility measurements. A remarkably large superconducting volume fraction of up to $\sim 10\%$ was found for $x > 0$, though $La_2CuO_{4+\delta}$ ($x = 0$), which oxygenated under the same conditions, showed a fraction of at most 0.2%. These results have been discussed in relation to the phase separation in $La_2CuO_{4+\delta}$ suggested by Jorgensen *et al.* The Bi-for-La substitution should introduce a random potential for the interstitial oxygen atoms and, thereby, suppress the segregation of the excess oxygen atoms. The large superconducting volume then results from the uniform oxygen distribution.

INTRODUCTION

It is widely known that insulating La_2CuO_4 can be rendered superconducting at $T_c \sim 40$ K by incorporating extra oxygen as well as by substituting A^{2+} (A = Ca,Sr,Ba) for La^{3+}.[1,2] However, oxygenated samples have shown poor superconducting properties in comparison with the A-substituted ones. This has been attributed to the experimental difficulty of oxidation using high oxygen pressures and to a low-temperature phase separation into an insulating stoichiometric phase ($\delta \sim 0$) and a metallic (superconducting) oxygenated phase ($\delta \sim 0.1$).[2] Recently, Ryder *et al.* reported a microstructure in their TEM observations at low temperatures likely to be due to the phase separation.[3] It suggested the evolution of an oxygen concentration wave with a periodicity of ~ 30 nm. If the phase separation results in such a mixed-phase microstructure, the usually observed small volume fractions are understandable as resulting from the combined effects of an easy magnetic flux trapping by the nonsuperconducting stoichiometric phase and an extensive flux penetration of the superconducting phase.

Substitution of trivalent cations for La^{3+} has been done in order to examine chemical pressure effects on superconducting and magnetic properties. Takeda *et al.* prepared $La_{2-x}Nd_xCuO_{4+\delta}$ ($0 \le x \le 0.4$) under high oxygen pressures (60 katm) and observed a large increase of the superconducting volume fraction with increasing x.[4] They started from an assumption that the substitution of smaller Nd^{3+} ions for La^{3+} would enhance the bond-length mismatch between the LaO and CuO_2 layers and, thereby, increase the excess oxygen content. However, what they observed was a puzzling combination of an almost negligibly small increase in oxygen content and a large increase in the volume fraction. Suppression of the phase separation has thus been suggested as the most likely effect of the substitution.

The $La_{2-x}Bi_xCuO_{4+\delta}$ system has been prepared by various workers under atmospheric pressures for $0 < x \le 0.1$ to find the composition dependence of the crystallographic and antiferromagnetic properties.[5,6] Takeda *et al.*, on the other hand, treated the same solid solution under high oxygen pressures and observed a superconducting transition at $T_c = 15$–25 K.[7] The Bi^{3+} substitution is interesting because Bi^{3+} has apparently an almost same ionic radius as La^{3+} but has a $(6s)^2$ lobe that La^{3+} and other rare-earth ions lack. The lobe often induces a local distortion of the surrounding atomic coordination. Therefore, it is expected that the substitution of Bi^{3+} would have a greater effect on the stability of the interstitial oxygen atoms sandwiched between a couple of LaO layers and so on the superconductivity of the $La_2CuO_{4+\delta}$ system.

In this paper, we report superconducting properties measured through dc magnetic susceptibility and dc resistivity as a function of bismuth and oxygen contents. The most interesting finding is that the volume fraction is rapidly increased by the substitution. We show that the miscibility gap existing in $La_2CuO_{4+\delta}$ is effectively closed, and a homogeneous superconducting phase is produced for $x > 0.05$.

