

## Cu Valence States in Superconducting Bi-Pb-Sr-Ca-Cu-O System

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Received December 19, 1989; in revised form April 4, 1990

The oxidation states of Bi, Pb, and Cu in the Bi-Pb-Sr-Ca-Cu-O (BPSCCO) system have been determined by a combination of volumetric measurement technique and iodometric titration. It was found that, in contrast to previous reports, the concentration of the  $\text{Cu}^{3+}$  ions decreased with increasing Pb content, and  $\text{Cu}^{3+}$  ions were absent in samples of  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_3\text{O}_{9.8}$ , while a  $T_c$  at 108 K and a  $J_c$  of greater than 12,000 A/cm<sup>2</sup> at 77 K were observed. The 110 K phase in BPSCCO was stabilized and showed a high tolerance to change in oxygen partial pressure during sintering. In Pb-doped materials, Bi appears to be trivalent while Pb was determined to be mixed-valence  $\text{Pb}^{4+}/\text{Pb}^{2+}$ . It is suggested that superconductivity in BPSCCO may result from a dynamic transfer of holes from Bi/Pb-O layers toward Cu-O<sub>2</sub> planes. © 1990 Academic Press, Inc.

### 1. Introduction

It has been reported by a number of authors (1-6) that the most striking common feature of Y-Ba-Cu-O (YBCO), BPSCCO, and Tl-Ba-Ca-Cu-O (TBCCO) superconductors is a valence of Cu greater than 2, indicating that the presence of  $\text{Cu}^{3+}$  or  $(\text{Cu-O})^+$  cluster is associated with the pairing mechanism thought to be crucial to superconductivity. It is understood that, for high- $T_c$  cuprates, superconductivity resides in the Cu-O<sub>2</sub> planes and requires either ox-

idation (*p*-type) or reduction (*n*-type) of these Cu-O<sub>2</sub> planes. This is well demonstrated by the correlation of the  $\text{Cu}^{3+}$  concentration with  $T_c$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . However, the location of the holes in BPSCCO remains unknown. By applying the approach used for YBCO to BPSCCO, a hole concentration ( $n - 2$ ), where  $n$  = formal copper valence, has been calculated and correlated with  $T_c$  on the basis of the presence of  $\text{Cu}^{3+}$  (5).

The extra oxygen content and thus copper valence are normally determined by thermo-

gravimetric measurement or iodometric titration (2, 5). However, the former measures only the relative weight change. Moreover, the weight loss due to the evaporation of Bi and, in particular, Pb makes the oxygen level assessment very unreliable. The latter method is sensitive not only to  $\text{Cu}^{3+}$  but also to  $\text{Bi}^{5+}$  and  $\text{Pb}^{4+}$ , so it is not feasible to determine the amount of oxygen solely associated with  $\text{Cu}^{3+}$ . Thus, the extra oxygen determined by this method may be incorrectly attributed to the presence of  $\text{Cu}^{3+}$  in BPSCCO.

In the present work, we report results that demonstrate that the  $\text{Cu}^{3+}$  concentration is depressed by Pb substitution for Bi and that  $\text{Cu}^{3+}$  ions are absent in  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_3\text{O}_{10-y}$  (2223), which showed a  $T_c$  at 108 K. The implication of the absence of  $\text{Cu}^{3+}$  is discussed.

## 2. Experimental Procedure

### 2.1 Sample Preparation and Characterization

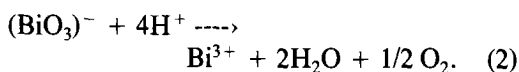
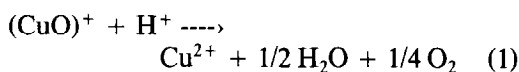
Samples were prepared from mixtures of  $\text{Bi}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{CuO}$  with variable starting compositions by standard powder metallurgical procedures: mixing, calcining at  $820^\circ\text{C}$  for 24 hr, pressing into pellets, and sintering at  $840^\circ\text{C}$  for up to 100 hr in  $\text{N}_2/\text{O}_2$  mixtures at oxygen partial pressures varying from 0.010 to 1.000 atm.

