

Stability of superconducting phases in Bi-Sr-Ca-Cu-O and the role of Pb doping

S. X. Dou, H. K. Liu, A. J. Bourdillon, M. Kviz, N. X. Tan, and C. C. Sorrell

School of Materials Science and Engineering, The University of New South Wales, P.O. Box 1, Kensington, New South Wales, Australia 2033

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The effects of heat treatment, partial oxygen pressure (P_{O_2}), and Pb substitution on the oxygen nonstoichiometry and on the stability of superconducting phases in the Bi-Sr-Ca-Cu-O systems were examined. The Pb substitution promoted and stabilized the 110-K phase, with a reproducible zero resistance at 107 K achieved in Pb-substituted samples. P_{O_2} hardly affects the superconducting transition temperature (T_c) in Pb stabilized samples while a large variation of T_c in Bi-Sr-Ca-Cu-O systems was observed by changing P_{O_2} from 0.01 to 1.0 atm. The Cu^{3+} concentrations determined by a volumetric measurement technique vary little with P_{O_2} over the range studied, so this ion is not critical for superconductivity in Bi-Sr-Ca-Cu-O, as it is in Y-Ba-Cu-O. The higher extra oxygen content obtained from iodometric titration is attributed to the oxygen associated with Bi^{5+} ions in $Bi-O_2$ layers which are not measured by the volumetric method. Such ions result from cationic vacancies. In doped 2:2:2:3 compounds, Pb^{4+} ions, most likely located in the Bi layers, lower the charge states of both Bi and Cu which are otherwise raised by cationic vacancies.

The knowledge of superconductivity in $BaPb_{1-x}Bi_xO_3$,¹ even though at much lower temperatures than the transition temperatures T_c in either $YBa_2Cu_3O_{7-x}$ (1:2:3) or in $Bi_2Sr_2Ca_2Cu_3O_{10+y}$ (2:2:2:3), suggests that multivalent Bi^{3+} , Bi^{4+} , or Bi^{5+} ions are important to superconductivity in (2:2:2:3) compounds^{2,3} as multivalent Cu is to 1:2:3 compounds.⁴ The Bi-Sr-Ca-Cu-O system has two distinct transition temperatures at 80 and 110 K.⁵ These are identified, respectively, with $Bi_2Sr_2CaCu_2O_{8+y}$ 2:2:1:2 and 2:2:2:3 phases.⁶⁻⁸ Much effort has been spent in promoting the volume fraction of the 110-K superconducting phase. Among procedures which have been found to increase the volume fraction of the higher- T_c phase are the following: (i) starting compositions with higher Ca and Cu content than in the stoichiometry of 2:2:2:3 compounds,⁸ (ii) substitutions of Pb for Bi up to 40% (Refs. 9 and 10), and (iii) heat treatments involving either long annealing times and quenching or annealing under low O_2 partial pressure.

In this paper the effects of (a) heat treatment, (b) Pb substitution, and (c) oxygen partial pressure (P_{O_2}) on the stability of superconducting phases in Bi-Sr-Ca-Cu-O are described, following examination by various techniques. (d) Conclusions are reached about the role of multivalent ions in superconducting Bi-Sr-Ca-Cu-O, and this leads to the identification of the mechanism for the stabilization of the 110-K phase by Pb doping.

The samples were prepared from appropriate mixtures of Bi_2O_3 , PbO, $SrCO_3$, $CaCO_3$, and CuO by standard solid-state reaction procedures.⁸ These procedures include codecomposition of the mixture prepared by drying a solution of Bi, Pb, Sr, Ca, and Cu nitrates; calcining at 800 °C for 6 h; pressing and sintering (once or twice with crushing and repressing) at a temperature between 850 and 870 °C for 6 h; annealing at a temperature between 820 and 845 °C for a time somewhere between 60 h and 12 d in an atmosphere, $1 > P_{O_2} > 0.01$; and finally quenching or cooling to room temperature in a furnace. A

starting composition corresponding to Bi:Sr:Ca:Cu = 1:1:1:2 was used in the present study.

