JOURNAL OF SOLID STATE CHEMISTRY **96**, 2–6 (1992)

Synthesis of Pb-Based Cuprate Superconductors by the Sol–Gel Method*

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Received June 14, 1991

The sol–gel method provides a convenient means for preparing lead cuprates of the types $Pb_2Sr_{2-y}Ba_y Ln_{1-x}Ca_xCu_3O_8$ (2213 type) with Ln = Y or rare earth and $Pb_{1-z}Cu_zSr_{2-y}Ba_yY_{1-x}Ca_xCu_2O_7$ (1212 type). Superconducting compositions of these two families showing sharp transitions can be prepared in a reproducible manner by this method.

Introduction

The sol–gel method is an excellent low-temperature route for the synthesis of oxide materials and is useful in producing materials in the form of very small particles and hence with enhanced reactivity in the solid state. The sol–gel method has been employed in the last three years for the synthesis of some of the cuprate superconductors as well. We have been interested in synthesizing the Pb-based cuprate superconductors which are new materials (*1*), the first member of the 2213 family of general formula $Pb_2Sr_2Ln_{1-x}Ca_xCu_3O_8$ (Ln = Y or rare earth) having been reported for the first time in 1988 (*2*). Part of the motivation for this study was that lead cuprates are somewhat difficult to synthesize reproducibly using a conventional ceramic method. The superconducting properties of these materials are critically dependent on the atmosphere in which they have been heat treated.

$Pb_2Sr_2Ln_{1-x}Ca_xCu_3O_{8+\delta}$ (Ln = Y or rare earth) with two CuO_2 sheets present in between two $(Pb_2Cu)O_2$ layers are prepared under low partial oxygen pressures in order to prevent the oxidation of Pb^{2+} and Cu^{1+} and thereby maintain the required local charge distribution (*3*). Recently superconducting lead cuprates of the general formula (Pb, Cu) Sr_2(Y, Ca)$Cu_2O_{7+\delta}$ with a crystal structure similar to that of the Tl-based 1212 type cuprates have been reported (*4*). The 1212 compounds have a crystal structure different from the 2213 cuprates and are prepared in an oxidizing atmosphere. In this article, we present the first successful synthesis of both these families of lead cuprates by the sol–gel method.

Experimental

Nitrate solutions of the relevant cations were prepared separately and then mixed in

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* Contribution No. 792 from the Solid State and Structural Chemistry Unit dedicated to Professor Paul Hagenmuller.

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0022-4596/92 $3.00

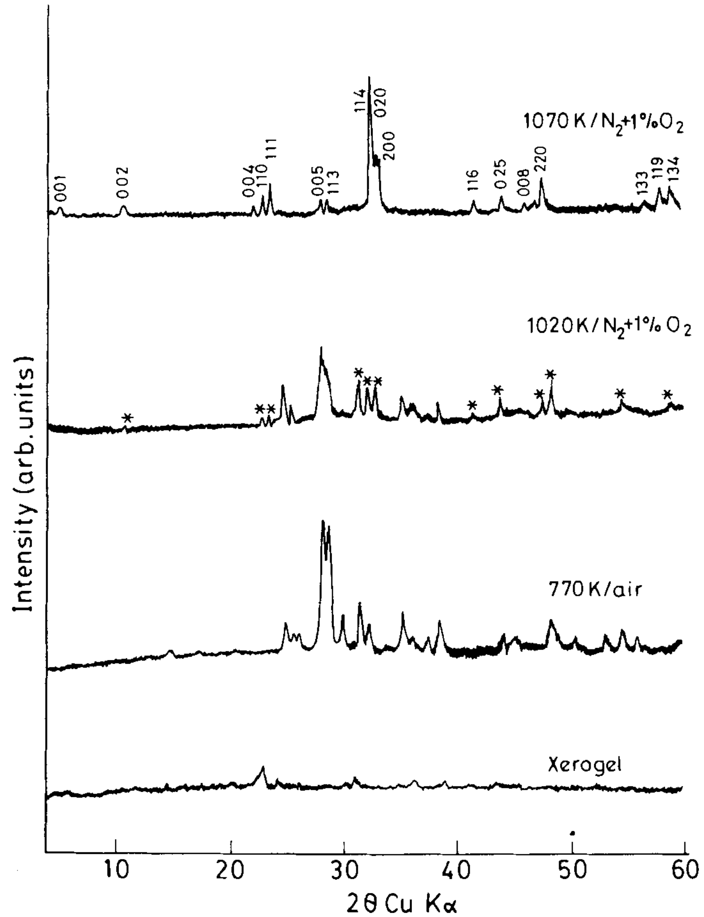

FIG. 1. Powder X-ray diffraction patterns showing the evolution of the superconducting $Pb_2Sr_2Dy_{0.5}Ca_{0.5}Cu_3O_8$ phase on heating the xerogel.