The electrical resistivity was measured by the standard four-probe dc technique with computer data logging. The  $J_c$  was measured by increasing the current through the sample until the voltage drop across the specimen exceeded  $1 \mu\text{V}$ . The ac magnetic susceptibility was measured by a mutual inductance method at 83 Hz. Microstructural and compositional studies were performed with a JEOL JXA-840 scanning electron microscope (SEM) equipped with a Link Systems AN10000 energy dispersive spectrometer (EDS). X-ray diffraction patterns were ob-

tained with a Philips type PW 1140/00 powder diffractometer with  $\text{CuK}\alpha$  radiation.

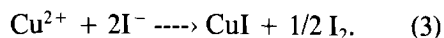
### 2.2 Determination of the Oxidation States

A volumetric measurement technique for determining the quantity of oxygen and associated  $\text{Cu}^{3+}$  ions has been previously established and reported (4). By combining this technique with iodometric titration, the oxidation states of Bi, Pb, and Cu in BSCCO and BPSCCO may be determined. In the volumetric measurement technique, a weighed specimen (0.500–1.000 g) is dissolved in dilute hydrochloric acid and the gas evolved is collected according to the reactions



By measuring the volume of  $\text{O}_2$  evolved, the total amount of  $\text{Cu}^{3+}$  and  $\text{Bi}^{5+}$  can be determined. It should be noted that this technique is unable to distinguish between  $\text{Cu}^{3+}$  and  $\text{Bi}^{5+}$  ions.

In the iodometric titration technique, a weighed specimen ( $\sim 0.050$  g) is first dissolved in dilute hydrochloric acid. After gas evolution, 10 vol% KI solution is added, which produces  $\text{I}_2$  according to the reaction

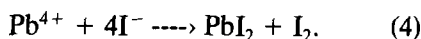


The solution is then titrated with a standardized sodium thiosulfate solution (0.036 N).

It should be pointed out that the aforementioned modification to conventional iodometric titration is important because, by dissolving the specimen in the acid solution, the  $\text{Cu}^{3+}$  and the  $\text{Bi}^{5+}$  ions can be eliminated, and the titration can follow immediately after adding KI to the solution. If the KI solution is added first, the specimen dissolution becomes very slow and does not

proceed to completion since precipitation of CuI results in a protective coating on the surface of the specimen. In this case, it is very difficult to assess whether the specimen is dissolved or not because there is always some precipitation present in the solution. Moreover, CuI has a strong catalytic effect on the reoxidation of the  $I^-$  ions. In this case, the titration error can be as large as 30%, depending on the period of time required for specimen dissolution. Thus, it is not possible to use the conventional iodometric titration technique to determine oxygen content.

In samples containing Pb, the following reaction occurs according to the electrochemical potentials (7)



In Pb-doped samples, Pb substitution reduces  $Bi^{5+}$  to  $Bi^{3+}$  so that the concentration of  $Pb^{4+}$  and  $Cu^{3+}$  can be determined separately.

It is necessary to point out that the term oxidation state is based on the nature of chemical bonding (8). By definition, the oxidation state of oxygen in compounds is two; and the oxidation states of cations are calculated according to the charge neutrality in the compounds. The real charges on atoms are normally less than the valence states, in particular, for highly covalent oxides such as cuprates. There are conflicting reports on the real charge distribution between Cu and O in cuprate superconductors. The holes may reside on a copper site, in the form of  $Cu^{3+}$ ; on an oxygen site, in the form of  $O^-$ ; or between the Cu-O bond, in the form of a cluster  $[Cu-O]^+$ . There is no evidence for the actual presence of  $Cu^{3+}$  in cuprate superconductors, and some experimental evidence shows that the holes are associated with  $O^{2-}$  rather than  $Cu^{2+}$  ions. The presence of  $O^-$  is revealed by oxygen K-edge X-ray absorption and electron energy loss (EELS) measurements (9-11). However,

Madelung energy calculations on hole conductivity in these compounds indicate that they tend to equalize the energies for holes on both Cu sites and O sites, allowing for delocalization and metallic conductivity, whereas semiconducting compounds are shown to have deep holes, self-trapped on the O sites (12).

