

## Effect of oxide additives on the properties of high temperature superconductor, $\text{YBa}_2\text{Cu}_3\text{O}_7$

K D CHANDRASEKARAN, U V VARADARAJU<sup>+</sup>,  
A BARADARAJAN and G V SUBBA RAO<sup>+</sup>

Department of Chemical Engineering, <sup>+</sup>Materials Science Research Centre, Indian Institute of Technology, Madras 600 036, India

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**Abstract.** The effect of oxide additives—CuO, SiO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub> and ZnO in 1–10 mol% on the sintering and superconducting properties of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  was studied. SEM studies indicated improvement of grain size and interconnectivity due to the additives, the best results being obtained with Bi<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub>. The superconducting transition temperature is unaffected ( $92 \pm 2$  K) even with 10 mol % of the additives. ZnO, however, decreases the  $T_c$  as expected.

**Keywords.** High temperature superconductors; effect of additives;  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

### 1. Introduction

The recent discovery of high temperature superconductivity in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  with a  $T_c^0$  of 91 K by Wu *et al* (1987) and Cava *et al* (1987) and extensively investigated by many others (Chu *et al* 1987; Dhar *et al* 1987; Engler *et al* 1987; Ganguly *et al* 1987; Hikami *et al* 1987; Hosoya *et al* 1987; Matsushita *et al* 1987; Nagarajan *et al* 1987; Paulose *et al* 1987; Rao *et al* 1987; Rao and Ganguly 1987; Srinivasan *et al* 1987; Subba Rao *et al* 1987a, b; Takagi *et al* 1987) aroused worldwide interest for a detailed study and possible technological exploitation using liquid nitrogen (b.p. 77 K) as the cryogen.  $\text{YBa}_2\text{Cu}_3\text{O}_7$  has outstanding superconducting properties (Dunlap *et al* 1987; Ellis 1987; Engler 1987; Xiao *et al* 1987; Narasimha Rao *et al* 1988; Rao 1988): a  $T_c$  of 91 K, well above the liquid N<sub>2</sub> temperature; highest critical magnetic field ( $H_{c2}$ ) known for any material (> 1500 kOe), short superconducting coherence length (15–20 Å) and *p*-type metallic behaviour. Oriented thin films of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  have shown critical currents ( $J_c$ ) of  $10^6$  A/cm<sup>2</sup> comparable to that of the low- $T_c$  conventional superconductors like Nb<sub>3</sub>Sn and Nb–Ti (Chaudhari *et al* 1987). However, studies on bulk and fabricated wires of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  showed, till now, disappointingly low  $J_c$  values: typically 150–500 A/cm<sup>2</sup> (Malik *et al* 1987; Sharma *et al* 1988) but in specially prepared wires, of the order of 7000 A/cm<sup>2</sup> (Jin *et al* 1987). This is attributed to the ceramic nature of the high  $T_c$  oxide material and poor interconnectivity of the grains (Jarvinen *et al* 1988; Kilcoyne and Cywinski 1987). In essence, the grain structure and 'twinned' nature of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is responsible for the low  $J_c$  encountered in bulk material. It is known that "pinning" centres incorporated into  $\text{YBa}_2\text{Cu}_3\text{O}_7$  can play a crucial role in increasing its  $J_c$ . These pinning centres can be foreign metal ions or impurities which however do not destroy the basic superconducting nature of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . As a prelude to this, effect of oxide additives on  $\text{YBa}_2\text{Cu}_3\text{O}_7$  w.r.t. the  $T_c$  behaviour, normal state resistivity, grain size and their interconnectivity need to be studied and optimized.

Effect of chemical substitution on the superconductivity and related properties of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  has been extensively studied in the literature (Dunlap *et al* 1987; Subba Rao *et al* 1987c; Varadaraju *et al* 1987; Xiao *et al* 1987; Narasimha Rao *et al* 1988; Rao 1988). Thus, while replacement of yttrium by other rare earth ions does not change the  $T_c$  of the compound, substitution at the Ba-site and particularly at the Cu-site by either an ion of the same valency (Sr, Ca or Zn, Ni) or aliovalent ions (e.g.  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ) drastically decreases the  $T_c$  of pure  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and at sufficiently high concentrations, destroys the superconducting property completely. Kile *et al* and Cywinski (1987) studied the effect of partial substitution of yttrium by bismuth and barium by lead in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and found that while the  $T_c$  remains unchanged, the normal state room temperature resistivity decreases by an order of magnitude. Both Bi and Pb oxides act as fluxes in the sintering process during the synthesis and changes in the morphology of the sintered grains were noted. However, there exists the possibility of the formation of impurity phases of the type,  $\text{BaBiO}_3$  and  $\text{BaPbO}_3$ , along with the substituted  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