the required molar ratio. A mixture of citric acid and ethylene glycol in the molar ratio 1 : 4 was then added slowly to the nitrate solution under constant stirring. The clear blue solution thus obtained was concentrated at 370–520 K in order to get a gel. The gel was then decomposed by heating at 770 K for 5 hr in air and the ash colored crystalline powder thus formed was subjected to different heat treatments in 1% O_2 + N_2 atmosphere or in O_2 atmosphere depending on whether the cuprate was of 2213 or 1212 type.

The phase purity of the cuprate samples was checked with powder x-ray diffraction patterns recorded with a JEOL JDX-8P diffractometer using Cu*Kα* radiation. Oxygen content of the samples was determined by thermogravimetric analysis in a flow of hydrogen at 770 K using a CAHN 131 TG system. Superconducting properties were characterized by both four probe DC resistivity and DC magnetic susceptibility. Transmission electron microscopy (TEM) studies were carried out using a JEOL JEM 200 CX microscope operated at 200 kV and the

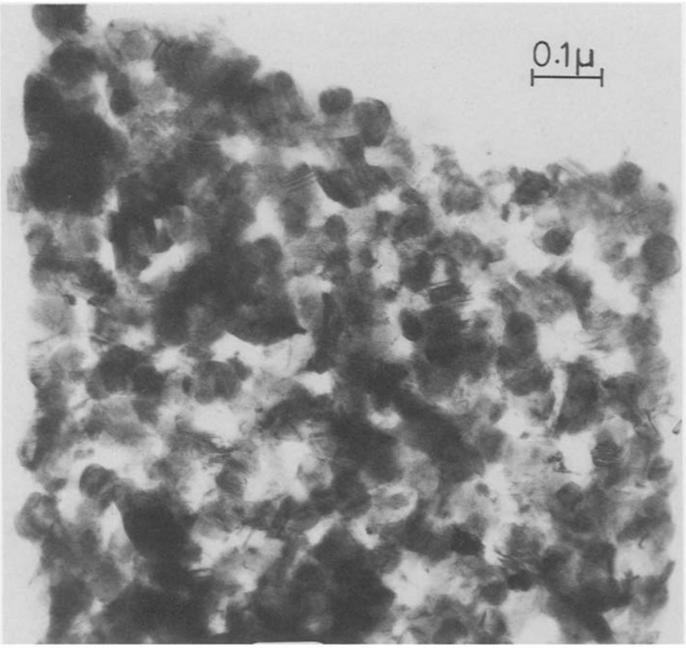

FIG. 2. Transmission electron micrograph of the fine powders obtained by heating the xerogel of $Pb_2Sr_2Dy_{0.5}Ca_{0.5}Cu_3O_8$ at 770 K in air for 3 hr.

samples were ground and dispersed on holey carbon grids in the usual manner.

Results and Discussion

In Fig. 1 we show the evolution of the X-ray diffraction pattern of a superconducting 2213 cuprate of the formula $Pb_2Sr_2Dy_{0.5}Ca_{0.5}Cu_3O_{8+\delta}$ as a function of the calcining temperature and of the atmosphere. On heating the xerogel in air at 770 K for 3–4 hr, we get crystalline powders containing primarily Sr_2PbO_4, Y_2SrO_4, and CuO. The particle size in these crystalline powders is hardly of the order of 0.05 μm as determined by electron microscopy. In Fig. 2 we show a typical electron micrograph of the precursor of $Pb_2Sr_2Dy_{0.5}Ca_{0.5}Cu_3O_{8+\delta}$ obtained by heating the xerogel in air at 770 K. The fine powders were pelletized and heated in a flowing stream of N_2 with 1% O_2 at 1070 K for 10 hr followed by quenching in liquid nitrogen to obtain the 2213 phase (Fig. 1). Heating the pellets of the fine powders in the 970–1020 K range gives only partial formation of the 2213 phase as can be seen from Fig. 1.

