Nitrate and Carbonate Methods for the Synthesis of Superconducting $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ and $Pb_{0.5}Sr_{2.5}Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$

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We have attempted to prepare the two new superconducting oxides, $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ and $Pb_{0.5}Sr_{2.5}Ca_{0.5}Cu_2O_{7-\delta}$, by heating the coprecipitated carbonates and by nitrate decomposition methods. The oxides so prepared show an onset of superconductivity ~74 and ~100 K, respectively. The minor phases occurring along with the superconducting ones were identified except for one X-ray reflection at $2\theta = 17.72°$. The dependence of phases formed upon the particular preparative conditions is also discussed.

Introduction

Two new superconducting oxides of the Pb–Sr–(Ca, Ln)–Cu–O system have been described recently. $Pb_2Sr_2ACu_3O_{8+\delta}$ (A = Ca, Ln) were first reported by Cava et al.[1] and almost simultaneously by a group at Du Pont.[2] Cava et al. have prepared $Pb_2Sr_2Ca_xLn_{1-x}Cu_3O_{8+\delta}$ for $0 \leq x \leq 0.5$ by heating predried and reacted Ca, Sr, Ln, and Cu oxides with PbO around 880 °C and a subsequent annealing in 1% oxygen atmosphere. They found these complex oxides to be superconducting, showing an onset around 70 K and zero resistance varying from 48 to 30 K depending on x and δ. They also suggest that the optimal composition, x, for this solid solution is 0.5; $x > 0.5$ gave multiphasic oxides.[1] Direct synthesis of these superconductors by heating the constituent oxides or carbonates has not been possible due to the stability of the $SrPbO_3$-based perovskite. Subramanian et al.[2] have prepared these superconducting oxides by heating the constituent oxides in sealed gold tubes. In reinvestigating the above results, Gasnier et al.[3] observed a two-step resistivity transition for $Pb_2Sr_2Ca_{0.25}Y_{0.75}Cu_3O_x$ showing zero resistance around 15 K. A similar two-step transition has been observed by Cava et al.[1] More recently, Goodman and co-workers[4] have attempted to investigate the coexisting phases in this system. They not only suggest that there is isomorphous substitution of Ca and Sr accompanying a random displacement of Pb but also reemphasize the result of the Bell labs group that the Pb–Sr–(Y,Ca)–Cu-oxides are yet to be fabricated as a single phase as their products contained low amounts of secondary compounds and amorphous materials.[4] In view of this, any new method to attempt the preparation of these superconducting oxides is worthwhile.

The second oxide in this family, $Pb_{0.5}Sr_{2.5}Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$, was reported by Roullion et al.[5] This compound was prepared by heating the constituent oxide mixtures, suitably mixed, pressed into pellets, and placed in an alumina crucible, in evacuated silica tubes at 875 °C for several hours.[5] This material exhibited an onset of superconductivity ~100 K and zero resistance around 53–45 K.

In our laboratory, we have been interested in preparing the new high-temperature superconductors by wet methods.[6,7] In this article we report our attempts to synthesize two representative members of the new family, $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ and $Pb_{0.5}Sr_{2.5}Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$, by simple wet methods such as the decomposition of the coprecipitated carbonates and nitrates. We also discuss the formation of the competitive phases depending on the preparative conditions.

Experimental Section

Both the oxides $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ and $Pb_{0.5}Sr_{2.5}Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$ were prepared by carbonate and nitrate decomposition methods. Stoichiometric amounts of $Pb(NO_3)_2$ (Fisher, ACS grade), $SrCO_3$ (Alfa, reagent grade), $CaCO_3$ (Aldrich, reagent grade), Y_2O_3 (99.99%), and CuO (Aldrich, 99.99%) were weighed and dissolved in 1:1 nitric acid. Care was taken that all the powder dissolves in nitric acid. The nitrate solution so formed was further used for both methods of preparation: (1) The nitrate solution was slowly evaporated on a water bath to obtain a solid mass which was later decomposed on a low flame. The resulting powder was ground and heated at 875–880 °C for 2–16 h in flowing 1:15 O_2:N_2 gaseous mixture. (2) An aqueous, stoichiometric solution of the nitrates containing metal ions was slowly dripped into an aqueous solution of sodium carbonate, taken in excess, under constant stirring. Complete precipitation of the metal ions was ascertained by adding concentrated Na_2CO_3 solution to the supernatant liquid. The precipitate thus obtained was washed with hot water and filtered several times until the filtrate showed (pH < 7). Washing of the precipitate was continued for a few more times to remove all detectable amounts of sodium ions. The precipitate was inserted into a furnace preheated to 850 °C. After 1 h of heating the sample was quenched to room temperature, ground, pressed into pellets and again put into the preheated furnace whose temperature was later increased from 850 to 875–880 °C in 1 h. At this temperature samples were fired for different periods, 2–16 h, under a reduced partial pressure of oxygen: 1:15 O_2:N_2 gaseous mixture. For comparison $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ was also prepared by the conventional ceramic method. The phasic purity of the resulting oxides was determined by the X-ray diffraction method on a Seifert-Scintag PAD-II diffractometer using Cu Kα radiation. Unit-cell parameters were calculated by least-squares fitting. Superconducting properties of these samples were detected in nearly zero magnetic

