Bull. Mater. Sci., Vol. 14, No. 2, April 1991, pp. 251–255. © Printed in India.

Effect of heat treatment and composition on the superconductivity in Pb–Sr–R–Ca–Cu–O oxide system

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Abstract. The effect of compositions, sintering temperatures and furnace atmospheres on the superconducting transition temperatures of several members of the series $Pb_2Sr_2R_{1-x}Ca_xCu_3O_z (0.0 \leqslant x \leqslant 0.7$, R = Y, Gd) has been studied. The effect of partial replacement of Pb, Ca and Y by In has also been studied. The shapes of the resistivity-temperature curves and the zero resistance temperatures are found to be extremely sensitive to the synthesis parameters employed. Superconductivity is not observed in samples treated in oxidizing atmosphere or heated at very high temperatures. Samples sintered in flowing nitrogen showed incomplete transition in resistivity starting at about 75 K and extending down to 15 K. A new and comparatively simple synthesis procedure involving treatment of the samples in vacuum has been employed to obtain nearly single-phase materials showing metallic behaviour. Using this procedure, samples of the above composition, but containing no Ca(i.e. $Pb_2Sr_2RCu_3O_z$, R = Y and Dy), are also found to be superconducting with zero resistance up to 48 K.

Keywords. Oxide superconductors; lead strontium; rare earth oxides.

1. Introduction

The discovery of high T_c oxide superconductors has triggered the search for new oxide systems. Three families of copper oxide-based high T_c superconductors based on $(La, M)_2CuO_4$, $LnBa_2Cu_3O_7$ and $(Tl, Bi)_m(Ba, Sr)_2Ca_{n-1}Cu_nO_{m+2n+2}$ are widely known. Further to these systems, Cava *et al* (1988) reported a new family superconductors whose general formula was given as $Pb_2Sr_2ACu_3O_{8+\delta}$ where A is a lanthanide or a mixture of Ln + Sr or Ca.

The oxygen content could be varied from $\delta = 0$ to $\delta = 1.8$ depending on synthesis conditions. However, samples with zero or large values of δ were not superconducting. These compounds could be synthesized only under mildly oxidizing conditions (1% O_2 in N_2). The structure was found to be orthorhombic and the simplest cell consistent with the observed X-ray intensities was reported to be c-centred with $a = 5.40$ A, $b = 5.43$ A and $c = 15.74$ A. They reported the largest flux expulsion in a Meissner experiment for $A = Y_{0.5}Ca_{0.5}$ with an onset of diamagnetism at 68 K. This compound showed a broad resistive transition beginning at 79 K with a zero resistance at 32 K. However, a single crystal with $A = (Dy, Ca)$ showed a resistive transition midpoint at 52 K and a zero resistance at 46 K. They also observed that compositions containing A = rare earth only (i.e. without Ca or Sr) were not superconducting. This observation was also confirmed by Subramanian *et al* (1989) and Rao *et al* (1989).

We have investigated the effect of synthesis conditions such as sintering temperatures and furnace atmospheres on the superconducting transition temperatures of several compositions in the series $Pb_2Sr_2R_{1-x}Ca_xCu_3O_z (0.0 \leqslant x \leqslant 0.7$, R = Y, Gd, Eu, Dy). The effect of partial replacement of Pb, Ca and Y by In has also been studied. Our

results show that it is possible to obtain superconductivity even in pure $Pb_2Sr_2RCu_3O_z$ under suitable synthesis conditions without any Ca or Sr addition. Indium can also be incorporated at site A instead of Ca.

2. Experimental

The samples for the present study were prepared by a two-step process. First, the precursor powders of the desired compositions were made by thoroughly mixing $SrCO_3$, R_2O_3, $CaCO_3$ and CuO powders. These mixtures were given two calcination treatments at 920 C and 940 C for 15 hr in air with an intermediate grinding. Stoichiometric quantities of PbO and/or In_2O_3 were added to these precursors and the mixture calcined at 800 C for 2 hr in air. The calcined material was then pressed into pellets and sintered at temperatures between 840 C and 880 C in air, or nitrogen atmosphere. For several samples, while the heating and soaking at the peak temperature were done in air, the cooling was done in a vacuum of 10^{-2} torr at 5 C/min. The transition temperatures were determined by four-probe d.c. resistivity measurements performed on a computer-controlled resistivity set-up.

