Bull. Mater. Sci., Vol. 14, No. 2, April 1991, pp. 161–166. © Printed in India.

Structural, electrical and magnetic properties of Y–Sr–Cu–O

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Abstract. Preparation, resistivity (ρ), field-cooled (FC) and zero field-cooled (ZFC) susceptibility (χ) of YSrCuO are reported. Zero ρ is observed at 72 K. FC χ shows a superconducting transition at 68 K and also an antiferromagnetic transition at 15 K which is due to $Y_2Cu_2O_5$ as deduced from electron diffraction and composition analyses. It is tentatively proposed that the Y-rich phase could be responsible for the observed superconductivity.

Keywords. YSrCuO; electron diffraction; EDX analyses; antiferromagnetism; superconductivity.

1. Introduction

Conflicting results have been reported as to the occurrence of superconductivity in $YBa_{2-x}Sr_xCu_3O_7$ especially for $x > 1$. Whereas, Veal *et al* (1987) reported that T_c decreases as x increases and in particular for $x > 1$, the compound looses its superconductivity, Oda *et al* (1987) found a tetragonal structure for $x = 2$ with $T_c = 80$ K. On the other hand, Zhang Qi-rui *et al* (1987) found $T_c = 90.5$ K in $Y_{1-x}Sr_xCuO_{3-y}$ for $0.375 < x < 0.5$ and Wu *et al* (1988) observed T_c^{on} at 92 K and zero resistance at $T_c = 85$ K in YSrCuO (nominal composition). In the absence of a detailed structure analysis, the main X-ray diffraction (XRD) peaks were indexed on the basis of Sr replacing Ba ions. It was also shown that this phase does not contain the 40 K phase whose composition was $Y_{0.9}Sr_{2.1}Cu_3O_y$ reported earlier by Mei *et al* (1987). While this work was in progress, Sunshine *et al* (1989) found that the $x = 2$ compound (the Sr analogue) does not form. In this paper, we report the preparation, electron diffraction, quantitative EDX analyses, resistivity (ρ) and magnetic susceptibility (χ) both field-cooled (FC) and zero field-cooled (ZFC) of the YSrCuO system.

2. Experimental techniques

Ceramic samples were prepared by mixing high purity Y_2O_3, $SrCO_3$ and CuO in the metal atom ratio 1:1:1 and calcining at 1200C in air for 2 hr. The calcined powder was ground, mixed with a binder, granulated and pressed in the form of discs under 3 ton/cm^2 pressure. These discs were sintered in air at 1200C followed by furnace-cooling. Four indium contacts were ultrasonically welded to a rectangular bar for

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electrical measurements. An alternating current (50 μA to 10 mA) was passed through the sample and the voltage was measured by a lock-in amplifier. Van der Pauw technique was used to calculate ρ. Faraday balance was used to measure χ in a field of $H = 600$ Oe. Electron diffraction was carried out on small platelets crushed in an agate morter. EDX analyses were performed in a Philips 505, 15 kV scanning microscope provided with an EDX Link Analytical AN 1000 spectrometer.

3. Results and discussion

The resistivity as a function of temperature of one of the samples is shown in figure 1. ρ at 300 K is quite high at 700 mΩ cm but decreases slowly with T. The superconducting onset is at 86 K and the zero resistivity is achieved at 72 K. The transition width is around 4 K.

The FC χ of the sample is shown in figure 2. χ starts decreasing at around 72 K and the diamagnetism sets in at 68 K. The diamagnetic susceptibility increases up to 40 K and shows a plateau between 45 and 35 K. It then slowly decreases reaching a value of 1×10^{-5} emu/g at 15 K before increasing up to 2×10^{-5} emu/g. We would like to attribute the maximum at 15 K to the antiferromagnetic transition of $Y_2Cu_2O_5$ ($T_N = 13$) reported earlier (Troc *et al* 1987). The EDX analyses also indicate the presence of $Y_2Cu_2O_5$ (see below and table 1). In figure 3 is shown the ZFC χ data which were not reported earlier. Starting from 8 K, the diamagnetic signal continuously decreases reaching 0 at 70 K without showing any maximum at 15 K nor any step at 40 K as was seen in the FC data. It is possible that the magnetic impurity is completely screened by the superconducting phase. Due to the high field used here, we are unable to estimate the Meissner fraction. However, we note that at 10 K, the ZFC χ is 30 times that of the FC χ indicating a relatively high screening effect.