Electrical resistivity was measured by the standard four-probe dc technique with computerized data logging. Microstructural and compositional studies were performed in a JEOL JSM 840 scanning electron microscope (SEM) equipped with a Link Systems energy dispersive spectrometer. X-ray diffraction patterns were obtained from a Philips-type PW 1140/00 powder diffractometer with Cu $K\alpha$ radiation. The oxygen content associated with labile ions (Cu^{3+} , Bi^{5+} , etc.) was determined by the volumetric measurement technique⁴ and by iodometric titration.³

Figure 1 shows the temperature-dependent dc voltage drop at T_c measured in samples annealed at 850 °C in $P_{O_2} = 0.067$ atm for times varied between 80 and 264 h. After 80 h the 110-K transition was not observed. SEM analysis showed that the major phase had a typical composition $Bi_2Sr_{1.6}Ca_{0.7}Cu_2O_{8+y}$ (i.e., based on the $T_c = 80$ K 2:2:1:2 phase).

With increasing annealing time the 2:2:1:2 phase gradually transforms to the 2:2:2:3 phase. After annealing for 200 h, the 2:2:2:3 phase occupies 85% by volume and the 110-K phase transition shows a large drop with T_0 at 90 K. A typical composition for this phase corresponds to Bi:Sr:Ca:Cu = 1.9:1.8:1.8:3.6 in which the ratio of Ca:Sr has increased from 0.46 after 80 h to 1 after annealing for 200 h. Further annealing results in a loss of Bi and the formation of nonsuperconducting phases such as $SrCaCu_4O_6$.

The temperature-dependent dc voltage drops in samples containing various levels of substitutional doping are shown in Table I. A T_0 of 107 K was recorded in samples containing a dopant concentration x of 20%, where $x = [Pb]/([Pb] + [Bi])$. These samples were heat treated at 850 K for over 200 h with two intermediate represses. SEM analysis showed that 2:2:2:3 compounds occupied 90% by volume with a typical composition corresponding

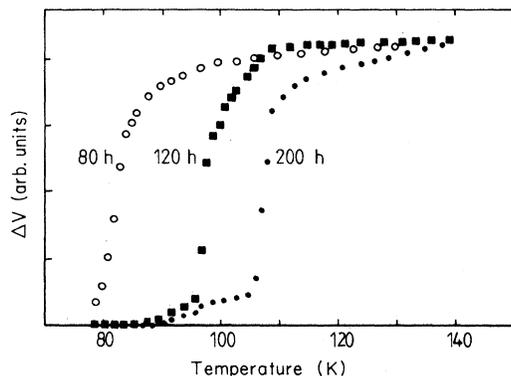


FIG. 1. Voltage drops showing the effect of annealing times (at 850°C and $P_{O_2}=0.067$ atm) on T_c in Bi-Sr-Ca-Cu-O samples.

to (Bi,Pb):Sr:Ca:Cu = 2.3:1.9:1.6:3.

After 20-h sintering the 2:2:1:2 phase dominates. X-ray diffraction patterns from samples with up to $x=40\%$ are basically the same as those from undoped material ($x=0$), except that the peaks are systematically shifted to higher angles with increasing Pb substitution. This results from a decrease in lattice parameter (Fig. 2) and unit-cell volume (by 3% when $x=40\%$). Since the ionic radius of Pb^{2+} [0.132 nm (Ref. 11)] is considerably larger than those of Bi^{3+} (0.11 nm), Ca^{2+} , Sr^{2+} , or Cu^{2+} , substitution for any of the latter ions would tend to increase the volume of the unit cell. If Pb occurs as Pb^{4+} (0.0915 nm), and substitutes for strongly charged Bi^{3+} , the observed decrease in the lattice parameter can be explained.