The fact that these materials are electronically metallic, even in the nonsuperconducting state, implies the existence of nonionic bonding without defined  $Cu^{3+}$  species on any given lattice site (13). Therefore, it may be assumed that holes are distributed between Cu and O to form a complex of the type  $[Cu^{3+}-O^{2-}] \leftrightarrow [Cu^{2+}-O^-]$ . It is, however, convenient to refer to  $Cu^{3+}$  and the  $[Cu-O]^+$  complex. The actual charge distribution cannot be determined by wet chemical methods; the wet chemical method used to measure the apparent level of  $Cu^{3+}$  by the authors (4) actually measures the hole concentration.

The same definition and rule may be used in the case of the extra oxygen in the Bi-O<sub>2</sub> layer; i.e., oxygen ions are always  $O^{2-}$ , the extra oxygens are referred to as  $Bi^{5+}$ , although the real charge on Bi may be lower than five.

### 3. Results and Discussion

Table I lists the results for the concentrations of  $Pb^{4+}$  and  $Cu^{3+}$ , as determined by a combination of the volumetric measurement technique and iodometric titration, together with the  $T_c$  and  $T_0$ , the heat treatment conditions, and the nominal starting compositions for the Bi-Pb-Sr-Ca-Cu-O samples. It may be seen that the concentration of  $Cu^{3+}$  ions decreases with increasing Pb dopant level when the nominal Cu content remains constant in the starting materials. Surprisingly,  $Cu^{3+}$  ions were completely absent when a starting composition of Bi/Pb/Sr/Ca/Cu = 1.6/0.4/1.6/2.0/3.0 was used. A

TABLE I

NOMINAL COMPOSITIONS,  $T_c$  AND  $T_0$ , AND CONCENTRATIONS OF  $Pb^{4+}$  AND  $Cu^{3+}$  IONS FOR SAMPLES IN THE Bi-Pb-Sr-Ca-Cu-O SYSTEM HEAT TREATED FOR 120 hr AT 840°C UNDER DIFFERENT OXYGEN PRESSURES

Nominal composition Bi/Pb/Sr/Ca/Cu	$P_{O_2}$ (atm)	$T_c^a$ (K)	$T_0^b$ (K)	$Pb^{4+}$ level (% of total Pb)	$Cu^{3+}$ level (% of total Cu)
1.0/0.0/1.0/1.0/2.0	0.067	105	91	—	6.0
0.8/0.2/1.0/1.0/2.0	0.067	109	106	41.3	4.1
0.8/0.3/0.8/1.0/2.0	0.209	108	104	58.3	1.5
0.8/0.3/0.8/1.0/2.0	0.050	105	104	30.0	1.5
0.8/0.2/0.8/1.0/1.5	0.067	108	103	60.0	0

<sup>a</sup> Midpoint of transition (10–90% of sigmoid).

<sup>b</sup> Zero resistivity (10 nV resolution).

temperature of zero resistivity ( $T_0$ ) of 104 K was achieved, as shown in Fig. 1. Furthermore, a value of  $J_c$  of 12,000 A/cm<sup>2</sup> at 77 K was achieved for a silver-clad tape of this material prepared by cold drawing, cold rolling, and heat treating at an oxygen partial pressure of 0.067 atm (14). These observations suggest that the  $T_c$  does not correlate with  $Cu^{3+}$  concentration in BPSCCO, contrary to the case of  $YBa_2Cu_3O_{7-x}$ . The present results are consistent with those obtained by the electrochemical method (15), in which it was found that the quantity of  $Cu^{3+}$  is only about 0.5–0.8% of total Cu in

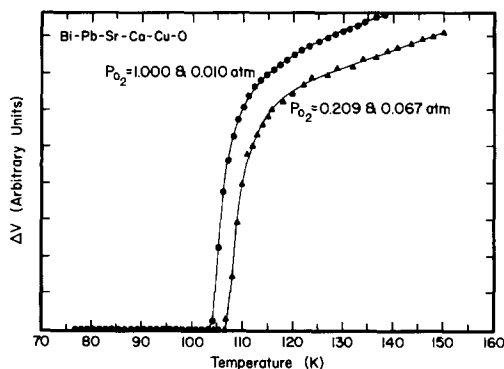


FIG. 1. Superconducting transitions for BPSCCO samples heat treated under various oxygen partial pressures.