EXPERIMENTAL

Samples of $La_{2-x}Bi_xCuO_{4+\delta}$ with $x = 0$, 0.05, 0.10, 0.15, and 0.20 were prepared by the usual ceramic method by firing mixtures of La_2O_3, Bi_2O_3, and CuO.[7] The pellets obtained were annealed at 600 °C for 60 h under 100 and 500 atm of oxygen. The powder x-ray diffraction measurements confirmed that the samples crystallize in the K_2NiF_4-type structure. The orthorhombicity decreased with increasing x. The simple tetragonal structure was obtained at room temperature for $x \ge 0.1$ ($P_{O_2} = 1$ atm) and $x \ge 0.05$ ($P_{O_2} = 100{,}500$ atm). Oxygen contents of the final products determined by iodometric titration were 0.02–0.03 (100 atm) and ~0.05 (500 atm), almost independent of the Bi content.[7]

Electrical resistivity of the pellets was measured by the four-probe method over a temperature range $20 \leq T \leq 300$ K. dc magnetic susceptibility was measured by using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, $MPMS_2$). To detect the Meissner signal, powdered samples were cooled in a field of 10 G, while a field of 1000 G was applied to measure the normal-state susceptibility.

RESULTS

The solid solution $La_{2-x}Bi_xCuO_{4+\delta}$ showed superconductivity only after being annealed under high oxygen pressures, implying an excess oxygen dopes the CuO_2 plane with carrier holes. Figure 1(a) displays the temperature dependence of magnetic susceptibility for $x=0.05$. As the annealing oxygen pressure increases, both the onset temperature T_c and the diamagnetic response increase. The value of $\chi_g = -2.618 \times 10^{-3}$ emu/g for $P_{O_2} = 500$ atm corresponds to a superconducting volume fraction of 12%, which is comparable to those of the $La_{2-x}A_xCuO_4$ (A = Ba,Sr) system. It is surprising that such a small amount of Bi increases the volume fraction so rapidly without any change in the excess oxygen content. The Bi-content dependence of these properties for $P_{O_2} = 500$ atm is shown in Fig. 1(b). T_c decreases monotonically with x, but χ_g shows a possibly more complicated dependence. Important results are summarized in Table I and Fig. 2. T_c is given in two ways: one is the temperature, where susceptibility just begins to decrease by more than $\sim 10^{-8}$ emu/g from a constant positive value for the normal state, and the other is the point where χ_g reaches 1% of its maximum value. The difference between the former and the latter is 3 K for $x=0$ and 5–7 K for $x>0$. As x increases from 0 to 0.2, T_c decreases, at first rapidly and then slowly, while the absolute value of the diamagnetic susceptibility at 5 K increases steeply at first and then slowly decreases. As for the effects of annealing oxygen pressure, T_c always changes by 3–5 K, while the change in χ_g is remarkable only for $x \leq 0.05$ as is clearly shown by the ratio χ_g(500 atm)/χ_g(100 atm) in Table I. These results will be consistently explained by assuming a suppression of the miscibility gap in a later discussion.

Figure 3 shows normal state susceptibility measured at $H = 1000$ G for samples of $x = 0, 0.05, 0.2$ annealed at 500 atm. As reported before, oxygenated $La_2CuO_{4+\delta}$ shows a cusp at ~250 K, which is assigned to the antiferromagnetic order of the stoichiometric component.[1] A small addition of Bi seems to lower this temperature to 140 K ($x=0.05$) and makes the cusp small. For $x \geq 0.1$ the cusp disappears, suggesting the disappearance of the antiferromagnetic component, i.e., the elimination of any phase separation.

Further evidence of the suppression of the phase separation has been seen in the temperature dependence of resistivity. Figure 4 shows the R-T curves for $x=0$ and

