Effect of bismuth replacement at barium site in Y–Ba–Cu–O system

RAM BILAS

Department of Physics, Indian Institute of Technology, Kanpur 208 016, India

MS received 2 June 1992; revised 31 December 1992

Abstract. X-ray diffraction, electron paramagnetic resonance, microwave absorption and resistivity measurements were carried out on $\text{YBa}_{2-x}\text{Bi}_x\text{Cu}_3\text{O}_7$ ($0 \leq x \leq 0.5$) superconductors in order to study the effect of bismuth on the structural and superconducting properties. A decrease in sintering temperature increased the amount of impurity phase. Transition from an orthorhombic (superconducting) phase to tetragonal structure produced no significant change in EPR zero-field signal at liquid nitrogen temperature (LNT). The non-resonance signal height decreased on higher concentration of bismuth. Sintered $\text{YBa}_{2-x}\text{Bi}_x\text{Cu}_3\text{O}_7$ superconductor had a strong EPR zero-field signal at LNT. We have evaluated particle size from XRD and EPR studies. The average particle size was about 0.4 μm .

Keywords. Oxide superconductor; bismuth impurity; microwave absorption.

1. Introduction

The discovery of La–Sr–Cu–O and Y–Ba–Cu–O oxide superconductor with T_c up to 90 K (Bednorz and Muller 1986; Kiloyne and Cywinski 1987; Muromachi *et al* 1987; Wu *et al* 1987; Iqbal *et al* 1988) has aroused a lot of interest in Y–Ba–Cu–O superconductor. Bismuth introduced into the Y–Ba–Cu–O (1–2–3) system to partially replace yttrium (Yang 1990) was reported to have improved grain contact by forming flux during sintering. It was used as an oxide additive in the Y–Ba–Cu–O system (Jung 1988; Takeyuki *et al* 1988) which possibly resulted in liquid phase sintering. It was also reported that the partial Bi substitution had an advantage, that Bi_2O_3 seemed to perform the function as an internal catalyst which favoured the growth of superconducting phase. Moreover, it is well known that bismuth oxide was used earlier as a nucleating agent in ceramic materials. The replacement of copper site by Bi in Y–Ba–Cu–O system was also investigated earlier (Yang *et al* 1990). The present investigation is concerned with partial replacement of barium site by bismuth to study the effect of Bi on structural and superconducting properties of $\text{YBa}_{2-x}\text{Bi}_x\text{Cu}_3\text{O}_{7-s}$ ($0 \leq x \leq 0.5$) high T_c superconductors.

2. Experimental

The samples were synthesized by the standard solid-state reaction technique. The constituents were weighed (wt.%) from powders of yttrium oxide (Y_2O_3), barium carbonate (BaCO_3), bismuth oxide (Bi_2O_3) and copper oxide (CuO) each of purity 99.9%. They were mixed and ground thoroughly in an agate pestle mortar. The grinding was repeated twice to achieve homogeneity.

After decomposing at 800°C/12 h the powder was pressed into pellet-form by applying a pressure of 8 tonnes/cm². The pellets (≈ 1.1 cm in dia. and 0.2 cm thick) were sintered in two different conditions. Under the first, some pellet samples were heated

at 950°C/12 h and furnace-cooled to room temperature in the presence of oxygen atmosphere and under the second, some other pellet samples were sintered at 950°C for 2 h and slowly cooled to 600°C. The samples were then kept at this temperature for 5 h.

XRD patterns of the samples were recorded using Rich-Scifert isodebyflex (model 2002) diffractometer with chromium (CrK_α) target. EPR spectra were recorded using Varian E-109 EPR spectrometer. The sample ($2 \times 2 \times 1 \text{ mm}^3$) was kept in a sealed quartz tube and a thermocouple sensor placed in contact with the sample. The temperature was controlled with a variable temperature controller with accuracy of $\pm 0.5 \text{ K}$. The frequency of the resonance cavity was measured using a standard g -marker, (DPPH) $g = 2.0036 \pm 0.0002$. The resistivity was measured using a standard four-probe technique. Knick precision constant current source (model 181) and Keithley nanovoltmeter were used for resistivity measurements.