$Bi_2Sr_2CaCu_2O_y$ , while no  $Cu^{3+}$  ions were detected in  $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_z$ .

A critical question concerning the absence of  $Cu^{3+}$  ions is whether internal oxidation/reduction takes place between the multivalent ions when dissolved in HCl. For example, if  $Bi^{3+}$  and/or  $Pb^{2+}$  are oxidized by  $Cu^{3+}$  so that  $Cu^{2+}$  results, then no  $O_2$  evolution would be observed. In order to determine this, aqueous solutions of HCl, HCl +  $BiCl_3$ , and HCl +  $PbCl_2$  were prepared. It is well known that  $YBa_2Cu_3O_{7-x}$  contains levels of  $Cu^{3+}$  that can be well characterized and defined (4). One pellet of  $YBa_2Cu_3O_{7-x}$  was sectioned into three pieces and each was dissolved in one of the three solutions. The amount of  $O_2$  evolved was then measured and the level of  $Cu^{3+}$  calculated. As shown in Table II, the results

TABLE II  
CONCENTRATION OF  $Cu^{3+}$  IONS IN  $YBa_2Cu_3O_{7-x}$   
DISSOLVED IN VARIOUS SOLUTIONS

Solution	HCl <sup>a</sup>	HCl + $BiCl_3$ <sup>b</sup>	HCl + $PbCl_2$ <sup>c</sup>
$Cu^{3+}$ level (% of total Cu)	21.02	21.17	21.28

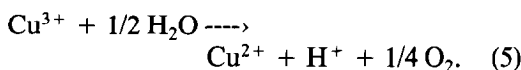
<sup>a</sup> 10/90 wt % HCl/H<sub>2</sub>O.

<sup>b</sup> 0.025 mol/liter.

<sup>c</sup> 0.036 mol/liter.

are quite consistent in that the dissolved  $\text{Bi}^{3+}$  and  $\text{Pb}^{2+}$  showed no interaction with the  $\text{Cu}^{3+}$ , which had a constant level for each solution. Therefore, the absence of  $\text{Cu}^{3+}$  cannot be attributed to the reduction to  $\text{Cu}^{2+}$  by  $\text{Bi}^{3+}$  or  $\text{Pb}^{2+}$ .

The standard-state electrochemical potentials for  $\text{Pb}^{4+}/\text{Pb}^{2+}$ ,  $\text{Cl}_2/\text{Cl}^-$ , and  $\text{O}_2/\text{H}_2\text{O}$  in acid solution have been determined to be 1.46, 1.36, and 1.23 V, respectively (7). The electrochemical potential for  $\text{Cu}^{3+}/\text{Cu}^{2+}$  is not known. Since  $\text{Cu}^{3+}$  is known not to be stable in  $\text{H}_2\text{O}$  (4, 16), then  $\text{H}_2\text{O}$  will be the first to be oxidized by  $\text{Cu}^{3+}$  according to the reaction



$\text{H}_2\text{O}$  is always a main component in the aqueous solution, so  $\text{Bi}^{3+}$  and  $\text{Pb}^{2+}$  cannot be oxidized to  $\text{Bi}^{5+}$  and  $\text{Pb}^{4+}$ , respectively, by  $\text{Cu}^{3+}$ , which is consistent with the experimental results.

A second question concerning the absence of  $\text{Cu}^{3+}$  ions is whether impurity phases had an effect on the measurements. It may be seen from X-ray diffraction patterns that the sample that exhibited the absence of  $\text{Cu}^{3+}$  ions contained nearly single-phase 2223, as shown in Fig. 2. Trace

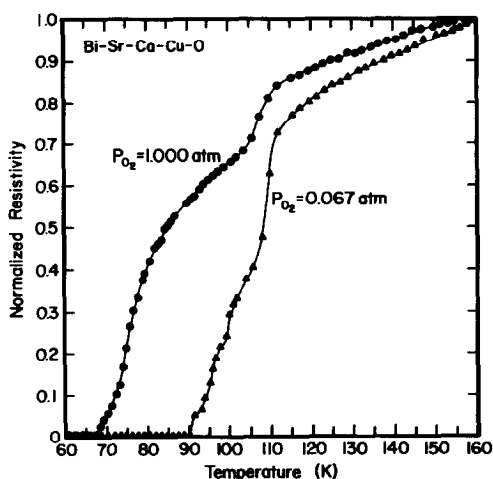


FIG. 3. Superconducting transitions for BSCCO samples heat treated under pure oxygen (1.000 atm) and 0.067 atm oxygen partial pressure.

