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Effect of nominal copper concentration in $YBa_2Cu_{3\pm x}O_{7-\delta}$ on the superconducting transition*

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Abstract. Variation of the copper concentration in the nominal composition $YBa_2Cu_{3\pm x}O_{7-\delta}$ markedly influences the superconducting transition. The transition occurs at the highest temperature with lower width, when $x = +0{\cdot}25$.

Keywords. Oxide superconductors; $YBa_2Cu_{3\pm x}O_{7-\delta}$.

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1. Introduction

The superconducting transition of $YBa_2Cu_{3\pm x}O_{7-\delta}$ in the 90–100 K region has been widely investigated (Chu *et al* 1987; Rao *et al* 1987a; Tarascon *et al* 1987) and the crucial role of oxygen in the superconductivity has been well established (Jorgensen *et al* 1987; Rao 1987; Rao *et al* 1987b). In spite of numerous investigations, the chemical factors as well as the preparative conditions which enable reliable and reproducible superconducting behaviour of this oxide are not entirely understood. For example, depending upon the method of preparation (Bhat *et al* 1987; Kini *et al* 1987) annealing (Yakhmi et *al* 1987) or soaking conditions (Mathews *et al* 1987) the transition temperature varies anywhere between 83 and 130 K. Some of the very high transition temperatures ($\sim$ 100 K) reported seem to be artifacts of preparative conditions and are not strictly reproducible over repeated cycles and the only feature where there is a general agreement amongst all workers seem to **be** the occurrence of superconductivity in $YBa_2Cu_3O_{7-\delta}$ around 95 ± 5 K. The sharpness of the transition is an important factor and it is necessary to find conditions that give sharp transitions in large scale preparations. The actual transition temperature in the 90–100 K region itself, not so significant, once T_c is above liquid nitrogen temperature. In this laboratory, we have examined the superconducting transition of $YBa_2Cu_3O_{7-\delta}$ prepared with different initial proportions of copper. The study has revealed that the transition is affected by the presence of Y_2BaCuO_5 phase and is considerably sharper when the starting composition has a slight excess of copper.

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2. Experimental

The compounds were prepared by the direct solid state reaction of high purity Y_2O_3, $BaCO_3$ and CuO. The nominal compositions studied were $YBa_2Cu_{3\pm x}O_{7-\delta}$ (x= −0·50, −0·25, 0·0, 0·25 and 0·50). The starting materials in the appropriate ratios were heated at 850°C for 24 h with intermittent grinding followed by pelletizing and sintering at 925°C for 12 h. The final heat treatment was given in oxygen atmosphere at 850°C for 6 h followed by slow cooling at the cooling rate of 50°C/h to room temperature.

X-ray powder diffractograms were recorded with a Phillips instrument using Ni filter and Cu K_α radiation. The four probe dc electrical resistance was measured in the range 60–300 K using a pumped liquid nitrogen cryostat. The electrical contacts were made on a sample of 1 x 1 x 8 mm, size with conducting silver epoxy (Elteck Corporation, India, 1228C).

3. Results and discussion

In table 1 the X-ray lattice parameters of the different compositions of $YBa_2Cu_{3\pm x}O_{7-\delta}$ for different x values between −0·50 to 0·50 are listed. All the compositions have the orthorhombic phase but in addition contain different amounts of Y_2BaCuO_5 or CuO. The percentage of Y_2BaCuO_5 progressively decreases with increase in x, while percentage of CuO becomes significant at high x values (table 1).

The room temperature resistance of the samples presented in table 1 decreases considerably as x increases from −0·50 to 0·50. The temperature variation of resistance is ploted as $R(T)/R(300)$, for the sake of convenience, in figure 1. Superconducting transitions were observed in all the cases but the width of the transition (ΔT_c defined as 10% to 90% of the transition), the onset temperature [$T_{c(ON)}$] and the zero resistance temperature [$T_{c(0)}$] vary considerably with the composition. The

Table 1. The unit cell parameters, percentages of Y_2BaCuO_5 and CuO phases, room temperature resistance, superconducting onset temperature, zero resistance temperature, midpoint of transition and width of transition for $YBa_2Cu_{3\pm x}O_{7-\delta}$ compositions.

x in $YBa_2Cu_{3\pm x}O_{7-\delta}$	Lattice parameters (Å) a	b	c	% of[a] Y_2BaCuO_5	% of CuO	$R_{(300)}$ mΩ	$T_{c(ON)}$ (K)	$T_{c(0)}$ (K)	T_c (K)[b]	ΔT_c (K)
−0·50	3·83	3·89	11·67	11	0	130	76	−50 K	68·0	15·0
−0·25	3·83	3·89	11.68	6	0	114·8	84·5	66.0	78·0	10·0
0·00	3·83	3·89	11·68	0	0	20·0	92.0	82·0	87·0	6·0
+0·25	3·83	3.89	11·67	0	2	17·8	100·0	92·9	96·0	3·5
+0·50	3·83	3·89	11·67	0	6	20·0	100·5	< 60[c]	—	—

(a) Estimated from X-ray diffractogram with an error of ±2%.
(b) T_c defined as midpoint of 10% to 90% of the transition.
(c) Saturates below 85 K to 6% of normal state value.