We have prepared several members of the 2213 family including the nonsuperconducting analogues, $Pb_2Sr_2LnCu_3O_8$, by the procedure described above. We have also prepared $Pb_2Sr_{1.75}Ba_{0.25}Y_{0.5}Ca_{0.5}Cu_3O_{8+\delta}$, wherein Sr is partly substituted by Ba by the sol–gel method. In Table I, we present the lattice parameters of the various members of the 2213 family of Pb cuprates prepared by us along with the superconducting properties. All of them have an orthorhombic symmetry and as *Ln* (Y or rare earth) in $Pb_2Sr_2LnCu_3O_8$ is replaced by Ca, the orthorhombic *a* and *b* parameters decrease and the *c* parameter increases. When the larger

TABLE I

STRUCTURE AND SUPERCONDUCTING PROPERTIES OF Pb CUPRATES

Compound	Lattice parameters a(Å)	b(Å)	c(Å)	Superconducting transition[a]
$Pb_2Sr_2YCu_3O_{8+\delta}$	5.412	5.428	15.75	Semiconducting
$Pb_2Sr_2Y_{0.75}Ca_{0.25}Cu_3O_{8+\delta}$	5.412	5.438	15.78	T_c, 50 K
$Pb_2Sr_2Y_{0.50}Ca_{0.50}Cu_3O_{8+\delta}$	5.396	5.420	15.77	T_c, 67 K
$Pb_2Sr_{1.75}Ba_{0.25}Y_{0.5}Ca_{0.5}Cu_3O_{8+\delta}$	5.424	5.456	15.83	T_c, 63 K
$Pb_2Sr_2DyCu_3O_{8+\delta}$	5.405	5.428	15.71	Semiconducting
$Pb_2Sr_2Dy_{0.5}Ca_{0.5}Cu_3O_{8+\delta}$	5.363	5.420	15.74	T_c, 62 K
$Pb_2Sr_2LuCu_3O_{8+\delta}$	5.399	5.432	15.77	Semiconducting
$Pb_2Sr_2Lu_{0.5}Ca_{0.5}Cu_3O_{8+\delta}$	5.385	5.412	15.78	T_c, 65 K
$Pb_{0.7}Cu_{0.3}Sr_2Y_{0.6}Ca_{0.4}Cu_2O_{7+\delta}$	3.818	—	11.83	Semiconducting
$Pb_{0.5}Cu_{0.5}SrBaY_{0.75}Ca_{0.25}Cu_2O_{7+\delta}$	3.839	—	11.91	T_c, 50 K

[a] Midpoint of the transition.

Ba^{2+} ion is substituted for Sr^{2+} in $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_8$, there is an increase in all three unit cell parameters.

In Fig. 3 we have shown the resistivity behavior of $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$ as a function of composition. When $x = 0.00$ the cuprate is insulating. The $x = 0.5$ composition shows a sharp superconducting transition with a T_c midpoint of 67 K. The $x = 0.25$ composition shows a T_c midpoint of 50 K. It is difficult to obtain such sharp transitions in ceramic preparations. It is noteworthy that the temperature coefficient of resistance of the $x = 0.5$ composition prepared by us is positive in the normal state and not negative as found in the ceramic preparation (5). Oxygen inhomogeneity has been considered to be responsible for the negative

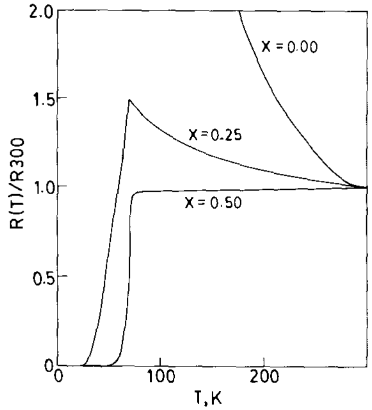

FIG. 3. Temperature variation of the normalized resistivity of $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$.

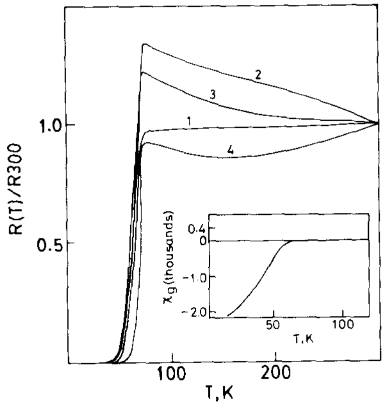

FIG. 4. Temperature variation of normalized resistivity of (1) $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_8$; (2) $Pb_2Sr_{1.75}Ba_{0.25}Y_{0.5}Ca_{0.5}Cu_3O_8$; (3) $Pb_2Sr_2Dy_{0.5}Ca_{0.5}Cu_3O_8$; and (4) $Pb_2Sr_2Lu_{0.5}Ca_{0.5}Cu_3O_8$. Inset shows the DC magnetic susceptibility of $Pb_2Sr_2Lu_{0.5}Ca_{0.5}Cu_3O_8$.