amounts of impurity phases  $\text{SrCaCu}_2\text{O}_4$ ,  $\text{Ca}_2\text{CuO}_3$ , and  $\text{Ca}_2\text{PbO}_4$  were observed by EDS but were not detected by X-ray diffraction analysis, indicating that these impurity phases are present at very low levels. These impurity phases were prepared separately and determined to have a negligibly small amount of  $\text{Cu}^{3+}$  (17). Thus, the impurities cannot be responsible for the absence of  $\text{Cu}^{3+}$  ions in the aforementioned samples.

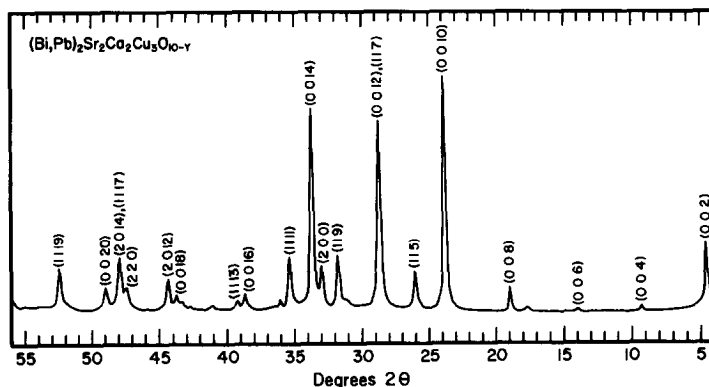


FIG. 2. X-ray diffraction pattern of a sample of nominal composition  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_3\text{O}_{10-y}$ .

TABLE III  
 $T_c$  AND CONCENTRATION OF  $\text{Cu}^{3+}$  FOR BSCCO  
 TREATED UNDER VARIOUS  $P_{\text{O}_2}$

Oxygen pressure (atm)	$T_c$ (K)	$T_o$ (K)	$\text{Cu}^{3+}$ level (% of total Cu)
1.000	90	67	5.4
0.200	105	67	5.7
0.067	105	92	6.0
0.010	85	72	5.7

Another interesting feature of these Pb-doped samples is the high tolerance of the  $T_c$  to variations in oxygen partial pressure. Figure 1 shows that  $T_c$  and  $T_o$  vary only by 3 K for changes in oxygen partial pressure during sintering between 1.000 and 0.067 atm. By contrast, the  $T_c$  for undoped BSCCO is highly sensitive to the oxygen partial pressure, as shown in Fig. 3. The two samples had the same starting composition,  $\text{Bi/Sr/Ca/Cu} = 1/1/1/2$ , and heat treatment conditions, except that the samples underwent final heat treatment under different oxygen partial pressures. The sample treated in pure oxygen had a  $T_o$  of 67 K, whereas the sample treated in 0.067 atm oxygen had a  $T_o$  of 91 K. It is noted that, when the oxygen partial pressure varied from 0.010 to 1.000 atm, the  $\text{Cu}^{3+}$  concentration remained nearly constant, as shown in Table III.

The temperature dependence of the ac magnetic susceptibility for these two samples is shown in Fig. 4. It is seen that the oxygen treatment depressed not only the transition temperature but also the proportion of the superconducting phase. This is in agreement with the resistivity measurements.