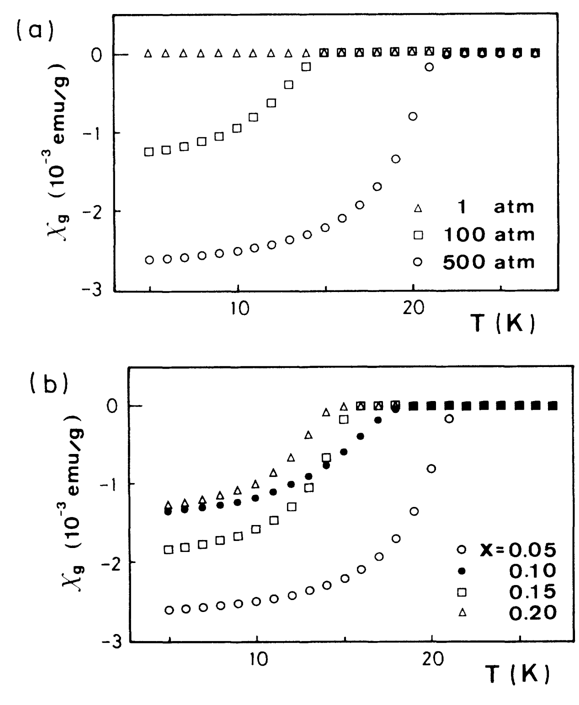

FIG. 1. Temperature dependence of the magnetic susceptibility of $La_{2-x}Bi_xCuO_{4+\delta}$ as a function of oxygen pressure applied for $x=0.05$ (a) and of Bi content for $P_{O_2} = 500$ atm (b). The data were collected using powdered samples on cooling in a field of 10 G.

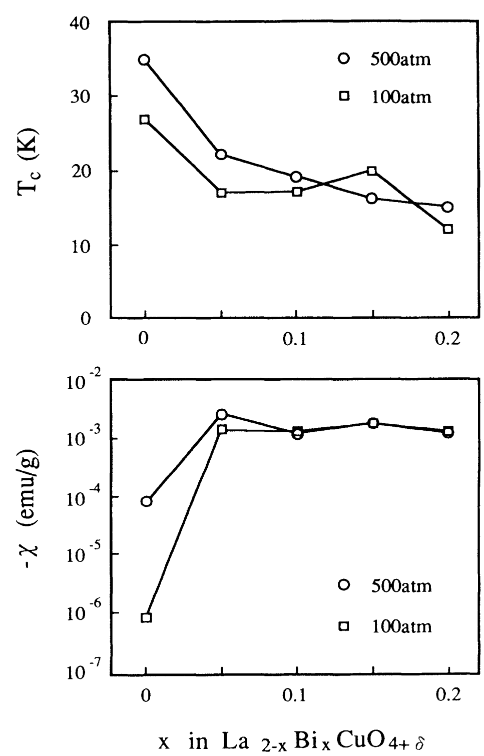

FIG. 2. Bi-content dependencies of T_c (1%) and of χ_g at 5 K.

TABLE I. Summary of magnetic susceptibility data.

x	P_{O_2} (atm)	T_c (K)[a]	Sample $\chi_g(10^{-3}$ emu/g) at 5 K	$\chi_g(500$ atm$)/\chi_g(100$ atm)
0	500	32–35	−0.032	37.6
		(35–37)[b]	(−0.075)[b]	
	100	27	−0.000 85	
0.05	500	22–29	−2.618	1.89
	100	17–23	−1.382	
0.10	500	19–25	−1.320	0.95
	100	17–22	−1.391	
0.15	500	16–22	−1.817	0.97
	100	20–25	−1.877	
0.20	500	15–21	−1.238	1.11
	100	12–17	−1.111	

[a]These values were obtained after slow cooling.
[b]T_c's determined in two ways (see text).

0.1. The broad hump around 200–250 K, which has been attributed to the phase separation,[3] is absent for $x \geq 0.5$. The suppression is quicker than that seen in the $La_{2-x}Nd_xCuO_{4+\delta}$ system where the hump survives until $x = 0.15$.