Figure 3 shows the effect of annealing time on the superconducting transition in Pb-doped samples. T_c mea-

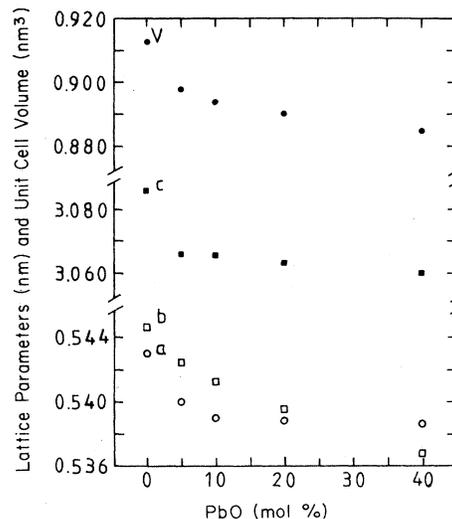


FIG. 2. Variations in unit-cell parameters in Pb-doped $Bi_2-Sr_2CaCu_2O_{8+y}$. Annealing time 20 h at 830°C.

surements and SEM analysis show that 120 h is sufficient to form the 110-K phase in Pb-doped samples, and this is about half the time needed in undoped samples. Thus Pb substitution accelerates 2:2:2:3 phase formation.

Prolonged annealing results in a loss of Pb, apparently due to evaporation of PbO. Minority phases, such as $SrCaCu_4O_6$ (0:1:1:4) and Ca_2PbO_4 , have been formed and identified by SEM and x-ray diffraction.

To measure the oxygen content of the superconductors two techniques have been used and compared: thermogravimetry and a volumetric method. Thermogravimetry has been widely used to determine the oxygen composition in

TABLE I. Effects of Pb doping levels and heat-treatment conditions on superconducting properties in Bi-Pb-Sr-Ca-Cu-O.

Annealing time (h)	Oxygen pressure P_{O_2}	T_c midpoint	T_0 1% of sigmoid	y^a	Cu ³⁺ percent of total Cu
BiSrCaCu₂O_{5.5+y}					
82	0.067	82	77	0.077 ± 0.002	7.7
120	0.067	97	80	0.075	7.5
200	0.067	105	90	0.058	5.8
240	1.0	90	< 77	0.054	5.4
240 ^b	0.2	105	80	0.057	5.7
240	0.067	105	82	0.060	6.0
240	0.01	85	< 77	0.057	5.7
Bi_{0.8}Pb_{0.1}SrCaCu₂O_{5.55+y}					
200	0.2	98	66	0.053	5.3
Bi_{0.8}Pb_{0.2}Sr₁Ca₁Cu₂O_{5.6+y}					
240	1.0	105	103	0.05	5.0
240	0.2	109	107	0.041	4.1
240	0.067	108	105	0.046	4.6
240	0.01	106	103	0.038	3.8
Bi_{0.8}Pb_{0.3}SrCaCu₂O_{5.6+y}					
200	0.2	107	104	0.015	1.5

^aSee formula.

^bQuenched.

1:2:3 compounds,¹² and in Bi-based superconductors, values for y as high as 0.5 and 1.4 have been reported^{2,13} in 2:2:1:2 compounds. Whereas 1:2:3 compounds had provided good reproducibility, Bi-based materials show a large scatter. This suggests that any change in oxygen content is masked by volatile Pb loss (PbO melts at 886°C). To obtain pure 2:2:2:3 compounds, corresponding adjustments should be made in the starting composition to compensate for the loss during sintering. For undoped Bi-Sr-Ca-Cu-O systems the thermogravimetric technique gives more consistent results since the rate of evaporation of Bi is slower than Pb.

Problems associated with metal evaporation are avoided in the volumetric method. The evolution of oxygen from superconductor specimens in acid solution is used to measure the concentration of Cu^{3+} ions in the material.⁴ Table I shows this concentration and corresponding values for y in the 1:1:1:2 compound. The results are reproducible and much lower than those reported from thermogravimetry.^{2,13} Although in the doped specimens y shows some variation over the range of P_{O_2} , T_c and T_0 show variations within only 3° after changes in P_{O_2} between 1 and 0.01. These variations prove that Pb-substituted 2:2:2:3 compounds form more easily than undoped material.

It is interesting to note that the Pb substitution for Bi suppressed the Cu^{3+} concentration (volume of oxygen released in acid solution), which correlates with T_c in other cuprate superconductors;⁴ whereas the T_c 's of the Pb-doped samples anticorrelate. This general observation is compounded with a particular example: When two specimens of different initial composition ($\text{Bi}_{0.8}\text{Pb}_{0.2}\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$ and $\text{Bi}_{0.8}\text{Pb}_{0.3}\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$) were fired in similar ways, T_c was unaffected, but the Cu^{3+} was greatly depressed in the latter case. If Cu^{3+} ions are not essential, the superconductivity most likely involves metallic d bands based on Cu^{2+} ions.