3. Results and discussion

The initial experiments were carried out on two compositions i.e. $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_z$ and $Pb_2Sr_2Gd_{1-x}Ca_xCu_3O_z$. The properties were found to be extremely sensitive to the sintering temperature and the furnace atmosphere employed. Superconductivity was not observed in samples treated in air. However some compositions, when heated up to 880 C in N_2 and quenched, showed onset of superconductivity at 75 K but zero resistance was not attained down to 15 K. The synthesis procedure was then modified and the samples, after heating in air, were cooled in a vacuum of $\sim 10^{-2}$ torr. This procedure yielded superconducting samples in both Y and Gd-based compositions. The XRD patterns of these samples were in good agreement with those reported by Cava *et al* (1988). While the onset temperature varied marginally, the zero resistance temperature depended on the composition and sintering temperature. These results are summarized in table 1. $T_c(R = 0)$ was higher in Y-samples than the Gd samples and was found to increase with Ca-content when the sintering temperature was raised from 860 to 880 C. $T_c(R = 0)$ generally reduced and resulted in incomplete transitions down to 15 K in some compositions. This could be due to formation of other phases as suggested by Cava *et al* (1988).

Table 1 also summarizes the effect of partial replacement of Pb, Ca and Y by indium in the nominal compositions. When In was substituted for Pb, $T_c(0)$ was found to increase (figure 1). When Ca was replaced by In, $T_c(0)$ reduced slightly (figure 2). However it is interesting to note that $Pb_2Sr_2Y_{0.4}In_{0.6}Cu_3O_z$ was also superconducting with a $T_c(0)$ of 37 K as compared to its calcium analogue, thus indicating that In substitutes at Ca site in these compounds.

The effect of vacuum cooling was then investigated on pure $Pb_2Sr_2RCu_3O_z$, R = Y, Gd, Eu and Dy samples and the results are given in table 2. While Gd and Eu compositions showed incomplete transitions, pure Y and Dy compositions (without Ca) sintered at 840 C were found to be superconducting with $T_c(0)$ of 46 K and 48 K, respectively (figure 3). As mentioned earlier, these pure compositions were reported to

Table 1. Zero resistance temperature of Pb–Sr–R–Cu–O compositions

Compositions	Zero resistance temperature	
Sintered at	860/Air/2 hr/ Cooled in vacuum	880/Air/2 hr/ Cooled in vacuum
$Pb_2Sr_2Y_{1-x}Ca_xCu_3O_z$		
$x = 0.4$	24 K	20 K
$x = 0.5$	34 K	NSC
$x = 0.6$	45 K	NSC
$Pb_2Sr_2Gd_{1-x}Ca_xCu_3O_z$		
$x = 0.3$	15 K	NSC
$x = 0.5$	20 K	15 K
$x = 0.7$	29 K	15 K
$Pb_{1.6}In_{0.4}Sr_2Y_{1-x}Ca_xCu_3O_z$		
$x = 0.4$	48 K	42 K
$x = 0.5$	43 K	41 K
$x = 0.6$	37 K	NSC
$Pb_2Sr_2Y_{0.4}Ca_{0.6-x}In_xCu_3O_z$		
$x = 0.2$	41 K	—
$x = 0.4$	38 K	—
$x = 0.6$	37 K	—
$Pb_2Sr_2Y_{0.2}In_{0.2}Ca_{0.6}Cu_3O_z$	27 K	—

NSC—Not superconducting down to 15 K

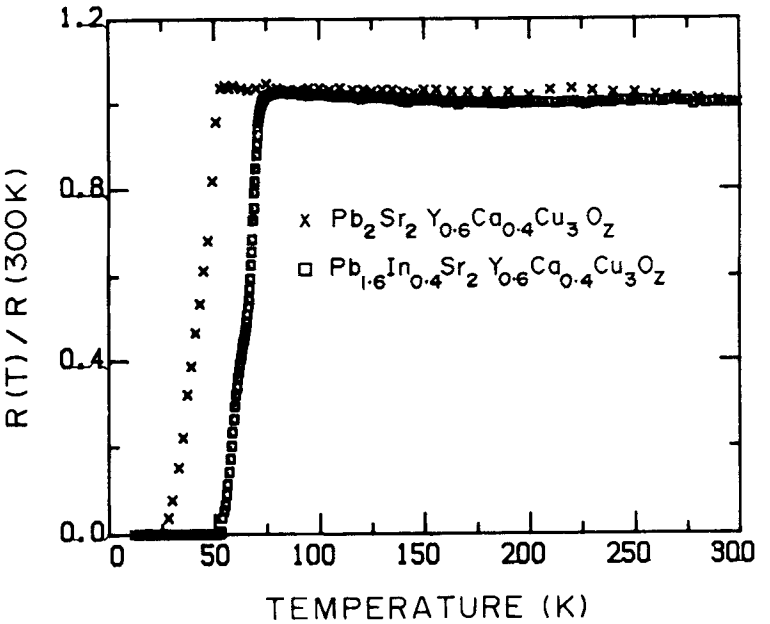

Figure 1. Resistance vs temperature plot for $Pb_{2-x}In_xSr_2Y_{0.6}Ca_{0.4}Cu_3O_z$ ($x = 0$ and 0.4).