Very recently, Ryder *et al.* reported from their ac resistivity and thermopower measurements that the cooling rate below room temperature affects the superconducting transition of oxygenated $La_2CuO_{4+\delta}$. Fast cooling effectively precludes the oxygen migration and gives a more homogeneous oxygen distribution leading to a lower T_c. Slow cooling, on the other hand, allows the phase segregation to produce an oxygen-rich part having a higher T_c. Stimulated by their work, we have examined the cooling rate dependence of magnetic susceptibility for the present system. The results are shown in Fig. 5. A powdered sample was at first cooled from room temperature to 5 K in about 10 s, warmed up to 60 K, and then magnetization was measured in a field of 10 G on cooling ("quench"). After that, the sample was warmed to 350 K, slowly cooled to 60 K with an average cooling rate of 0.5 K/min, and magnetically measured on cooling ("slow cool"). In the case of $La_2CuO_{4+\delta}$ a significant change of the superconducting properties was observed as reported by Ryder *et al.* [Fig. 5(a)]. T_c rose by 3 K, and the diamagnetic signal was about twice as large after the slow cooling. On the other hand, such a change was not detected in the Bi-doped samples [Fig. 5(b)].

DISCUSSION

The direct and indirect evidence obtained in the present work to conclude the disappearance of the miscibility gap in the $La_{2-x}Bi_xCuO_{4+\delta}$ system are as follows: (1) large superconducting volume fraction for $x \geq 0.05$, (2) T_c dependence on x at a given oxygen content, (3) increase of the superconducting volume fraction with δ observed only for $x < 0.1$, (4) disappearance of the cusp in the χ-T curve for $x \geq 0.1$, (5) disappearance of the broad hump in the R-T curve for $x \geq 0.05$, and (6) disappear-

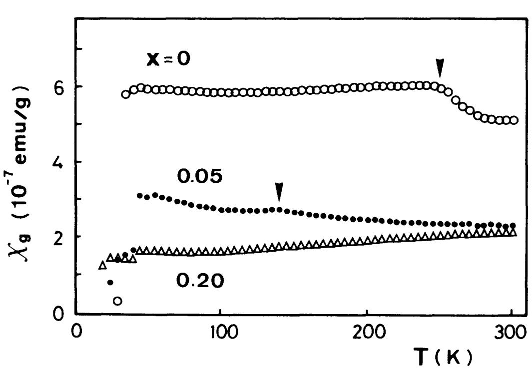

FIG. 3. Temperature dependence of magnetic susceptibility for $x = 0$, 0.05, and 0.20 annealed in 500 atm oxygen. The cusp around 250 K shifts to lower temperatures with increasing x and disappears for $x \geq 0.10$. The jump around 44 K seen for $X = 0.05$ and 0.2 is probably due to slight contamination of the samples by Bi_2CuO_4.

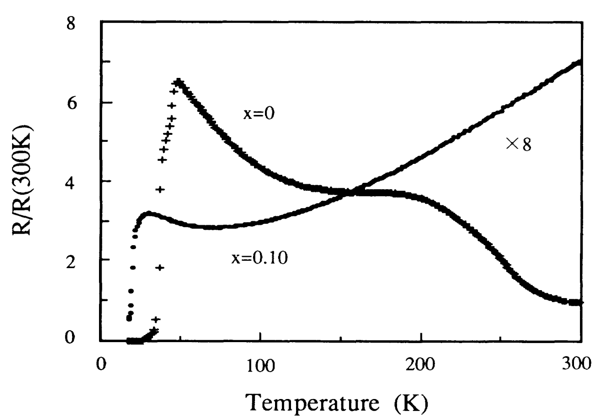

FIG. 4. Temperature dependence of normalized resistivity for $x = 0$ and 0.10 treated in 500 atm oxygen. The broad hump at 200–250 K for $x = 0$, which is attributed to the phase separation, disappears for $x \geq 0.05$.

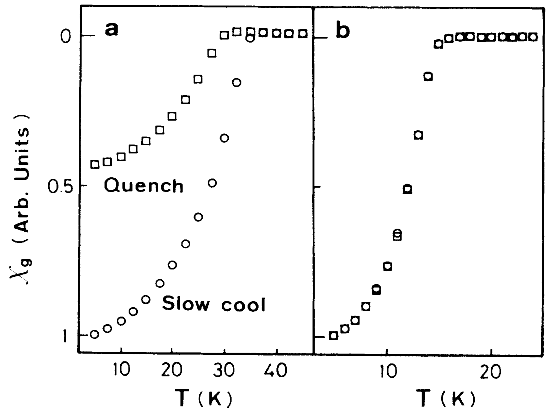

FIG. 5. Cooling rate dependence of the Meissner curve for $x=0$ (a) and $x=0.05$ (b), both oxygen treated at 500 atm. The cooling processes expressed by terms "quench" and "slow cool" are described in the text.

