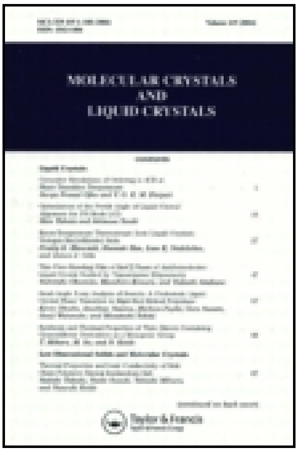

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Chemistry of Bismuth-Based High-T_c Superconductors

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CHEMISTRY OF BISMUTH-BASED HIGH-T_c SUPERCONDUCTORS

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Abstract 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 Cu^{3+} ions decreased with increasing Pb content, and Cu^{3+} ions were absent in samples of $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_2Cu_3O_{9.8}$, while a T_c at 108 K and a J_c of greater than 12,000 A/cm^2 at 77 K were observed. In Pb-doped materials, Bi appears to be trivalent while Pb was determined to be mixed-valence Pb^{4+}/Pb^{2+}. It is suggested that superconductivity in (BPSCCO) may result from a dynamic transfer of holes from Bi/Pb-O layers towards Cu-O_2 planes.

INTRODUCTION

It has been reported by a number of authors[1-6] that the most striking common feature of Y-Ba-Cu-O (YBCO), Bi-Pb-Sr-Ca-Cu-O (BPSCCO), and Tl-Ba-Ca-Cu-O (TBCCO) superconductors is a valence of Cu greater than 2. It is understood that, for high-T_c cuprates, superconductivity resides in the Cu-O_2 planes and requires either oxidation (p-type) or reduction (n-type) of these Cu-O_2 planes. This is well demonstrated by the correlation of the Cu^{3+} concentration with T_c in $YBa_2Cu_3O_{7-x}$. However, the location of the holes in (BPSCCO) remains unknown. The extra oxygen content and thus copper valence are normally determined by thermogravimetric measurement or iodometric titration.[2,5] However, the former measures only the relative weight change. The latter method is sensitive not only to Cu^{3+} but also to Bi^{5+} and Pb^{4+}, so it is not feasible to determine the amount of oxygen solely associated with Cu^{3+}. Thus, the extra oxygen determined by this method may be incorrectly attributed to the presence of Cu^{3+} in (BPSCCO). In the present work, we report results that demonstrate that the Cu^{3+} concentration was depressed by Pb substitution for Bi and the Cu^{3+}

ions are absent in $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_2Cu_3O_{10-y}$ (2223), which showed a T_c at 108 K. The implication of the absence of Cu^{3+} is discussed.

EXPERIMENTAL PROCEDURE

Sample Preparation and Characterisation

Samples were prepared from mixtures of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, and CuO with variable starting compositions by standard powder metallurgical procedures: mixing, calcining at 820°C for 24h, pressing into pellets, and sintering at 840°C for up to 100h in N_2/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 d.c. 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 μV. 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 obtained with a Philips type PW 1140/00 powder diffractometer with CuKα radiation.

Determination of the Oxidation States

A volumetric measurement technique for determining the quantity of oxygen and associated 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:

$$(CuO)^+ + H^+ \dashrightarrow Cu^{2+} + 1/2H_2O + 1/4O_2 \qquad (1)$$

$$(BiO_3)^- + 5H^+ \dashrightarrow Bi^{4+} + 5/2H_2O + 1/4O_2 \qquad (2)$$

By measuring the volume of O_2 evolved, the total amount of Cu^{3+} and Bi^{5+} can be determined. It should be noted that this technique is unable to distinguish between Cu^{3+} and Bi^{5+} ions.