The fact that, when these samples were immersed in dilute HCl, no gas evolution was detected demonstrates the absence not only of  $\text{Cu}^{3+}$  ions but also of  $\text{Bi}^{5+}$  ions. The depression of the  $\text{Cu}^{3+}$  and  $\text{Bi}^{5+}$  concentrations is attributed to the presence of tetra-

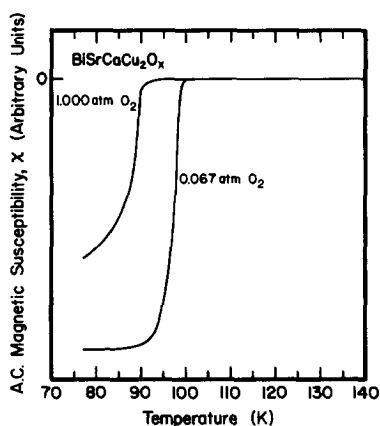


FIG. 4. Temperature dependence of ac susceptibility for BSCCO samples heat treated under pure oxygen and 0.067 atm oxygen partial pressure.

valent Pb ions.  $\text{Pb}^{4+}$  ions cannot be detected by the volumetric measurement technique since  $\text{Pb}^{4+}$  ions are stable in HCl. However, the concentration of  $\text{Pb}^{4+}$  ions can be determined by iodometric titration according to reaction (4). The presence of  $\text{Pb}^{4+}$  ions as a function of the total Pb content showed some variation, depending on the initial Pb content and the oxygen partial pressure (Table I).

The presence of tetravalent Pb ions was

TABLE IV  
 STRUCTURAL LAYER CHARGE DISTRIBUTION IN  
 HIGH- $T_c$  SUPERCONDUCTORS

YBaCuO charge	BiSrCaCuO charge	TlBaCaCuO charge
1 2 3 7	2 2 1 2 8	2 2 1 2 8
Y 1.5+	Ca 1+1	ca 1+
$\text{CuO}_2$ 2-	$\text{CuO}_2$ 2-	$\text{CuO}_2$ 2-
BaO	SrO	BaO
	BiO 1+	TlO 1+
CuO 1+		
	BiO 1+	TlO 1+
BaO	SrO	BaO
$\text{CuO}_2$ 2-	$\text{CuO}_2$ 2-	$\text{CuO}_2$ 2-
Y 1.5+	Ca 1+	Ca 1+

also evident, as indicated by the following factors: The lattice parameters decreased with increasing Pb dopant levels, indicating the small ionic size and high charge of  $\text{Pb}^{4+}$  (Fig. 5); and tetravalent Pb ions were observed in the secondary phase  $\text{Ca}_2\text{PbO}_4$  in BPSCCO materials.

In a previous paper (18), we have shown that in Pb-doped  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10-y}$ , the TEM phase contrast in corresponding superlattices is much reduced, suggesting that  $\text{Pb}^{4+}$  reduces  $\text{Bi}^{5+}$  to  $\text{Bi}^{3+}$  ions and promotes the superconducting 110 K phase (19). A recent work by Fukushima *et al.* (20) has also shown the same change in the structural modulation in Pb-doped samples. They explained these changes in the structural modulation by a decrease in additional oxygen in the Bi-O layer, which is in agreement with the present results. The additional oxygen in the Bi-O<sub>2</sub> layers proposed by Fukushima *et al.* (20) was assumed to be in the form of  $\text{O}^-$ , which is equivalent to  $\text{Pb}^{4+}$  ions in the Bi-O<sub>2</sub> layer according to the present work because oxygen ions were defined as  $\text{O}^{2-}$ .

It has been established (1) that, in high- $T_c$  superconducting materials, the Cu-based states that are oxidized toward formal tri-

valency (i.e., average Cu valence greater than 2) are capable of accepting electron pair fluctuations to achieve locally the closed-shell configuration  $d^{10}$ , and hence are essential to superconductivity. Furthermore, the hole concentration has been described in terms of  $(n-2)$  per atom, where  $n$  = formal copper valence, with a good correlation with the  $T_c$  having been observed (5).

Recently, Raveau *et al.* (21) have reviewed the three types of cuprate superconductors and concluded that the mixed valence of copper, involving a partial oxidation of  $\text{Cu}^{2+}$  into  $\text{Cu}^{3+}$ , is absolutely necessary for superconductivity. Through substitution of the divalent and the trivalent ions on the Cu sites in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , some workers have shown that the superconductivity resides in the Cu-O<sub>2</sub> planes, with the Cu-O chains acting only as a reservoir of holes and coupling the Cu-O<sub>2</sub> planes through charge transfer. The only important role of the Cu-O chains may be that their formation results in  $\text{Cu}^{3+}$  in the Cu-O<sub>2</sub> planes (8). Thus both the planes and the chains have delocalized electron behavior and should be represented as having  $\text{Cu}^{3+}$  and  $\text{Cu}^{2+}$  mixed states. However, the amount of  $\text{Cu}^{3+}$  ions that can be chemically determined is not greater than 1/3 of the total Cu; i.e., the amount of Cu in the chain positions. This indicates that the average copper valence in the Cu-O<sub>2</sub> planes is slightly greater than two.