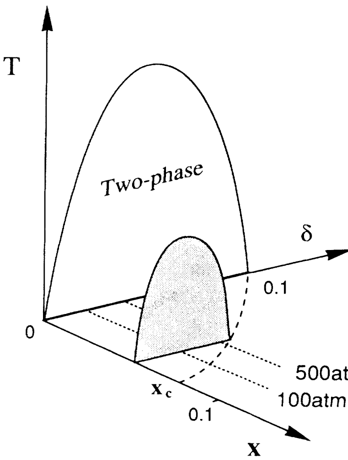

FIG. 6. Schematic phase diagram for $La_{2-x}Bi_xCuO_{4+\delta}$. The miscibility gap existing at $x=0$ tends to close with increasing x. The critical Bi content x_c is between 0.05 and 0.10.

ance of the cooling rate dependence of the χ-T curve for $x \geq 0.05$.

These results are qualitatively explained by assuming a schematic δ-x-T phase diagram illustrated in Fig. 6. The miscibility gap existing between $\delta \sim 0$ and 0.1 for $x=0$, diminishes as x increases, and disappears at a critical Bi content x_c: x_c may be between 0.05 and 0.10. For $0 \leq x < x_c$ two phases coexist at low temperatures: antiferromagnetic $La_{2-x}Bi_xCuO_4$ and superconducting $La_{2-x}Bi_xCuO_{4+\delta'}$. δ' in the latter decreases toward δ with increasing x, a random potential introduced into the LaO layers precluding the oxygen coagulation. The "speciality" of Bi^{3+} substitution can be recognized in the fact that x_c is much larger in the case of the Nd-for-La substitution.

As x increases at a constant δ value, within the two-phase region δ' of the superconducting phase gradually decreases, but its volume fraction increases. In the single-phase region, on the other hand, δ' does not vary with x (equal with δ). T_c thus decreases, but the Meissner signal increases with x in the two-phase region, while both of them are constant in the single-phase region as seen in Fig. 2. The observed slight decrease in T_c for $x>0.05$ may be due to the randomness ensuing from the substitution. Other experimental results can be consistently interpreted using this phase diagram.

The solid solution of the single-phase region may prove to be a suitable sample to study in greater detail superconductivity induced by excess oxygen.

CONCLUSION

Superconducting properties of the solid solution $La_{2-x}Bi_xCuO_{4+\delta}$ with $0 \leq x \leq 0.2$ and $0 \leq \delta \leq 0.05$ produced at high oxygen pressures have been examined by dc magnetic susceptibility measurements. The results have clearly shown that the miscibility gap existing for $x=0$ is suppressed by the Bi substitution.

ACKNOWLEDGMENT

This work was supported by a "Grant-in-Aid for Scientific Research on Chemistry of New Superconductors" from the Ministry of Education, Science, and Culture.

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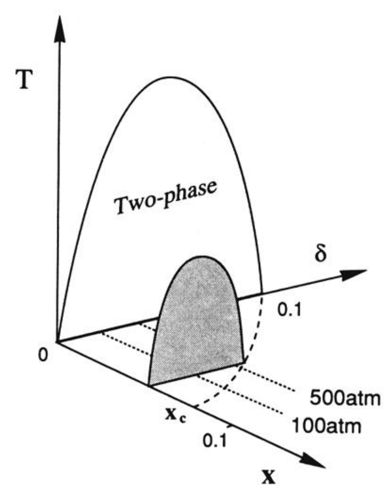

FIG. 6. Schematic phase diagram for $La_{2-x}Bi_xCuO_{4+\delta}$. The miscibility gap existing at $x=0$ tends to close with increasing x. The critical Bi content x_c is between 0.05 and 0.10.