Quantitative analyses of a part of the above sample were performed by EDX spectrometer. The surface area analysed was $130 \times 130\,\mu m^2$. The material seems to

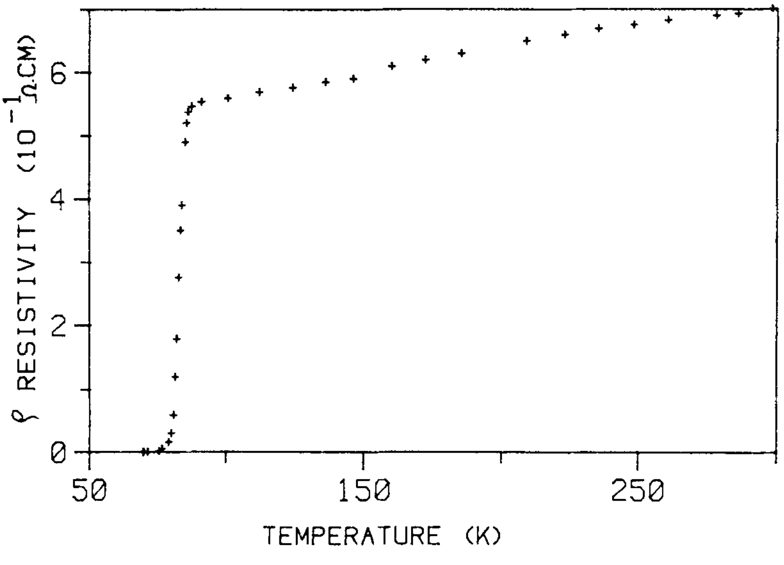

Figure 1. Resistivity (ρ) as a function of temperature of YSrCuO.

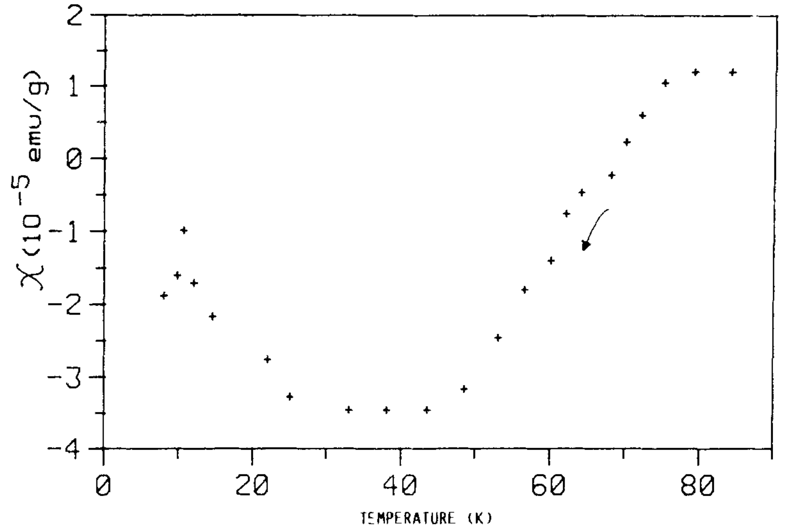

Figure 2. Magnetic susceptibility (χ) as a function of temperature of YSrCuO cooled in a field of 600 Oe.

Table 1. EDX analyses of the sample YSrCuO.

A. $Y_xSr_yCu_zO_z$ type compounds		B. Insulating compounds	
$Y_{1.5}Sr_2Cu_3O_7$	17%	Y_2SrO_4	24%
$YSrCuO_4$	6%	$Y_2Cu_2O_5$	18%
$YSr_2Cu_4O_8$	5%	$SrCuO_2$	2%
Other random compositions	21%	$YCuO_2$	2%
average composition	$Y_1Sr_1Cu_{1.35}O_4$	$Sr_2Cu_5O_7$	<2%
		$Sr_3Cu_4O_7$	<2%
		$Y_2Cu_4O_7$	<1%
		$SrCu_2O_3$	<1%

have mainly the $Y_{1.25}SrCuO_4$ composition. In addition, 94 punctual analyses were (2.5 μm^3 in volume) carried out to define the various compositions of the above mentioned surface. A wide variety of compositions were found as in table 1. One can divide the data into two groups—(i) $Y_xSr_yCu_zO_t$ type compounds which may be superconductors and (ii) ternary compounds with and without Cu most of which are known to be non-superconductors. The average composition of type i is found to be $YSrCu_{1.35}O_4$. About 17% of our sample has a composition slightly richer in Y compared to the nominal 1–2–3 composition. The sample prepared by Zhang Qi-rui *et al* (1987) is richer in both Y and Sr. Note that none of these authors have analysed the composition of their sample. Of the insulating compounds (type ii), one can identify $Y_2Cu_2O_5$ as revealed by the antiferromagnetic transition observed at 15 K. Often, we found Al and Ba contamination in our samples. In fact, one could write the general composition as $Y_xSr_yCu_z\,Al_{0.02-0.3}Ba_{0.01-0.3}O_t$. Let us note that Sunshine *et al* (1989) indeed report the observation of such compounds (with Al substituted at the Cu site) and find $a = b = 3.84$ and $c = 11.28$ Å but do not observe superconductivity as reported here by us.

