Science is built up with facts, as a house with stones, but a collection of facts is no more a science than a heap of stones is a house.

.... Poincare
INTRODUCTION

High temperature superconductivity in oxides of La-Ba(Sr)-Cu-O system having the $K_2NiF_4$ structure [1-4] and of the Y-Ba-Cu-O system [5,6] possessing the perovskite structure has stimulated intensive studies on this and related systems. Since the discovery of superconductive Y-Ba-Cu-O with the onset at about 90 K by Wu et al [5] which was followed by independent discoveries by Zhao et al [7] and Hikami et al [8], intensive studies have been directed to identify the phases responsible for superconductivity. The Y-Ba-Cu-O system has been investigated with various molar ratios (1:1, 3:2, 2:1) of (Y, Ba:Cu) [5, 8-15]. From a careful study [16] of the $Y_2O_3$-BaO-CuO phase diagram, the 90 K superconducting compound was identified as $Y_1Ba_2Cu_3O_{7-δ}$ and almost all researchers concentrate on composition in
the vicinity range of Y$_1$Ba$_2$Cu$_3$O$_{7.4}$. It was found [17] that the temperature of zero resistance is the highest at (Y + Ba)/Cu = 1 and tends to decrease with increase in the ratio due to phase segregation and multiphase formation. Since Y$_1$Ba$_2$Cu$_3$O$_{7.4}$ is superconducting well above liquid nitrogen temperature, it holds much promise. The main characteristic features of YBCO are found to be [18,19]:

(i) It is a type II superconductor.

(ii) Hall carrier density = 4 x 10$^{21}$ cm$^{-3}$ for a material of resistivity $\sim$ 400 $\mu$S cm just above the $T_c$.

(iii) $dH_c/dT = 2$T/K.

BCS coherence length $\approx$ 1.4 nm, London penetration depth $\approx$ 200 nm and Mean free path $\approx$1.2 nm.

(iv) $H_c (0) \sim 1$ T.

(v) $H_d (0) \sim 120$ T.

(vi) Critical current density (in ceramic samples) $\sim$ 10$^8$ A/cm$^2$ at 77 K.

Depairing current density: 10$^7$-10$^8$ A/cm$^2$ (estimated).

Many investigators have found that $T_c$ and sharpness of the transition in Y$_1$Ba$_2$Cu$_3$O$_{7.4}$ are very sensitive to sintering temperature and atmosphere and correspondingly to the degree of nonstoichiometry, $\delta$ [20-24]. It is therefore essential to determine the exact oxygen composition under different conditions of sample preparation and heat treatment. Fig.8.1 shows that the condition for superconductivity behaviour in Y$_1$Ba$_2$Cu$_3$O$_{7.4}$ lies in a region of high oxygen content (which corresponds to high copper oxidation states) and low temperatures [25,26] and that the material at high temperatures behaves electrically like a metal. The tetragonal phase of YBCO, Y$_1$Ba$_2$Cu$_3$O$_8$ is insulating and the orthorhombic phase with high oxygen content is metallic. Phases with intermediate oxygen composition have been reported in the literature [27-29].

The purpose of the present investigation is to prepare pure, homogeneous and reproducible single phase high $T_c$ bulk superconducting Y$_1$Ba$_2$Cu$_3$O$_{7.4}$ samples under two different conditions and to determine the oxygen nonstoichiometry value ($\delta$), total copper content and Cu(III)/Cu(II) ratio. Attempt was also made to examine the compositional dependence of $T_c$ and structure of Y-Ba-Cu-O with Y to (Y+Ba)
Fig. 8.1. A schematic diagram for the electronic behaviour of Y$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ showing the location of the superconductive state.
ratio equal to 0.4 and (Y+Ba) to Cu equal to 1.0 and 1.5. The resistivity and ac susceptibility measurements for the samples slowly cooled after sintering in air and oxygen atmosphere were also made and the close correlation between composition, structure and superconducting behaviour of $Y_{1.8}Ba_2Cu_3O_{7.3}$ are discussed.