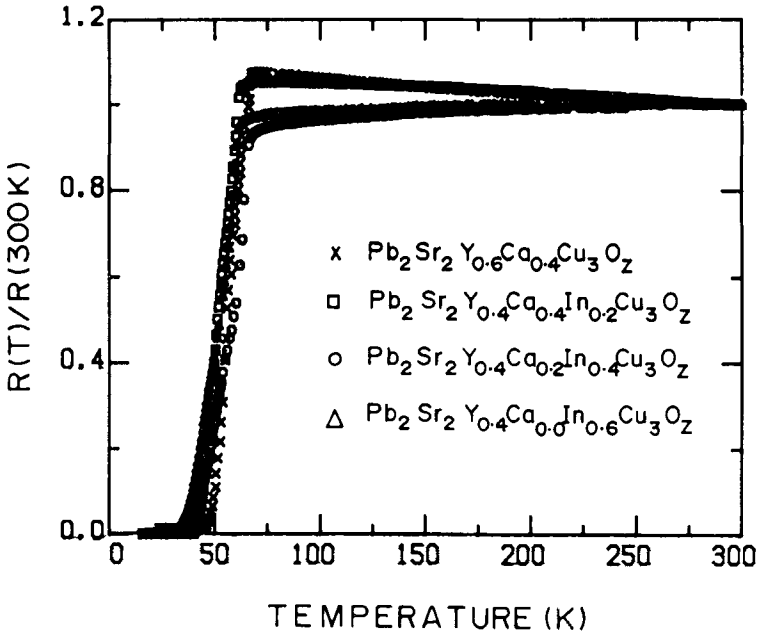

Figure 2. Resistance vs temperature plot for $Pb_2Sr_2Y_{0.4}Ca_{0.6-x}In_xCu_3O_z$($x = 0, 0.2, 0.4$ and 0.6).

Table 2. Zero resistance temperatures of Pb-Sr-R-Cu-O compositions sintered at 840 C/air/2 hr cooled in vacuum.

Composition	T_c(R = 0)
$Pb_2Sr_2YCu_3O_z$	46 K
$Pb_2Sr_2GdCu_3O_z$	NSC
$Pb_2Sr_2EuCu_3O_z$	NSC
$Pb_2Sr_2DyCu_3O_z$	48 K
$Pb_2Sr_2Y_{1-x}In_xCu_3O_z$	
$x = 0.4$	25 K
$x = 0.5$	25 K
$x = 0.6$	38 K
$x = 0.7$	NSC
$x = 1.0$	NSC

NSC—Not superconducting down to 15 K

be nonsuperconducting by other workers. It may be mentioned here that the ionic radii of Y^{3+} and Dy^{3+} are comparable while those of Gd^{3+} and Eu^{3+} are slightly higher. This could be a cause of incomplete transition and perhaps pure compositions based on Gd, Eu and other rare-earths may also show superconductivity under suitable synthesis conditions.

In conclusion, we have shown that In can be substituted at Ca site, and pure $Pb_2Sr_2RCu_3O_z$ compositions can be made superconducting under modified synthesis conditions.

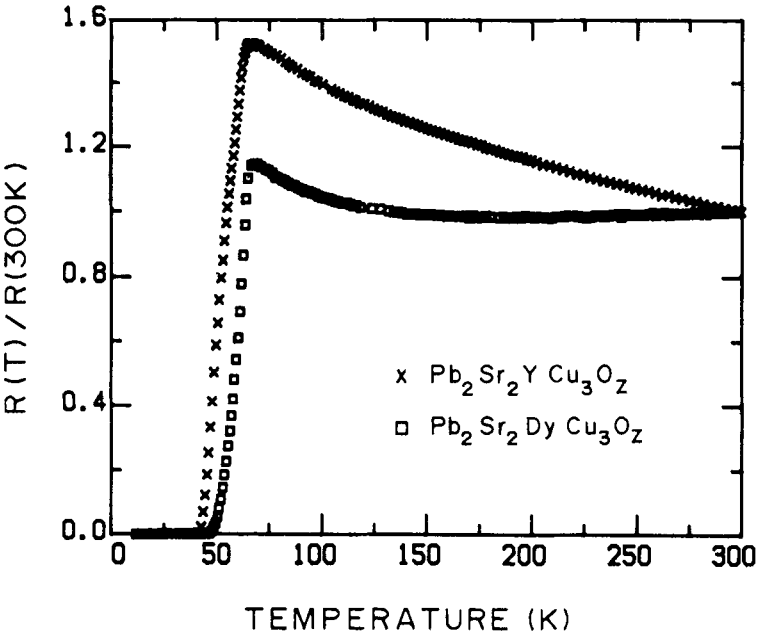

Figure 3. Resistance vs temperature plot for $Pb_2Sr_2RCu_3O_z$(R = Y and Dy).

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