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Effect of the Oxidation State of Pb on the Superconducting Transition Temperature of $Bi_{2-x}Pb_xSr_2CaCu_2O_{8+\delta}$

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Abstract—A procedure is developed for determining the Pb^{4+} concentration in Pb-substituted Bi-based 2212 superconductors. The effect of the $Pb^{4+} : Pb^{2+}$ ratio on the superconducting transition temperature of 2212 is studied. The results indicate that the highest T_c is offered by $Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_{8+\delta}$ containing the smallest amounts of Pb and Cu in their higher oxidation states.

INTRODUCTION

Partial Pb substitution on the Bi site in $Bi_2Sr_2CaCu_2O_{8+\delta}$ (2212) markedly increases the critical parameters of this superconductor and, in addition, changes its oxygen stoichiometry [1–3]. An important point is that Pb has a variable valence, which adds complexity to the effects of composition and heat-treatment conditions on the properties of 2212.

As shown previously [3], there is an optimal Pb content ($x \simeq 0.2$) which maximizes the superconducting transition temperature T_c and critical current density of 2212. This finding can be interpreted as indicating that the properties of Pb-substituted 2212 depend on the $Pb^{4+} : Pb^{2+}$ ratio. To address this issue, the concentrations of Bi and Pb in their higher oxidation states must be determined separately. However, given that the redox potentials of Bi and Pb differ little, such determination presents inherent difficulties [3, 4].

The objective of this work was to develop a procedure for determining the Pb^{4+} concentration in the presence of Bi^{5+} and to analyze the effect of the $Pb^{4+} : Pb^{2+}$ ratio on the T_c of Pb-substituted 2212.

EXPERIMENTAL

Ceramic samples for this investigation were prepared by melting appropriate starting mixtures, followed by liquid quenching and ceramming [5]. As in an earlier study [3], the mixtures contained K_2CO_3 in order to accelerate the formation of 2212.

T_c was measured by a standard four-probe technique with an accuracy of 0.5 K, at a transport current of 5 mA.

The procedure for determining the Pb^{4+} concentration in Bi–Pb–Sr–Ca–Cu–O superconductors takes advantage of the ability of Pb^{4+} to form stable, soluble acetates, in contrast to Cu^{3+} and Bi^{5+}. Upon dissolution of a Bi-based superconductor sample in warm glacial acetic acid, Cu^{3+} and Bi^{5+} convert to Cu^{2+} and Bi^{3+}, leading to oxygen release, while Pb^{4+} forms a tetraacetate soluble in acetic acid. The amount of the tetraacetate can be determined by the standard permanganate or dichromate method.

In our analyses, an about 0.3-g fine-particle 2212 sample (expected amount of Pb^{4+}, from 0.01 to 0.05 g) was placed in a dry 100-ml flask and then, after adding glacial acetic acid (5 ml), dissolved in it on a cooling water bath. After cooling to room temperature, the resultant solution, if containing a precipitate, was passed through a dry glass filter and collected in a titrating flask containing 50 ml of water and 10 ml of an $Fe(ClO_4)_2$ solution (2 M in $HClO_4$). Next, the flask and glass filter were washed twice with 2.5 ml of glacial acetic acid. The solution thus obtained was titrated by a $KMnO_4$ solution (or $K_2Cr_2O_7$ with phenylanthranilic acid as the indicator). Before titration, concentrated H_3PO_4 (0.5 ml) was added to bind the Fe^{3+} ion. As a blank solution, we used a mixture of a $Fe(ClO_4)_2$ solution (10 ml), glacial acetic acid (10 ml), and water (50 ml). The table presents the titration results for Pb_3O_4 and two 2212 compositions differing in Pb content.

The total Pb content was determined by a standard titration procedure. The relative uncertainty in Pb^{4+} concentration was ±3%. The $Bi^{5+} + Pb^{4+}$ and Cu^{3+} concentrations were determined as described previously [3].

RESULTS AND DISCUSSION

We studied $Bi_{2-x}Pb_xSr_2CaCu_2O_{8+\delta}$ samples with $x = 0.1–0.5$, which were quenched from the synthesis temperature (840°C). Chemical analysis data (Fig. 1) demonstrate that, with increasing Pb content, the amount of Pb^{4+} rises, while the $Pb^{4+} : Pb_{total}$ percentage ratio decreases from ≃75 to ≃60%. In contrast to Bi and Cu, most of the Pb is in its higher oxidation state. This finding agrees well with the conclusion drawn by Sequeira *et al.* [6] based on neutron diffraction data that the Pb substituted on the Bi site is in the oxidation state 4+.