In the iodometric titration technique, a weighed specimen (~0.050 g) is first dissolved in dilute hydrochloric acid. After gas evolution, 10 vol% KI solution is added, which produces I_2 according to the reactions:

$$Cu^{2+} + 2I^- \text{ ----> } CuI + 1/2I_2 \qquad (3)$$

$$Bi^{4+} + 4I^- \text{ ----> } BiI_3 + 1/2I_2 \qquad (4)$$

The solution is then titrated with a standardised sodium thiosulfate solution (0.036 N). In samples containing Pb, the following reaction occurs according to the electrochemical potentials[7]:

$$Pb^{4+} + 4I^- \text{ ----> } PbI_2 + I_2 \qquad (5)$$

By combining the results from equations (1) to (4), the concentration of Cu^{3+} and Bi^{5+}, if present, can be determined separately. In Pb-doped samples, Pb substitution reduces Bi^{5+} to Bi^{3+} so that the concentration of Pb^{4+} and Cu^{3+} can also be determined separately.

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_o, 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 temperature of zero resistivity (T_o) of 108 K was achieved, as shown in Figure 1. Furthermore, a value of J_c of 12,000 A/cm^2 at 77 K was achieved for a silver-clad tape of this material.[9] 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.[8] In this work,[8] it was found that the quantity of Cu^{3+} is only about 0.5 -0.8 %

of total Cu in $Bi_2Sr_2CaCu_2O_{8+z}$, while no Cu^{3+} ions were detected in $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_{10-y}$.

TABLE I Nominal compositions, T_c and T_o, and concentrations of Pb^{4+} and Cu^{3+} ions for samples in the Bi-Pb-Sr-Ca-Cu-O system heat treated for 120h at 840°C under different oxygen pressures.

Nominal Composition Bi /Pb /Sr /Ca /Cu	P_{O_2} (atm)	T_c[a] (K)	T_o[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	0.209	105	108	95.0	0
0.8/0.2/0.8/1.0/1.5	0.067	108	103	60.0	0

a) Midpoint of transition (10-90% of sigmoid)
b) Zero resistivity (10 nV resolution)

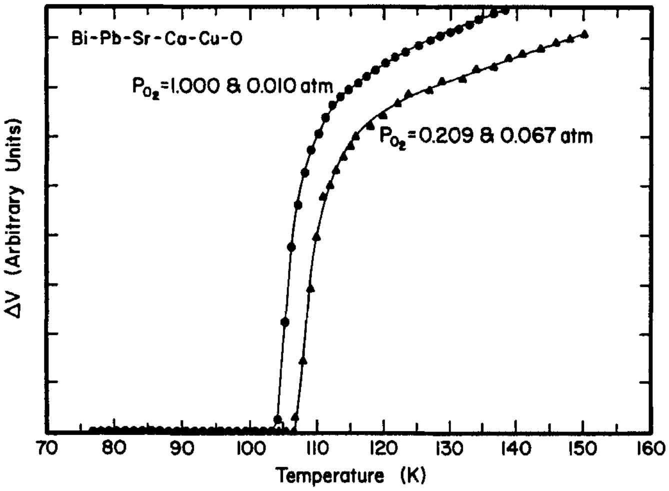

FIGURE 1 Superconducting transitions for (BPSCCO) samples heat-treated under various oxygen partial pressures.

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

TABLE II Concentration of Cu^{3+} ions in $YBa_2Cu_3O_{7-x}$ dissolved in various solutions.

Solution	HCl[a]	HCl + $BiCl_3$[b]	HCl + $PbCl_2$[c]
Cu^{3+} Level (% of Total Cu)	21.02	21.17	21.28