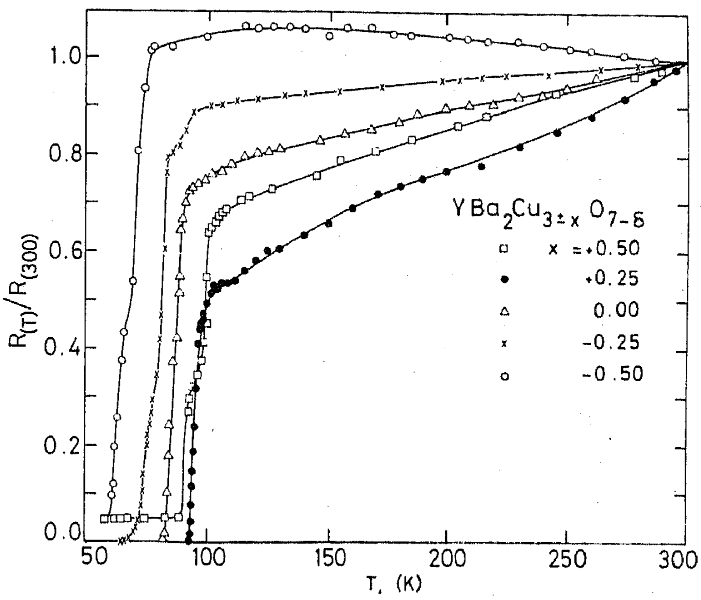

Figure 1. Temperature versus $R(T)/R(300)$ plots of nominal compositions $YBa_2Cu_{3\pm x}O_{7-\delta}$ for different values of **x**.

resistance ratio (defined as the ratio of normal state resistance just before the onset of T_c to the room temperature resistance) and the behaviour of resistance in the normal state also vary with the composition. Our sample with the ideal composition $YBa_2Cu_3O_{7-\delta}$, show $T_{c(ON)}$ and $T_{c(0)}$, at 93 and 84 K respectively. The samples with $x < 0$ showed lower $T_{c(ON)}$ and $T_{c(0)}$ in addition to which they had higher resistance ratios. Sample with $x = 0{\cdot}25$ had a resistance ratio of 0·5 and the $T_{c(ON)}$, $T_{c(0)}$ and ***AT,*** are 100, 92.9 and 3.5 K respectively. However, with $x = +0{\cdot}5$, the resistance ratio increases to 0·65 and though the $T_{c(ON)}$ is 100 K, the resistance saturates below 85 K to *6%* of the room temperature value and does not go to zero. Our best sample with $x = 0{\cdot}25$ could withstand a critical current of 1·9 **A** at 77 K in the configuration measured, which corresponds to a critical current of 190 A/cm^2. Resistivity experiments repeated on the same samples after exposure to 100% humidity at 363 K for 24 h showed no sign of deterioration of superconducting properties.

In the Y-Ba-Cu-O system, the three component phase diagram has been worked out recently (Roth *et al* 1987). It shows the presence of two stable phases, $YBa_2Cu_3O_7$ and Y_2BaCuO_5 in addition to many ternary phases. Another interesting feature is the existence of a partially melting region with Cu excess over $YBa_2Cu_3O_7$. This feature has been successfully exploited in growing sizable single crystals of superconducting compounds (Schneemeyer *et al* 1987). In the present study, since all the sample were heat treated identically, the relative proportion of $YBa_2Cu_3O_{7-\delta}$ and Y_2BaCuO_5 is dependent on the copper concentration. The effect of small amounts of semiconducting phase Y_2BaCuO_5 on the superconducting properties is clearly demonstrated in the present studies. The variation of resistance in the normal state can be thought of as arising from the weighed sum of metallic $YBa_2Cu_3O_7$ and semiconducting Y_2BaCuO_5 behaviour. In a way the resistance ratio is a measure of the amount of the semiconducting phase. Co-existence of the semiconducting phase seems to lower the $T_{c(ON)}$ and $T_{c(0)}$ and also affect the nature of resistivity curve above T_c.

Samples of $YBa_2Cu_3O_{7-\delta}$ prepared under similar conditions having identical X-ray powder diffraction patterns had a range of $T_{c(ON)}$, $T_{c(0)}$ and resistance ratios. It Seems likely that this variation is due to small amounts of the semiconducting phase present in the matrix below the detection level of X-ray diffraction technique. Concentration gradients are hard to eliminate in ceramic processing where starting materials are of finite grain size. By the law of chemical equilibrium it is possible to shift the reaction in favourable direction by using excess concentration of one of the components. In the present case the (YBa) :Cu ratio is 1 : 1 for the superconducting phase and 3 : 1 for the semiconducting phase. The result of 8·33% excess copper shows that it produces the best results. The present results also show that the stoichiometric sample does contain some semiconducting phase, though undetected by X-rays. This is eliminated by taking slight excess of copper. It is possible that varying copper concentration also affects the intergranular characteristics or grain boundaries, Since the presence of grain boundaries is an essential feature of superconductivity in polycrystalline materials, the presence of other related phases could also play a role. For example superconducting samples of such oxides prepared by low temperature method generally seem to give low T_c because of the small particle size and absence of grain boundaries.

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