Figure 2 shows the $Bi^{5+} + Pb^{4+}$ and Cu^{3+} concentrations as functions of Pb content. At low degrees of substitution ($x \leq 0.2$), the $Bi^{5+} + Pb^{4+}$ concentration increases slightly with x, while the Cu^{3+} concentration drops to zero, presumably, because the equilibrium

$$Pb^{2+} + 2Cu^{3+} \rightleftharpoons Pb^{4+} + 2Cu^{2+}$$

shifts to the right. As x increases further, the Pb^{4+} concentration rises substantially, and Cu^{3+} appears again because the above equilibrium shifts to the left. In an earlier study [3], Pb-substituted 2212 samples with $x = 0.2$, containing no Cu^{3+}, were also found to offer the highest T_c, the smallest transition width, and the largest superconducting volume. Together with the ordering of cations [2], primarily in the Sr, Ca, and Bi sites, upon Pb^{2+} incorporation into the Sr and Ca sublattices, the absence of Cu^{3+} must have a positive effect on superconducting properties, because Cu^{3+} gives rise to lattice distortions in both undoped 2212 and Pb-substituted materials with $x > 0.2$.

As shown earlier [3, 7], heat treatment has a strong effect on the critical parameters of Pb-substituted 2212. Critical roles are played by both the annealing temperature and atmosphere. In particular, the highest $T_c(R = 0)$ of 96 K was achieved by heat-treating $Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_{8+\delta}$ at 700°C and an oxygen partial pressure of $\sim 10^3$ Pa. The effect of heat-treatment conditions on T_c is illustrated in Fig. 3 (the annealing duration was 10 h). The nonmonotonic behavior of T_c around 400°C is associated with the metastable state of the samples [3] (longer term annealing leads to a gradual decrease in T_c).

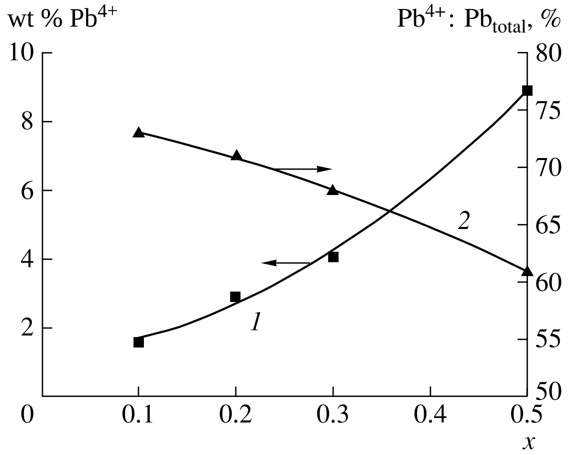

Fig. 1. (*1*) Weight percent of Pb^{4+} and (*2*) $Pb^{4+} : Pb_{total}$ percentage ratio as functions of Pb content.

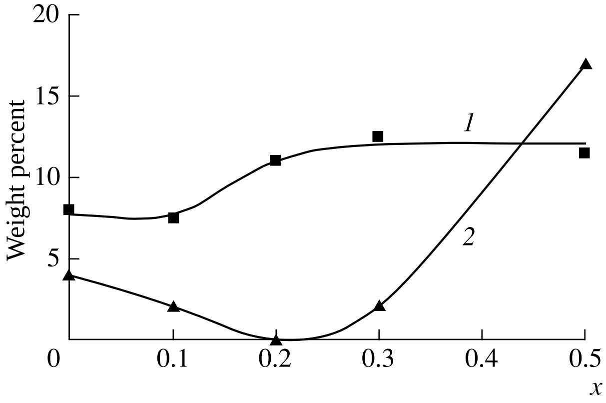

Fig. 2. Weight percent of (*1*) $Bi^{5+} + Pb^{4+}$ and (*2*) Cu^{3+} as functions of Pb content.