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Table I. Preparative Conditions for Various Samples Prepared by the Nitrate and Carbonate Methods

sample no.	composition	method	thermal treatment[a] temp, °C (time, h)
1a	$Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$	nitrate	880 (16)
1b	$Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$	carbonate	880 (4)
1c	$Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$	carbonate	880 (8)
1d	$Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$	solid state	930 (24)
2a	$Pb_{0.5}Sr_{2.5}Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$	nitrate	875 (12)
2b	$Pb_{0.5}Sr_{2.5}Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$	carbonate	875 (16)

[a] All samples were preheated for 1 h at 850 °C.

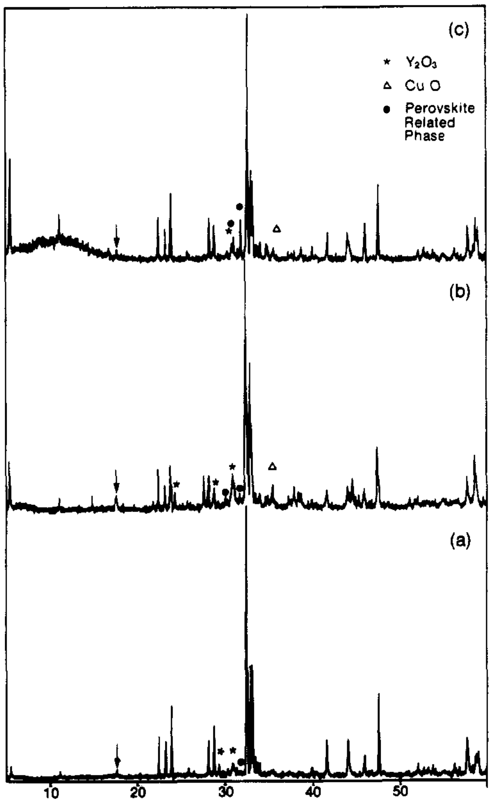

Figure 1. X-ray diffraction patterns of $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ after heating at 880 °C in (a) nitrates for 16 h (sample 1a), (b) carbonates for 4 h (sample 1b), and (c) carbonates for 8 h (sample 1c) in a 1:15 O_2:N_2 gaseous mixture. The mysterious peak at 5.00 Å (2θ = 17.71°) is shown by an arrow. Other impurity peaks are also shown.

field (50 mT) by using a magnetic induction technique.[8] Four-probe resistivity measurements were also carried out to characterize the superconducting properties of these samples. The products were also analyzed by inductively coupled plasma (ICP) arc analysis for the possible presence of sodium in the bulk.

Results

An X-ray diffraction pattern with a high amorphous background showing broad peaks corresponding to $SrCO_3$, $CuCO_3$, $CaCO_3 \cdot H_2O$, and $PbCO_3$ was observed for the coprecipitated carbonates. The solid mass obtained by the nitrate decomposition and the coprecipitated carbonates were given different thermal treatments. The products were analzyed by ICP for the possible presence of sodium, and no detectable amounts of sodium were observed. Details about the thermal processing are given in Table I. To avoid confusion during the following discussion, we will use the sample numbers as shown in Table I.