3. Results and discussion

Figure 1 shows X-ray patterns for samples with $x = 0.0, 0.1, 0.2, 0.3$ and 0.5 . The system showed orthorhombic nature up to $x = 0.2$ doping of Bi and after that the samples became multiphase for $x = 0.3$ and 0.5 . As x increased another group of peaks emerged with increased intensity which was identified as YBa_2BiO_6 and CuO (Yang *et al* 1990). No impurity peaks other than these three could be found in the patterns. The YBa_2BiO_6 phase co-existed with 1-2-3 and varied only in the composition range. When $x = 0.5$, the XRD pattern mainly consists of YBa_2BiO_6 and CuO with the 1-2-3 peaks hardly discernible. When bismuth replaces part of Ba in 1-2-3 composition a proportional phase of YBa_2BiO_6 is formed (Blower and Greeves 1988).

The lattice parameters a, b, c (950/12 h) for this series have been calculated (table 1). With different concentrations of Bi from X-ray diffraction patterns, it appeared that d -values increased with substitution of Bi in the Ba plane. The orthorhombic phase decreased and tetragonal phase increased at higher Bi concentrations. The system formed tetragonal structures lowering the superconducting transition (T_c).

The broadening of some of the particular peaks i.e. 103, 005, 123 has been considered. The average grain-size estimated from XRD patterns is given in table 2. Half-line width depends upon two factors, the particle (grain-size) and the lattice strain (lattice distortion). Normally the grain size of the material is $1 \mu\text{m}$. Thus, line broadening seems to be due to lattice strain as is evident from the lattice parameter as shown in figure 2. The line broadening passes through a maxima around $x = 0.1$ of Bi substitution. Thus it seems that substitution of Bi in $\text{YBa}_{2-x}\text{Bi}_x\text{Cu}_3\text{O}_{7-s}$ lattice is maxima and corresponds to the maximum incorporation of Bi.

The EPR spectra are shown in figure 3. A small zero-field signal appears at $x = 0.2$, after which the compound became multiphase and its signal amplitude zero field decreased. The spectra were recorded in a small piece ($2 \times 2 \times 1 \text{ mm}$) from the compound. The room temperature EPR signal consisted of a peak typical of $s = \pm 1/2$ species, showing the g -value anisotropy. Since the expected paramagnetic species should arrive from $\text{Cu}^{2+}/\text{Cu}^{3+}$, it is clear from the EPR spectra that dominant valence is Cu^{2+} from the orthorhombic symmetry Cu^{2+} which will show the g -value anisotropy. The presence of only two resolved components with $g_{\parallel} = 2.0 \pm 0.02$ and

Figure 1. X-ray diffraction patterns of $YBa_{2-x}Bi_xCu_3O_{7-\delta}$ ($0 \leq x \leq 0.5$) samples.

Table 1. Variation of lattice parameters for $YBa_{2-x}Bi_xCu_3O_{7-\delta}$ ($0 \leq x \leq 0.5$) heat-treated at $950^\circ\text{C}/12\text{ h}$.

x	a (Å)	b (Å)	c (Å)	v (Å) ³
0.0	3.80	3.87	11.67	171.70
0.1	3.84	3.91	11.71	175.91
0.2	3.81	3.88	11.68	172.27
0.3	3.85	3.92	11.72	176.96
0.5	3.88	3.95	11.75	180.17

Table 2. Average particle size for $\text{YBa}_{2-x}\text{Bi}_x\text{Cu}_3\text{O}_{7-\delta}$ ($0 \leq x \leq 0.5$) heat-treated in different conditions.

X	Particle size (μm) (950°C/12 h)		Particle size (μm) (950°C/2 h + 600°C/5 h)	
	XRD	EPR	XRD	EPR
0.0	0.40	0.41	0.31	0.41
0.1	0.34	0.41	0.25	0.41
0.2	0.43	0.41	0.34	0.41
0.3	0.33	—	0.34	—
0.5	—	—	0.38	—

Figure 2. Lattice volume change with increase in x -value of the system $\text{YBa}_{2-x}\text{Bi}_x\text{Cu}_3\text{O}_{7-\delta}$ ($0 \leq x \leq 0.5$).

$g_{\perp} = 2.13 \pm 0.02$ further indicates the axial symmetry of Cu^{2+} environments. The fact that $g_{\parallel} \leq g_{\perp} \leq 2$ indicates that ground state orbital of Cu^{2+} is $dx^2 - dy^2$ (Bhat *et al* 1987; Blazey *et al* 1987).