**EXPERIMENTAL**

Specimens of $Y_{0.4}Ba_{0.6}Cu_3O_{6.6}$, $Y_{1.2}Ba_{1.8}Cu_2O_{7.2}$ and $Y_{1.8}Ba_2Cu_3O_{7.4}$ were prepared by high temperature solid state reaction of 3N pure $Y_2O_3$, $BaCO_3$ and $CuO$ mixed in the desired composition. The stoichiometric mixtures were calcined in air in a recrystallized alumina boat at 1100 K for 16 hours. Subsequently the mixtures were subjected to second calcination at 1150 K for 16 hours for obtaining homogeneous powders. Two calcination steps were found to be enough for obtaining homogeneous single phase YBCO powder. It was found that when the reaction temperature was less than 1100 K, undecomposed $BaCO_3$ was left. The double calcined powder was subjected to extended grinding in agate planetary mill to vary its particle size distribution and surface area. The mixtures were ground to 150 mesh powders and these powders were cold-pressed (100 MPa) into pellets (13 mm dia x 2-3 mm thick) and sintered at 1170 K for 15 h in air and were slowly cooled (20 K/h) to room temperature to avoid degradation of the quality of the sample. Another set of pellets prepared under similar conditions were sintered at 1170 K for 15 hours in $O_2$ atmosphere and slowly cooled to 303 K to maintain the $O_2$ content very close to 3 or 7 depending on the compounds. Single phase $Y_{1.8}Ba_2Cu_3O_{7.4}$ samples were obtained by sintering at 1170 K. When the samples were sintered at temperatures $> 1170$ K, they had two or three phases. Slowly cooled Y-Ba-Cu-O has an orthorhombically distorted oxygen deficient perovskite structure whereas rapidly quenched ones are tetragonal.

The crystal structure of the slowly cooled samples was determined by XRD (Philips powder X-ray diffractometer), at room temperature using CuK$_\alpha$ line. The resistance was measured using the standard four-probe technique in the temperature range 303-70 K. Voltage and current leads were made by applying silver epoxy at four corners to which platinum wires were soldered with indium. The temperature dependence of ac susceptibility was made by an ac mutual inductance method at 317 Hz and 0.05 Oe. The temperature of the sample was monitored by a calibrated
copper-constantan thermocouple, to an accuracy of ±0.5 K. The infrared absorption spectra of the samples were recorded in the range 200 - 4000 cm⁻¹ using Pye Unicam SP3 300 infrared spectrophotometer. Iodometric titrations were also carried out to determine the effective copper oxidation level and as a result the oxygen content in Y-Ba-Cu-O samples. Sodium thiosulphate titrant was standardised against 5N pure copper. Starch indicator was added immediately before the end point. The Cu(II) and Cu(III) content of YBCO was measured by two iodometric titrations [30].

RESULTS AND DISCUSSION

X-ray diffraction profiles on the Y₁Ba₂Cu₃O₇₋δ samples showed that oxygen-sintered (sample A) and air sintered (sample B) samples [Fig. 8.2] were almost single phase and the observed reflections were characteristic of orthorhombic perovskite structure. The unit cell parameters for the samples sintered in air and oxygen are a = 0.3828 nm, b = 0.3897 nm, c = 1.169 nm and a = 0.3817 nm, b = 0.3883 nm, c = 1.168 nm respectively.