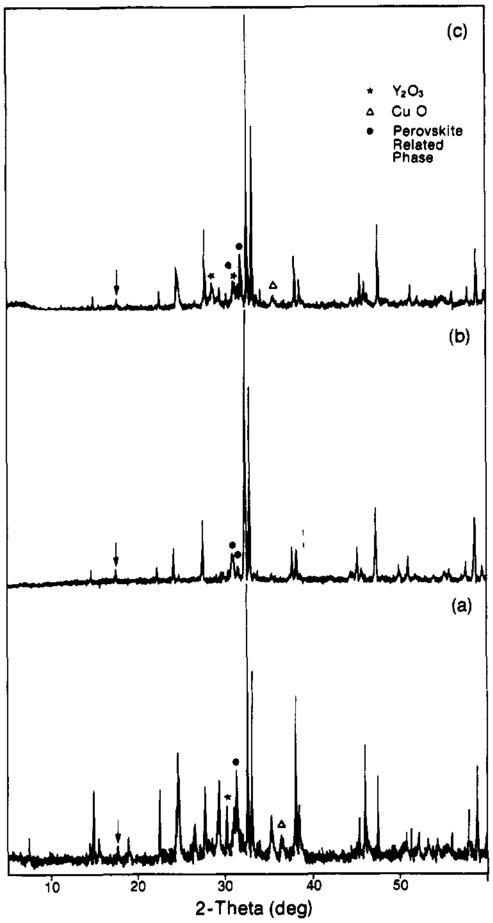

Figure 2. X-ray diffraction patterns of (a) $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ heated in air (sample 1d); (b) nitrate decomposition of $Pb_{0.5}Sr_{2.5}Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$ heated for 12 h (sample 2a); (c) $Pb_{0.5}Sr_{2.5}Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$ by carbonate method (sample 2b). All samples were heated at 875° C. Peak at 5.00 Å (2θ = 17.72°) and other impurity peaks are also shown.

In Figure 1 we show the X-ray diffraction patterns of samples 1a–c. Sample 1a shows a diffraction pattern with sharp peaks belonging to $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ and weak impurity lines belonging to Y_2O_3 (Figure 1a). Impurity lines corresponding to both yttrium oxide and copper oxide were observed for the sample prepared by the decomposition of the coprecipitated carbonates (Figure 1b). However, a longer heating time resulted in the disappearance of the lines belonging to yttrium oxide and the evolution of new lines corresponding to the $SrPbO_3$-related perovskite phase in addition to CuO lines (Figure 1c). As suggested in the literature,[1] this superconducting oxide forms in a narrow region of temperature under stringent preparative conditions. Even in the wet method, this crucial dependence of the formation of the superconducting phase and the coexistence of other competititive phases on the preparative conditions makes it harder to prepare pure superconducting $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$. An X-ray diffraction pattern of sample 1a was indexed on an orthorhombic unit cell with a = 5.386 (2), b = 5.418 (2), and c = 15.83 (5) Å. High-frequency impedance measurements on these samples are shown in Figure 3. Both samples 1a and 1c show broad superconducting transitions around 74 K. Resistivity measurements show a similar superconducting transition with onset around 74 K and zero transition ~48 K (inset of Figure 3). However, some preparations did show two-step transitions as observed by Gasiner et al.[3]

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[8] Mohan Ram, R. A.; Clearfield, A.; Kobiela, P. S.; Kirk, W. P. *Physica C* **1990**, *166*, 125.

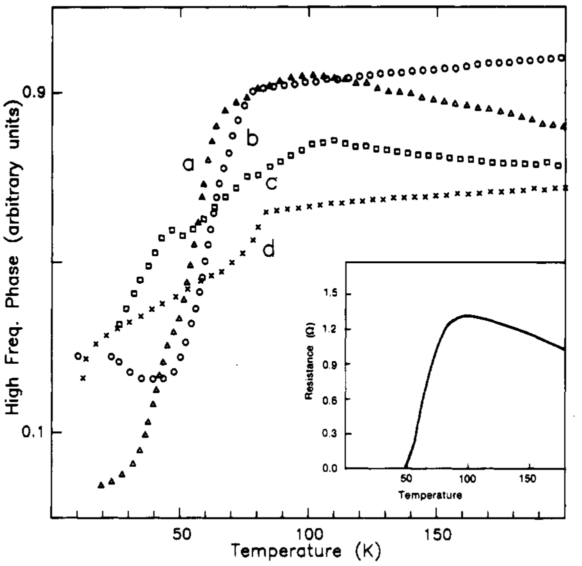

Figure 3. High-frequency impedance curves of (a) $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ by the nitrate method (sample 1a); (b) $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ by the carbonate method (sample 1c); (c) $Pb_{0.5}Sr_{2.5}Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$ by the nitrate method (sample 2a); (d) $Pb_{0.5}Sr_{2.5}Ca_{0.5}Cu_2O_{7-\delta}$ by the carbonate method (sample 2b). The inset shows the resistivity curve for sample 1a.