Figure 4 displays the $Pb^{4+} : Pb_{total}$ data for the samples heat-treated at temperatures in the range 400–700°C in an oxygen atmosphere ($p_{O_2} \sim 10^5$ Pa), air ($p_{O_2} \sim 10^4$ Pa), and argon ($p_{O_2} \sim 10^3$ Pa). With increasing heat-treatment temperature and decreasing p_{O_2}, the Pb^{4+} concentration decreases, as would be expected. The data in Figs. 3 and 4 are strongly correlated: the highest T_c ($t = 700$°C, $p_{O_2} \sim 10^3$ Pa) corresponds to the smallest relative Pb^{4+} concentration ($Pb^{4+} : Pb_{total} \simeq 50\%$). This finding is in line with the assumption [2] that Pb substitution leads to a better compositional order, since this is only possible if Pb is in the oxidation state 2+ and substitutes for Bi on Sr and Ca sites, which produces stronger lattice distortions.

Titration results for Pb_3O_4 and 2212 solutions

Sample no.	wt % Pb^{4+}	Sample no.	wt % Pb^{4+}
Pb_3O_4		$Bi_{1.5}Pb_{0.5}Sr_2CaCu_2O_y$	
1	30.21	1	8.84
2	29.97	2	8.91
3	30.83	3	8.92
4	30.09	$Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_y$	
5	30.12	1	2.93
6	30.15	2	2.94
Average	30.15	3	2.94
Nominal	30.22		

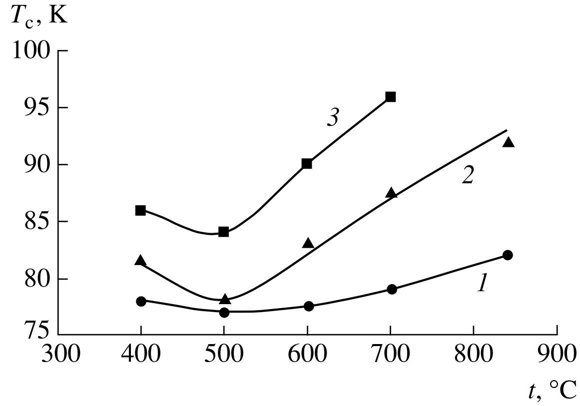

Fig. 3. T_c of $Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_{8+\delta}$ as a function of annealing temperature at oxygen partial pressures p_{O_2} ~ (*1*) 10^5, (*2*) 10^4, and (*3*) 10^3 Pa; annealing duration of 10 h.

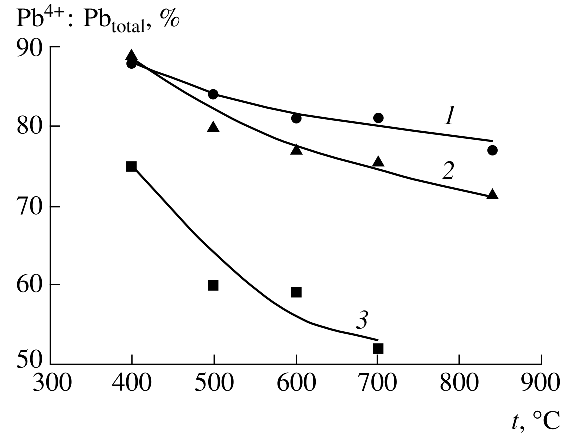

Fig. 4. Pb^{4+} : Pb_{total} percentage ratio as a function of annealing temperature for $Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_{8+\delta}$ annealed at different oxygen partial pressures; (*1*–*3*) same as in Fig. 3.

In addition, Pb^{2+} produces oxygen vacancies necessary for the ordering of excess oxygen, which improves the homogeneity and stabilizes the structure of 2212 [3, 8, 9]. This is supported by the fact that the oxygen content of the material heat-treated at 700°C and p_{O_2} ~ 10^3 Pa ($y = 8.03$) is close to the stoichiometric value [3]. As a result, the structural modulation disappears and the defect density decreases [10, 11], since excess oxygen resides in regular sites, instead of being incorporated in Bi layers, where it displaces Bi atoms and distorts the coordination polyhedra of Cu [12]. At the same time, the hole concentration in the system ($\delta = 0.13$ [3]) remains sufficient for the superconducting transition to occur at a relatively high temperature.

CONCLUSIONS

With increasing heat-treatment temperature and decreasing oxygen partial pressure, the Pb^{4+} content in the Bi–Pb–Sr–Ca–Cu–O system decreases. The highest T_c is offered by the $Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_{8+\delta}$ material heat-treated at 700°C and p_{O_2} ~ 10^3 Pa, which contains the smallest amounts of Pb and Cu in their higher oxidation states. Both factors improve the structural perfection of the 2212 superconductor.

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