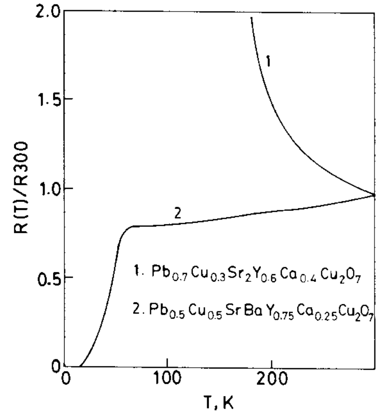

FIG. 5. Temperature variation of the normalized resistivity of 1212 type lead cuprates.

temperature coefficient of resistance found in some of the samples. The oxygen content of the superconducting samples prepared by us, as determined from thermogravimetric analysis, is around 8.3. The preparative features and properties of the products are reproducible in the sol–gel method unlike in the case of ceramic samples.

In Fig. 4 we have given the resistivity curves of a few superconducting compositions prepared by the sol–gel method, wherein 50% of the *Ln* site in $Pb_2Sr_2LnCu_3O_8$ is substituted by Ca. All of them show sharp superconducting transitions as also verified by magnetic measurements (see inset of Fig. 4). In Fig. 4 we also show the effect of partial substitution of Ba for Sr in $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_8$ in the superconducting transition. Substitution of Ba lowers the T_c. In $Pb_2Sr_{1.75}Ba_{0.25}Y_{0.5}Ca_{0.5}Cu_3O_8$, the temperature coefficient of resistance in the normal state is slightly negative unlike in $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_8$.

In the case of 1212 cuprates, xerogels of $Pb_{0.7}Cu_{0.3}Sr_2Y_{0.6}Ca_{0.4}Cu_2O_7$ and $Pb_{0.5}Cu_{0.5}SrBaY_{0.75}Ca_{0.25}Cu_2O_7$ were calcined at 770 K for 3–4 hr in air to get very fine crystalline powders. The powders were pressed into pellets and heated at 1170 K in air for 12 hr followed by annealing in oxygen at the same temperature. The 1212 phase starts forming even at 1070 K. Solid state synthesis of these compounds requires temperatures as high as 1270 K in an O_2 atmosphere whereas by the sol–gel method we are able to get nearly monophasic $Pb_{0.7}Cu_{0.3}Sr_2Y_{0.6}Ca_{0.4}Cu_2O_7$ and $Pb_{0.5}Cu_{0.5}SrBaY_{0.75}Ca_{0.25}Cu_2O_7$ at 1070 K. X-ray diffraction patterns of $Pb_{0.7}Cu_{0.3}Sr_2Y_{0.6}Ca_{0.4}Cu_2O_7$ and $Pb_{0.5}Cu_{0.5}SrBaY_{0.75}Ca_{0.25}Cu_2O_7$ could be indexed on a tetragonal unit cell with the parameters $a \sim 3.8$ Å and $c \sim 11.8$ Å (Table I). When Ba is partially substituted for Sr in $Pb_{0.5}Cu_{0.5}Sr_2Y_{0.75}Ca_{0.25}Cu_2O_7$, both *a* and *c* parameters increase.

Figure 5 shows the resistivity curves as a function of *T* of $Pb_{0.7}Cu_{0.3}Sr_2Y_{0.6}Ca_{0.4}Cu_2O_7$ and $Pb_{0.5}Cu_{0.5}SrBaY_{0.75}Ca_{0.25}Cu_2O_7$ prepared by the sol–gel method. $Pb_{0.7}Cu_{0.3}Sr_2Y_{0.6}Ca_{0.4}Cu_2O_7$ is semiconducting and $Pb_{0.5}Cu_{0.5}SrBaY_{0.75}Ca_{0.25}Cu_2O_7$ is superconducting with a T_c midpoint of 50 K.

Acknowledgment

The authors thank the Department of Science and Technology and the University Grants Commission for support of this research.

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