All the reflections in YₓBa₁₋ₓCuO₂ₓ (sample C), Y₁₋ₓBaₓCu₂O₄ₓ (sample D) could be indexed as an orthorhombic phase. The similarity of the XRD patterns of C and D samples indicates that the bulk superconductivity is realised in the common structure. This also indicates that strict stoichiometry is not necessary for obtaining a superconducting state. The X-ray diffraction peaks due to this orthorhombic phase did not shift in these samples having different nominal compositions of (Y+Ba) to Cu. The X-ray diffraction patterns of the samples C and D are shown in Fig. 8.3. A closer examination shows that the relative intensity of the diffraction peaks are greater in the sample C than in the sample D and the diffraction peaks are sharper for sample C than for sample D. The calculated unit cell parameters were a = 0.3829 nm, b = 0.3888 nm and c = 1.1667 nm which were consistent with those previously reported [31-33] for Y-Ba-Cu-O compound. From the unit cell dimensions, the virtual bond length of Cu-O is estimated to be 0.192 - 0.195 nm, assuming that the cubic perovskite structure is orthorhombically distorted without changing the atomic parameters. The value is much lower than 0.213 nm, the ordinary Cu-O bond length for Cu(II) ion in octahedral environments [34,35]. This apparent contraction may be partly explained by the decrease in coordination number of copper ions and considerable displacement of atoms from the special position of the ideal perovskite,
Fig. 8.2. X-ray diffraction profile of $Y_1Ba_2Cu_3O_{7-\delta}$ (sintered in oxygen).
Fig. 8.3. X-ray diffraction patterns of $Y_{0.4}Ba_{0.6}Cu_2O_3$-$\delta$ (Sample C) and $Y_{1.2}Ba_{1.8}Cu_2O_7$-$\delta$ (Sample D).
which are mostly caused by introduction of a large amount of oxygen vacancy. However, the extraordinary high \( T_c \) in these compounds strongly suggests actual contraction of Cu-O bonds.

Temperature dependence of resistivity [Fig. 8.4] for 123 samples sintered in oxygen and air are metallic between 303-95 K and resistivity starts to drop sharply at about 95 K. The sample \( \Lambda \) sintered in oxygen showed zero resistivity at 93 K with a sharp transition width of 1 K and the resistivity is less than 2 milliohm-cm at 303 K. On the other hand the sample sintered in air demonstrated the zero resistivity temperature of slightly lower value (90 K, with a transition width of 3 K) and the room temperature resistivity was 8 milliohm-cm.

The temperature dependence of resistivity for the samples C and D is shown in Fig. 8.5. The behaviour is characteristic of metallic between 303-90 K. Here also the resistivity drops sharply at about 95 K and becomes zero at 92 and 90 K respectively. The sharp transition observed in both the samples implies that the samples were homogeneous and the major phase is superconducting. The two samples, C and D exhibited similar temperature dependence of resistivity except that the transition is slightly narrower for sample C. Samples C and D show a distinct superconducting transition and \( T_c \) values at onset, mid point and zero resistance respectively are as follows: 95, 93 and 92 K for sample C and 95, 92 and 90 K for sample D. The resistivity just above the onset of superconducting transition was approximately 3.5 to 4.5 milliohm-cm. The transition width (10-90%) was about 3 K and it is likely that the superconducting phase is dominant in both the samples. The transition width and the temperature dependence of resistivity above the transition temperature were found to be strongly dependant on the sintering temperature. It is seen that Y-Ba-Cu-O with \((Y+Ba)/Cu\) ratios varying from 1.0 to 1.5 exhibit superconductivity with zero resistance at temperatures higher than liquid nitrogen. Although the two oxides have nearly the same onset \( T_c \) values of 95 K, the temperature of zero resistance is the highest (92 K) at \((Y+Ba)/Cu = 1\) and tends to decrease with increase in the ratio of \((Y+Ba)\) to \(Cu\).

From the temperature dependence of ac susceptibility for the four samples \( \Lambda, B, \) and \( D \) [Figs. 8.6 & 8.7], it is seen that at room temperature all the samples were paramagnetic and on cooling, a transition to diamagnetic state occurred at 95 K. The diamagnetic signal saturated at 93 and 90 K for the sample sintered in oxygen and air.
Fig. 8.4. Temperature dependence of resistivity for $Y_1Ba_2Cu_3O_{7-\delta}$ (A-sintered in oxygen, B-sintered in air).
Fig 8.5. Temperature dependence of resistivity for $Y_{0.4}Ba_{0.6}CuO_3\delta$ (Sample C) and $Y_{1.2}Ba_{1.8}Cu_2O_7\delta$ (Sample D).
Fig. 8.6. Temperature dependence of ac susceptibility for $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (A-sintered in oxygen, B-sintered in air).
Fig. 8.7. AC susceptibility versus temperature for $Y_{0.6}Ba_{0.6}CuO_{3-d}$ (Sample C) and $Y_{1.2}Ba_{1.8}Cu_2O_{7-d}$ (Sample D).
respectively. From the resistivity and ac susceptibility measurements, it has been confirmed that samples C and D were superconductors with $T_c(0)$ values of 92 K and 90 K respectively. The quality of the superconducting phase is magnified by rendering both resistive and inductive transitions much sharper.