a) 10/90 wt% HCl/H_2O
b) 0.025 mol/l
c) 0.036 mol/l

The standard state electrochemical potentials for Bi^{4+}/Bi^{3+}, Pb^{4+}/Pb^{2+}, Cl_2/Cl^-, and O_2/H_2O in acid solution have been determined to be 1.59 V, 1.46 V, 1.36 V, and 1.23 V, respectively.[7] The electrochemical potential for Cu^{3+}/Cu^{2+} may be assumed to be greater than that for Bi^{4+}/Bi^{3+}, 1.59 V. It is clear that H_2O will be the first to be oxidised by Cu^{3+} according to reaction (1). So Bi^{3+} and Pb^{2+} cannot be oxidised to Bi^{4+} and Pb^{4+} by Cu^{3+} in aqueous solutions, which is consistent with the experimental results. A second question concerning the absence of Cu^{3+} ions is whether the 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 Cu^{3+} ions contained nearly single-phase 2223, as shown in Figure 2. Trace amounts of impurity phases $SrCaCu_2O_4$, Ca_2CuO_3, and Ca_2PbO_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 Cu^{3+} in negligibly small amounts.[11] Thus, the impurities cannot be

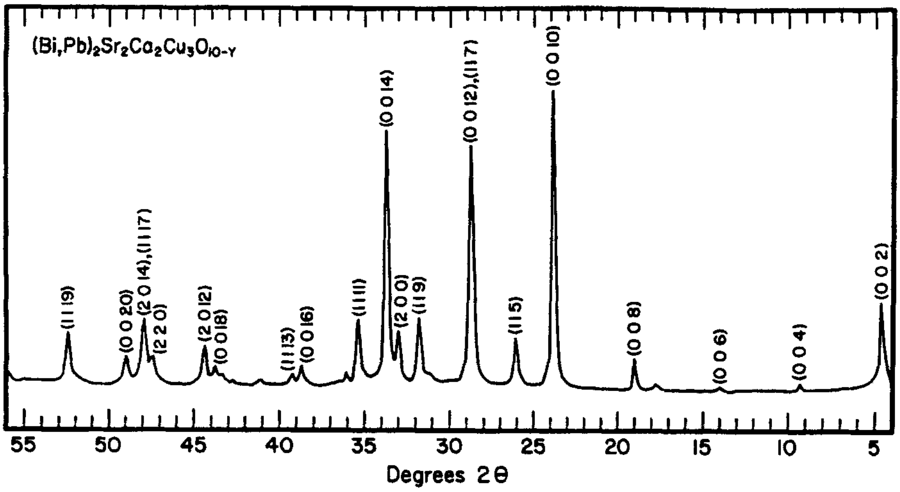

FIGURE 2 X-ray diffraction pattern of a sample of nominal composition $Bi_{1.6}Pb_{0.4}Sr_{1.6}Ca_2Cu_3O_{10-y}$.

responsible for the absence of Cu^{3+} ions in the aforementioned samples. 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 by only 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 Figure 3. The two samples had identical compositions, Bi/Sr/Ca/Cu/O = 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_c of 108 K and T_o of 67 K, whereas the sample treated in 0.067 atm oxygen had a T_c of 105 K and a T_o of 91 K. It is noted that, when the oxygen partial pressure varied from 0.010 to 1.000 atm, the Cu^{3+} conc$_{hc}$tration remained nearly constant, as shown in Table III. This indicates that the oxygen uptake or release during the change in P_{O_2} takes place in the Bi-O_2 layers rather than the Cu-O_2 layers.

The fact that, when these samples were immersed in dilute HCl, no gas evolution was detected demonstrates the absence not only of Cu^{3+} ions but also of Bi^{5+} ions. The depression of the Cu^{3+} and Bi^{5+} concentrations is attributed to the presence of tetravalent Pb ions. Pb^{4+} ions cannot be detected by the volumetric measurement technique