A critical current density of 330 A/cm² was recorded in a Pb-doped pellet with $x=0.4$, while an increased value of 1200 A/cm² was recorded from a cold-rolled silver-

sheathed tape. The increase is supposedly due to preferred orientation of microcrystals.

Without Pb substitution, superconducting properties in pure Bi-Sr-Ca-Cu-O are very sensitive to P_{O_2} (Table I and Fig. 4). This sensitivity is illustrated as follows. Samples were heat treated at 850°C for 20 h under different atmospheres. It is seen that the samples treated in air with quenching by removal from the furnace or treated in $P_{\text{O}_2}=0.067$ atm show large voltage drops at 105 K with tails to T_0 at 80 and 82 K, respectively; whereas the samples treated in $P_{\text{O}_2}=1$ or 0.01 atm show a large shift of T_c to lower temperatures with T_0 well below 77 K.

SEM analysis revealed that the majority phase (~85% by volume) had typical compositions: Bi:Sr:Ca:Cu = 2:1.6:1.9:3.2 with minor phases such as $\text{SrCa}_{1.5}\text{Cu}_{3.2}\text{O}_{5.7}$. All these samples contain similar phase assemblage and composition.

The concentration of Cu^{3+} and associated oxygen, y per unit formula, were determined by the volumetric technique. Here values for y were much smaller than corresponding values measured thermogravimetrically (0.4–1.4).¹³ y was independent of P_{O_2} , contrary to an earlier experience with another high- T_c superconductor 1:2:3 compounds.¹⁴ Assuming that the thermogravimetric results are influenced by metal loss, the volumetric measurement implies that the variations in T_c are not due to changes in Cu^{3+} and associated oxygen concentrations. The multivalence of Bi must also be considered.

When samples from the Bi-Sr-Ca-Cu-O system were dissolved in dilute HCl, precipitation was observed from the slow-cooled samples but not from the quenched specimens. In the former case the dark brown precipitate dissolves after 1 h. Since Bi_2O_3 dissolves in HCl without precipitation, it appears that Bi^{5+} ions are present in the slow-cooled samples, but not in the quenched ones. This suggests that Bi^{5+} ions cause the associated depression in T_c . These ions will tend to increase the oxygen content in Bi-O layers, enlarging the Bi-Bi separation and increasing resistance in these layers.¹⁵

Confirmation of the presence of Bi^{5+} ions in the Bi-Sr-Ca-Cu-O system is obtained from a comparison of results from volumetric measurements with those from iodometric titration³ and from a $\text{Fe}^3/\text{Fe}^{2+}$ reduction/

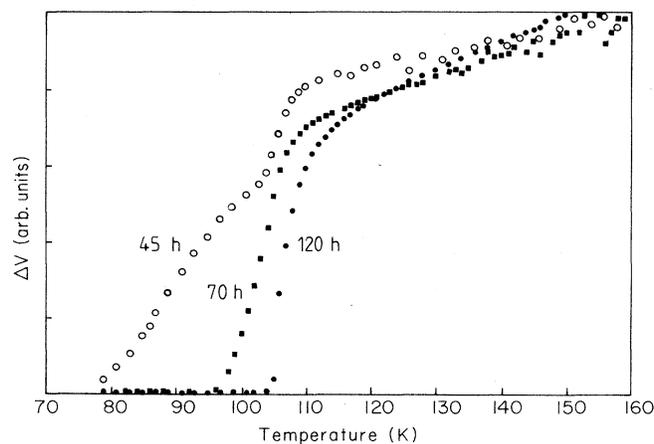


FIG. 3. Temperature-dependent resistivity showing effects of annealing time (at 840°C with $P_{\text{O}_2}=0.067$ atm) on superconducting transitions in Pb-doped samples.