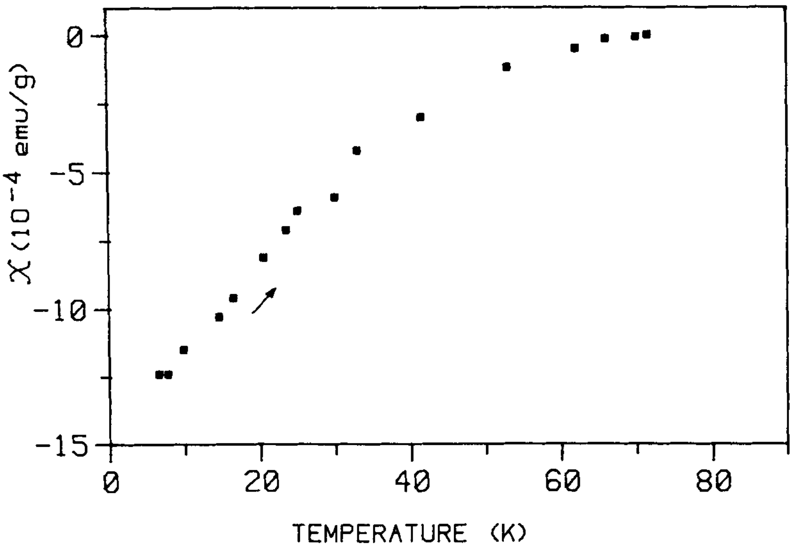

Figure 3. Zero field-cooled magnetic susceptibility (χ) as a function of temperature of YSrCuO.

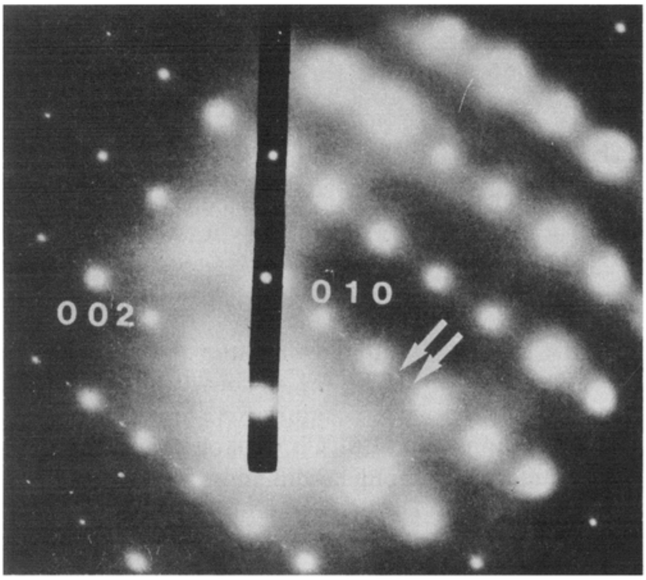

Figure 4. Electron diffraction pattern of $Y_2Cu_2O_5$ (zone axis: 1 0 0). Arrows indicate a superstructure.

The EDP indicates a great variety of spot and ring patterns. The thin (50 to 100 nm thick) crystals do not present apparent defects and grain boundaries. The major part of the crystals seems to correspond to Y_2SrO_4 and $Y_2Cu_2O_5$ (figure 4) as also indicated by our EDX data. Further, in coexistence with these, some patterns show the presence of numerous segmented rings (figure 5). These can be indexed according

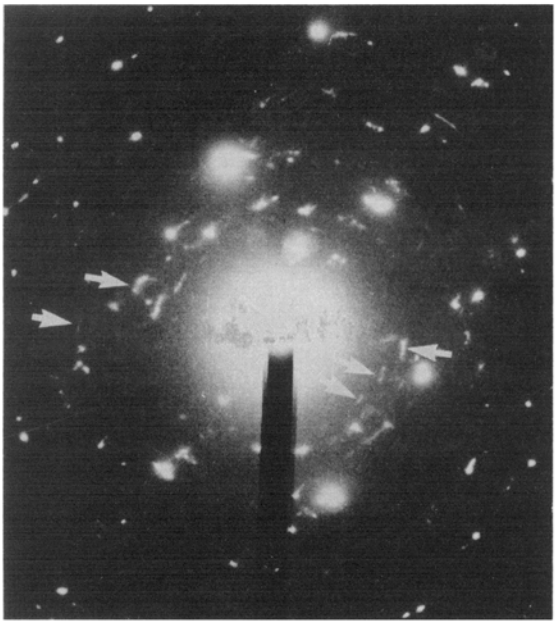

Figure 5. The small segmented rings, indicated by arrows, show that very small YSrCuO$_t$ crystals are embedded inside an oxide matrix (large spots).

to the tetragonal structure ($a = b = 3.77$ A and $c = 13.25$ A) as reported by Mei *et al* (1987). On the other hand, we did not succeed in indexing any of these with an orthorhombic structure as claimed by Wu *et al* (1988). It is possible that the tetragonal structure exists for a certain range of compositions of $Y_xSr_yCu_zO$. Hence the superconductivity observed in our sample is tentatively attributed to Y-rich part of the YSrCuO system of type i (table 1). At the present stage, however, the contribution due to $YSr_2Cu_4O_8$ cannot be neglected.

4. Conclusions

We have shown that superconductivity is indeed observed at $T > 70$ K in a multiphase sample of nominal composition YSrCuO synthesized at 1200 C. The phase responsible is tentatively attributed to YSrCuO rich in Y and having a tetragonal structure. An anomaly observed at 15 K in the field-cooled measurements is attributed to the antiferromagnetic transition of $Y_2Cu_2O_5$ identified by EDX and electron diffraction analyses.

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