In BPSCCO, the Cu-O chains were replaced by Bi-O<sub>2</sub> planes. Tarascon *et al.* (22) have proposed that the charge reservoir in Bi-based materials is the Bi-O<sub>2</sub> layer. By using a combination of the volumetric measurement technique and modified iodometric titration, the presence of  $\text{Cu}^{3+}$  and  $\text{Bi}^{5+}$  in undoped BSCCO has been detected (19) while, in Pb-doped materials (BPSCCO), the only mixed-valence element is Pb ( $\text{Pb}^{4+}/\text{Pb}^{2+}$ ), which may be important to superconductivity. It is sug-

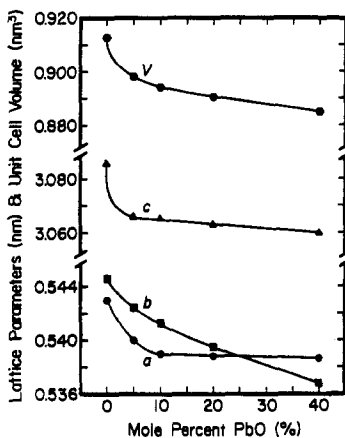
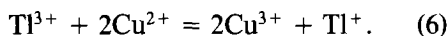
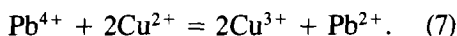


FIG. 5. Variation of the unit cell parameters of 2223 with increasing Pb dopant levels in BPSCCO.

gested that superconductivity in these materials could result from a dynamic transfer of the holes from the mixed-valence Bi-O<sub>2</sub> layers toward the Cu-O<sub>2</sub> planes, as proposed by Raveau *et al.* (23) for thallium-based compounds according to the reaction



For BPSCCO, it could be



This charge transfer takes place instantaneously between the Cu-O<sub>2</sub> planes and the Bi-O<sub>2</sub> layers. Thus, no excess Cu<sup>3+</sup> ions can be chemically detected.

In addition, the mixed-valence state Pb<sup>4+</sup>/Pb<sup>2+</sup> acts as a sink for oxygen, hence providing a buffering effect for oxygen pressure change. Thus, the *T<sub>c</sub>* of the Pb-doped Bi-Sr-Ca-Cu-O system was scarcely affected by changing the oxygen partial pressure from 0.010 to 1.000 atm.

Unlike mixed-valence Pb<sup>4+</sup>/Pb<sup>2+</sup>, which does not change the charge balance or the oxygen content significantly, mixed valence Bi<sup>5+</sup>/Bi<sup>3+</sup> has a limited range of variation since the Bi<sup>5+</sup> ions increase the oxygen content in the Bi-O<sub>2</sub> layers, enlarging the Bi-Bi separation and increasing the resistance in these layers (24). Mixed-valence Bi<sup>5+</sup>/Bi<sup>3+</sup> acts as a reservoir of holes and transfers the charge to the planes. However, the charge transfer is hindered by the increase in the resistance in the Bi-O<sub>2</sub> layers. Therefore, the *T<sub>c</sub>* of BSCCO is more sensitive to changes in the oxygen partial pressure than for BPSCCO. This is in agreement with the result reported by Fukushima *et al.* (20), who found that the Pb substitution for Bi decreased the additional oxygen in the Bi-O<sub>2</sub> layer, explaining the modulation change and subsequent enhancement in *T<sub>c</sub>*.

### Acknowledgments

The authors are grateful to Dr. N. Savvides and Mr. D. W. Hensley for assistance in the measurement of

the *T<sub>c</sub>* of a sample. Financial support from Metal Manufactures Ltd. and the Commonwealth Department of Industry, Technology and Commerce is gratefully acknowledged.

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