Iodometric titration analysis indicated that the oxygen sintered and air sintered YBCO samples have the formula $\text{Y}_1\text{Ba}_2\text{Cu}_3^+\text{Cu}^{2+}_{0.84}\text{Cu}^{2+}_{2.39}\text{O}_{6.99}$ and $\text{Y}_1\text{Ba}_2\text{Cu}_3^+\text{Cu}^{2+}_{0.71}\text{Cu}^{2+}_{2.29}\text{O}_{6.68}$ respectively. The oxygen deficiency value, $\delta$ and Cu(III)/Cu(II) ratio are 0.10 and 0.369 for samples sintered in oxygen and 0.15 and 0.310 for samples sintered in air respectively. The studies indicated that sintering in oxygen flow followed by slow cooling in oxygen atmosphere seems to be more effective for sufficient oxygen incorporation which improves the transition temperature and sharpness of the transition.

The infrared spectra of samples C and D at room temperature are shown in Fig.8.8. A number of bands were observed in the region 200-1000 cm$^{-1}$ and these are attributed to the lattice vibrations of Y-Ba-Cu-O. The calculated vibrational modes [36] assuming orthorhombic space group agree well with the observed values. The calculated values are given in brackets in the figure. This supports that the orthorhombic structure gives rise to high $T_c$ superconductivity in Y-Ba-Cu-O compounds.

Y-Ba-Cu-O materials are very sensitive to preparative details. The materials become superconducting when sintered at 1170 K in air or in oxygen atmosphere. Otherwise the sample becomes a semiconductor or an insulator. The insulating sample displays a different X-ray spectrum from that of the superconducting phase whereas the semiconducting material exhibits a similar spectrum. In both cases heat treatment in oxygen can make the sample a superconductor with the same orthorhombic structure. This shows that the oxygen concentration as well as structure plays an important role in superconductivity.

The cooling rate from a sintered state is also critical to the superconducting property because rapidly quenched samples were always insulators whereas the slowly cooled material was a superconductor. The sample cooled at medium rate is semiconducting at higher temperatures but becomes superconducting at sufficiently low temperatures which is usually lower than the critical temperature of the slowly
cooled sample of the same composition. Y-Ba-Cu-O compounds have tetragonal symmetry at the sintering conditions and transformed into orthorhombic symmetry during the slow cooling process because the samples absorb oxygen during cooling process. The $T_c$ in the tetragonal Y-Ba-Cu-O is 20 K lower than in the orthorhombic sample and the temperature dependence of resistivity is semiconducting. The nature of oxygen vacancy distribution is probably influencing the resistivity and $T_c$.

CONCLUSIONS

The normal state resistivity and $T_c$ in Y$_1$Ba$_2$Cu$_3$O$_{7-\delta}$ depend on the sintering atmosphere. The oxygen deficiency value, $\delta$ and (Cu(III)/Cu(II)) ratios are 0.10 and 0.369 for samples sintered in oxygen and 0.15 and 0.310 for samples sintered in air respectively. Sintering in oxygen flow followed by slow cooling in oxygen atmosphere seems to be more effective for sufficient oxygen incorporation which improves the transition temperature and sharpness of the transition.

The superconductivity of Y-Ba-Cu-O with different (Y,Ba):Cu molar ratio indicates that the temperature of zero resistance is the highest (92 K) at (Y + Ba)/Cu = 1 and tends to decrease with increase in the ratio of (Y + Ba) to Cu. A sharp transition at 95 K with a width of approximately 3 K was observed for the samples with 1:1 and 3:2 ratio.
REFERENCES