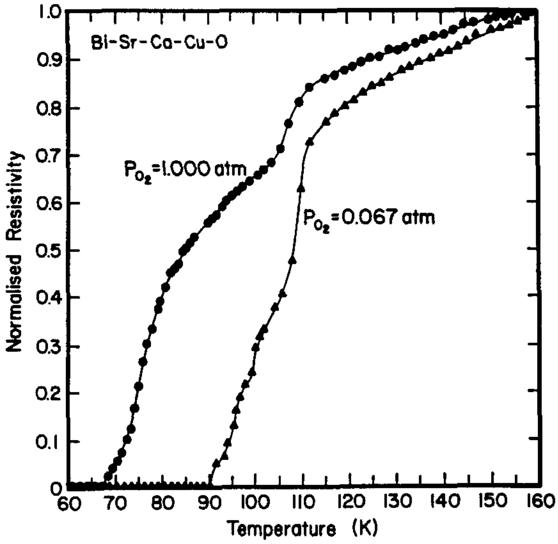

FIGURE 3 Superconducting transitions for (BPSCCO) samples heat-treated under pure oxygen (1.000 atm) and 0.067 atm oxygen partial pressure.

TABLE III Oxygen partial pressure, T_c and T_o, and concentration of Cu^{3+} for (BSCCO) treated under various P_{O_2}.

Oxygen Pressure (atm)	T_c (K)	T_o (K)	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

since Pb^{4+} ions are stable in HCl. However, the concentration of Pb^{4+} ions can be determined by iodometric titration according to reaction (5).

The presence of Pb^{4+} ions as a function of the total Pb content showed considerable variation, depending on the initial Pb content and the oxygen partial pressure (Table I).

The presence of tetravalent Pb ions was 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 Pb^{4+}; and tetravalent Pb ions were observed in the secondary phase Ca_2PbO_4 in (BPSCCO) materials. Recently, Raveau et al.[12] have reviewed the three types of cuprate superconductors and concluded that the mixed valence of copper, involving a partial oxidation of Cu^{2+} into Cu^{3+}, is absolutely necessary for superconductivity. Through substitution of the divalent and the trivalent ions on the Cu sites in $YBa_2Cu_3O_{7-x}$, some workers have shown that the superconductivity resides in the $Cu\text{-}O_2$ planes, with the Cu-O chains acting only as a reservoir of holes and coupling the $Cu\text{-}O_2$ planes through charge transfer. The only important role of the Cu-O chains may be that their formation results in Cu^{3+} in the $Cu\text{-}O_2$ planes.[13] In (BPSCCO), the Cu-O chains were replaced by $Bi\text{-}O_2$ planes. Tarascon et al.[14] have proposed that the charge reservoir in Bi-based materials is the $Bi\text{-}O_2$ layer. By using a combination of the volumetric measurement technique and modified iodometric titration, the presence of Cu^{3+} and Bi^{5+} in undoped (BSCCO) has been detected[15] while, in Pb-doped materials (BPSCCO), the only mixed-valence element is Pb (Pb^{4+}/Pb^{2+}). The mixed-valence states Bi^{5+}/Bi^{3+} in (BSCCO) and Pb^{4+}/Pb^{2+} in (BPSCCO) may be important to superconductivity. It is suggested that superconductivity in these materials could result from a dynamic transfer of the holes from the mixed-valence $Bi\text{-}O_2$ layers toward the $Cu\text{-}O_2$ planes, as proposed by Raveau et al.[16] for thallium-based compounds. For (BSCCO), it could be:

$$Bi^{5+} + 2Cu^{2+} = 2Cu^{3+} + Bi^{3+} \tag{7}$$

For (BPSCCO), it could be:

$$Pb^{4+} + 2Cu^{2+} = 2Cu^{3+} + Pb^{2+} \tag{8}$$

This charge transfer takes place instantaneously between the $Cu\text{-}O_2$ planes and the $Bi\text{-}O_2$ layers. Thus, no excess Cu^{3+} ions can be chemically detected.

Further, the mixed-valence state Pb^{4+}/Pb^{2+} acts as a sink for oxygen, hence providing a buffering effect for oxygen pressure change. Thus, the T_c of (BPSCCO) was scarcely affected by changing the oxygen partial pressure from 0.010 to 1.000 atm.

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