X-ray diffraction patterns of $Pb_{0.5}Sr_{2.5}Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$ prepared by the nitrate decomposition and by the carbonate method are shown in Figure 2 along with that of a sample of $Pb_2Sr_2Ca_{0.5}Sr_{0.5}Cu_3O_{8+\delta}$ prepared in air (sample 1d). The X-ray diffraction lines are much sharper than those reported in the literature, and the unit-cell dimensions calculated for sample 2a are $a = b = 3.821$ (2) Å and $c = 11.86$ (5) Å, comparing well with those reported in the literature.[1-3] In the impedance measurements sample 2a shows an onset of superconductivity around 100 K but also exhibits a step around 50 K (curve c in Figure 3). Sample 2b shows an onset of superconductivity ~80 K. The resistivity measurements show a wide transition with an onset around 100 K and zero resistance around 20 K. These transitions with large transition widths may have their direct dependence on the oxygen content of the superconducting oxide rather than the impurity phases present. However, we did not attempt to estimate the oxygen content of our samples since they were not pure monophasic oxides. Impedance measurements on some samples of $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ and also sample 2a show two-step transitions, possibly suggesting one or more superconducting phases,[3] although this was not obvious from the X-ray diffraction patterns. These steps and the broad transitions involved with these samples may be due to the presence of sample regions with varying oxygen content, δ.[1]

Discussion

In what follows, we would like to mention some of the observations made during our preparations, in addition to some already known in the literature, that bear upon the crucial dependence of these oxides on preparative conditions: (1) Oxide mixtures with nominal starting compositions of $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ when heated in air at 930 °C for a day gave a majority of the tetragonal phase corresponding to $Pb_{0.5}Sr_{2.5}Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$ with small amounts of CuO and the expected phase. Some lead volatilization undoubtedly occurred under these conditions. (2) A starting composition of $Pb_{0.5}Sr_{2.5}Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$ (both the nitrate and carbonate methods) heated at 875 °C in a reduced oxygen atmosphere and cooled slowly to room temperature yields a major phase corresponding to $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ together with an another phase with a layer thickness of 13.1 Å. We are continuing our investigation on this phase. (3) Superconducting oxides prepared by the nitrate decomposition method resulted in products with lesser amount of impurity phases than those of the carbonate method. (4) X-ray diffraction patterns of all our samples invariably showed a peak at a d spacing of 5.00 Å ($2\theta = 17.72°$), which are unable to account for as belonging to any of the known superconducting or impurity phases. (4) The impurity peak observed by Subramanian et al.[2] for $Pb_2Sr_2Ca_{0.5}Cu_3O_{8+\delta}$ at a d of 5.90 Å ($2\theta = 15°$) is in fact the ⟨002⟩ reflection of $Pb_{0.5}Sr_{2.5}Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$. (5) All oxides were good superconductors only when they were quenched from their firing temperatures in a reduced atmosphere of oxygen. Samples that were thus quenched were nearly monophasic and were black, showing good superconducting properties, whereas a slight change in oxygen partial pressure, firing temperature, and/or cooling rate resulted in pellets with a black surface and a greenish brown bulk material exhibiting poor superconducting properties. Therefore, it is likely that the superconducting phases are stable at high temperatures and are quenched into nonequilibrium states. Our superconducting oxides degraded with time: 10 days after preparation, samples preserved in air (in screw-capped vials) were found to be semiconducting, showing room temperature resistance of the order of a few ohms. We believe that detailed degradation studies of these superconducting oxidss are worth investigating. Our X-ray diffraction patterns contained very narrow peaks and a good baseline, indicating good crystallinity for our samples, in particular for $Pb_{0.5}Sr_{2.5}Ca_{0.5}Y_{0.5}CU_2O_{7-\delta}$ as compared to that reported by Roullion et al.[5]

In conclusion, we have attempted to prepare $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ and $Pb_{0.5}Sr_{2.5}Ca_{0.5}Y_{0.5}Cu_2O_{7-\delta}$ by wet methods such as nitrate decomposition and coprecipitated carbonates. Although our preparations did not give monophasic oxides but had small amounts of impurity phases, these were simple methods involving single-step heating schedules compared to the multistep procedures reported in the literature (for example, the $Pb_2Sr_2Ca_{0.5}Y_{0.5}Cu_3O_{8+\delta}$ phase prepared from the nitrate decomposition method was almost pure). In addition to some already known, we have pointed out some salient features involving the preparation of these oxides that are complicated not only by the presence of various competitive coexisting phases but also by the random substitution of Ca and Sr and the random ordering of Pb. Although we have had some success in preparing these superconducting oxides by the simple wet methods described above, we believe that other soft routes to prepare pure, monophasic Pb–Sr–(Ca,Y)–Cu–oxides should be investigated that may throw more light on these new complex oxide superconductors.

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