Transition from normal to superconducting state takes place between 72 K and 92 K and this has also been recorded at LNT temperature (figures 3–6). There is a very strong signal in the superconducting phase at very low field (0–50 G). The estimated EPR spectral parameters are given in table 3. The samples $x = 0.0, 0.1, 0.2$ are shown near zero-field microwave absorption signal (figures 4, 6) but no signal ($x > 0.3$) of the system has been observed due to its glassy nature. The average grain-size is estimated from EPR to be $\approx 0.4 \mu\text{m}$. We have compared the particle size determined from XRD and EPR and they are given according to the following formula (Blazey *et al* 1987) $S = \phi/2H_{c1}$ where, ϕ is $2.0678 \times 10^{-7} \text{ G/cm}^2$ and S , the loop area.

The average particle size is nearly the same from EPR and XRD (table 2). From resistivity data superconducting transition (T_c) was observed for system $\text{YBa}_{2-x}\text{Bi}_x\text{Cu}_3\text{O}_{7-\delta}$ by temperature dependence of resistivity. In spite of irregularities of porosity of the samples, the contact was important for measurement. It appears from the graph that the normal state resistance behaviour is metallic. The deviation

Figure 3. EPR spectra of YBa₂Cu₃O₇: Bismuth doped system at room temperature. (The samples were prepared at 950°C/12 h in presence of oxygen).

Figure 4. Low field absorption spectra of YBa_{2-x}Bi_xCu₃O_{7-δ} ($0 \leq x \leq 0.5$) at liquid nitrogen temperature for forward and reverse sweeps. (The Bi wt% are shown against the spectra (950°C/12 h)).

Figure 5. EPR spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Bi doped system at room temperature. The samples were prepared at $950^\circ\text{C}/2\text{ h} + 600^\circ\text{C}/5\text{ h}$ in presence of oxygen.

Figure 6. Low field absorption spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Bi doped samples at liquid nitrogen temperature for forward and reverse sweeps. (The Bi wt% are shown against the spectra (samples were prepared by $950^\circ\text{C}/2\text{ h} + 600^\circ\text{C}/5\text{ h}$ in presence of oxygen)).

Figure 7. The typical plots of temperature dependence of resistance of pure and 0.1 wt% Bi doped of $\text{YBa}_2\text{Cu}_3\text{O}_7$.

Table 3. EPR and non-resonant microwave absorption data of $\text{YBa}_{2-x}\text{Bi}_x\text{Cu}_3\text{O}_{7-\delta}$ ($0 \leq x \leq 0.5$).

x	$H_{0 \text{ Peak}}$ (G)	Resonance absorption signal (cm)	Non-resonance absorption signal (cm)
0.0	25	0.00	6.4
0.1	25	0.22	5.0
0.2	25	0.31	3.6
0.3	—	0.40	—
0.5	—	2.14	—

towards zero from the linear dependence in resistivity was observed near T_c . It was also observed that the superconducting transition temperature decreased with Bi concentration.

4. Conclusion

New composition of high T_c superconductor $\text{YBa}_{2-x}\text{Bi}_x\text{Cu}_3\text{O}_{7-\delta}$ with $x \leq 0.5$ have been prepared by the usual ceramic method. The superconducting phase and crystallites exhibited very small average particle size i.e. $0.4 \mu\text{m}$, from EPR as well as X-ray diffraction studies.

Acknowledgements

The author is grateful to Dr Prem Chand and Mr S V Sharma for valuable suggestions.

References

- Bednorz J G and Muller K A 1986 *Z. Phys.* **B64** 189
- Bhat S V, Ganguly P and Rao C N R 1987 *Pramana - J. Phys.* **28** L425
- Blower S K and Greaves C 1988 *Solid State Commun.* **68** 765

- Blazey K W, Muller K A and Bednorz J G 1987 *Phys. Rev.* **B36** 7241
- Iqbal Z, Eckhard H, Reidinger F, Bose A, Barry J C and Ramakrishna B L 1988 *Phys. Rev.* **B38** 859
- Jung J, Frank J P, Miner Wa A and Mohamed M A K 1988 *Phys. Rev.* **B37** 7510
- Kiloyne S H and Cywinski R 1987 *J. Phys. D. (Appl. Phys.)* **20** 1327
- Muromachi E T, Uchida Y, Matsui Y and Kato K 1987 *Jpn. J. Appl. Phys.* **26** L476; **26** 619
- Takeyuki S, Tsutomu Y, Akinori K, Sashi M and Hisashi S 1988 *J. Mater. Sci. Lett.* **7** 926
- Wu M K, Ashburn J R, Torng C J, Hor P H, Mang R L, Gao L, Huang Z J, Wang Y Q and Chu C W 1987 *Phys. Rev. Lett.* **58** 908
- Yang N, Liu R S, Wang W N and Wu P P 1990 *J. Mater. Sci.* **25** 4758