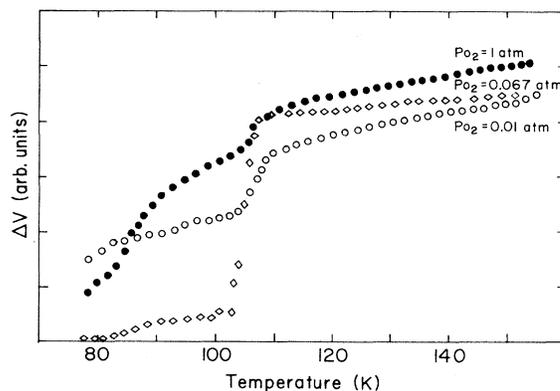


FIG. 4. Effects on P_{O_2} on T_c in Bi-Sr-Ca-Cu-O. Annealing time 200 h at 850°C.

oxidation method.¹⁶ The first gives a value for Cu^{3+} concentration of 7.7% whereas the latter two gave reported values of 15% and 17%, respectively. The higher values wrongly attribute excess oxygen to Cu^{3+} because the reduction/oxidation reaction does not distinguish the effects of Bi^{5+} ions from those of Cu^{3+} .

The concentration of Cu^{3+} ions is much less in 2:2:2:3 than in 1:2:3 compounds and furthermore, the first of these also typically contains minority second phases such as $\text{SrCaCu}_2\text{O}_{4+y}$ and $\text{SrCaCu}_4\text{O}_{6+y}$, both of which we have found to contain labile ions. Thus Cu^{3+} ions have a much reduced importance in the newer systems.

With the above information we are able to assess the role of Pb in stabilizing the higher- T_c 2:2:2:3 phase, which is structurally distinguished from 2:2:1:2 compounds in having an extra CuCaO_2 layer. We consider first charge distributions in other high- T_c systems (with T_c 's above 77 K) in the light of present results.

In 1:2:3 compounds there is a charge distribution across the unit cell illustrated by the layers shown in Table II. The Cu atom in the central layer is raised in valence from its normal Cu^{2+} to Cu^{3+} in order to make the sum of cationic charges even, like oxygen; though a possible alternative description is Cu^{2+}O^- for a delocalized electron.

The concentration of Cu^{3+} correlates with superconducting properties, such as T_c and J_c .^{4,17} In the nonsuperconducting tetragonal phase, the central plane is reduced to Cu^+ ions with the emission of oxygen.¹⁷ However, a superconducting tetragonal phase may be made by doping, e.g., with Fe.⁴ These data suggest that superconductivity in this system is associated with Cu^{3+} ions.

There is some evidence for such vacancies: First, the titration and volumetric experiments described above show some presence of Bi^{4+} or Bi^{5+} , and of some Cu^{3+} , though the concentration of Cu^{3+} is less than one-fifth of that found in 1:2:3 compounds.^{4,8} Second, superlattices ob-

TABLE II. Charge distributions on structural layers in 1:2:3 compounds (Ref. 17) and 2:2:2:3 compounds (Ref. 18).

Atomic layer	Net charge	Atomic layer	Net charge
		BiO	1+
Y	$\frac{3}{2}+$	SrO	...
CuO_2	2-	CuO_2	2-
BaO	...	Ca	2+
Cu^{3+}O	1+	CuO_2	2-
BaO	...	Ca	2+
CuO_2	2-	CuO_2	2-
Y	$\frac{3}{2}+$	SrO	...
		BiO	1+

served in electron microscopy^{19,20} and in scanning tunneling microscopy²¹ also indicate vacancies. The superlattices have been found to vary with Pb doping. We ascribe the chemical effects described above to cationic vacancies. The relative independence of T_c to P_{O_2} in Pb-doped specimens indicates the comparative absence of anionic vacancies.

The fact that the T_c 's of the Pb-doped samples have a comparatively high tolerance to P_{O_2} shows that the PbO substitution for Bi plays a role not only in accelerating the formation of the 2:2:2:3 phase but also in modifying the change equilibria. The Pb appears to be tetravalent for three reasons: lattice parameter changes indicate a small atomic size; Pb is tetravalent in the second phase Ca_2PbO_4 observed; and finally, iodometric measurements suggest high oxidation states. Assuming that Pb substitutes on the Bi layers for reasons of atomic size, it will tend to force both Bi^{5+} ions to Bi^{3+} and also the Cu^{3+} to Cu^{2+} as observed. The high charge state on Pb may also affect the the vacancy concentrations.

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