On the other hand, studies on the effect of oxide additives on the  $T_c$  behaviour of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  are limited (Dou *et al* 1987; Jarvinen *et al* 1988). Jarvinen *et al* (1987) studied the effect of 22 oxide additives (10 mol%) on the  $T_c$  and resistivity behaviour of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . Significant findings are: (i)  $\text{ZrO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{BaO}$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{Sb}_2\text{O}_3$  produced only a small but detectable change in the resistivity vs. temperature curves (including the transition temperature,  $T_c$ , of 90 K), compared with the pure reference material. (ii)  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and transition metal oxides such as  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{NiO}$  and  $\text{MoO}_3$  were found to strongly affect the  $T_c$  as well as the width of the transition,  $\Delta T_c$ . (iii) Addition of silver oxide,  $\text{Ag}_2\text{O}$ , has the beneficial effect of increasing the steepness of the superconducting transition (and hence decrease of  $\Delta T_c$ ). The beneficial effect of Ag or  $\text{Ag}_2\text{O}$  addition has been noted by other workers (Malik *et al* 1988; Sharma *et al* 1988). (iv) In cases where the oxide additive has only a minor effect on  $T_c$ , the X-ray diffraction (XRD) patterns indicated the retention of the orthorhombic phase of the original reference material. In addition, the presence of impurity phases was detected for the additives  $\text{Nb}_2\text{O}_5$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{SnO}$ ,  $\text{WO}_3$  and  $\text{Bi}_2\text{O}_3$ . Intensity of select (001) reflections of the orthorhombic phase of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  were found to increase with the following additives:  $\text{Bi}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$ . This indicates that the grains of the superconducting material are 'oriented' preferentially. (v) Additives like  $\text{Fe}_2\text{O}_3$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MoO}_3$  which have a drastic effect on  $T_c$  showed only the tetragonal phase of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and not the orthorhombic phase as can be expected.

In the present work, results of the studies on the effect of oxide additives  $\text{CuO}$ ,  $\text{ZnO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{SiO}_2$  in various proportions (ranging from 1–10 mol %) to  $\text{YBa}_2\text{Cu}_3\text{O}_7$  are reported. The oxides  $\text{ZnO}$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{SiO}_2$  are the usual well-known sintering aids employed in the fabrication of oxide ceramics, which will improve the grain structure.  $\text{CuO}$  and  $\text{Y}_2\text{O}_3$  are chosen in the present study because they form one of the components of the high  $T_c$  '123' phase. Preliminary studies by other workers have shown that the stability and  $T_c$  of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  can be improved by  $\text{CuO}$  addition during processing (Subba Rao *et al* 1987b; Umarji and Nanjundaswamy 1987).

## 2. Experimental

### 2.1 Bulk synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and additive compositions

Pure  $\text{YBa}_2\text{Cu}_3\text{O}_7$  in 250–300 g batches was synthesized by the high temperature solid state reaction of the constituent oxides and carbonates in stoichiometric proportions. The purity and source are:  $\text{Y}_2\text{O}_3$  (99.99%; Indian Rare Earths Ltd., Kerala);  $\text{BaCO}_3$  [99.5%; Glaxo Laboratories (India) Ltd., Bombay];  $\text{CuO}$  [99.9%; prepared from copper metal rod/powder (99.9%; Loba-Chemie IndoAustralanal Co., Bombay) by dissolution in AR  $\text{HNO}_3$  and decomposition of the nitrate above  $800^\circ\text{C}$  in air]. The starting materials were thoroughly mixed in a planetary agate ball mill (Fritsch, W. Germany) for one hour and the mixture calcined in air at  $950^\circ\text{C}$  for 24 h and cooled. The calcined powder was reground and pressed into lugs (4 cm dia; 1–2 cm thick containing about 50–75 g of material) and heated in air again for 24 h at  $950^\circ\text{C}$ . The lugs, which were black in colour at this stage, were then crushed and ground to fine powder and used as the raw material for additive preparations. No oxygen treatment was carried out at this stage.

Ten gram batches of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , along with the required amount of single additives, each corresponding to 1–10 mol% of  $\text{CuO}$  (99.9%),  $\text{Y}_2\text{O}_3$  (99.99%),  $\text{SiO}_2$  (99.9% BDH, chromatographic grade),  $\text{Bi}_2\text{O}_3$  (99.8%; Alfa Ventron, USA) and  $\text{ZnO}$  (99.0%; Loba) were thoroughly mixed using an agate mortar and pestle, pressed into pellets (8 mm or 12 mm dia; 1–2 mm thick using a WC-lined stainless steel die and plungers and pressure of 3–4 t) and heated at  $930$ – $950^\circ\text{C}$  for 24 h. The grinding, heating and cooling were repeated. The pellets were then oxygen-treated at  $900^\circ\text{C}$  in a tubular furnace for 24 h and subsequently at  $600^\circ\text{C}$  for an additional 24 h and then slowly cooled to room temperature by furnace shut-off maintaining the oxygen flow throughout the experiment.

### 2.2 Characterization and physical studies

The additive-containing phases along with the control sample (with no additive) were characterized by powder X-ray diffraction (Philips unit;  $\text{Cu K}_\alpha$ -radiation, Ni-filter; 35 kV; 20 mA) and bulk density. Superconducting behaviour was examined by the 'coil test' (previously calibrated with  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ; details are described in Varadaraju *et al* 1989) and by the four-probe dc electrical resistivity as a function of temperature. The resistivity apparatus shown in figure 1 is a modified version originally used by Janaki (1985). The measurement is based on the van der Pauw's method modified by Montgomery (1971). Liquid  $\text{N}_2$  bath was used as the coolant to obtain temperatures in the range 80–300 K. Ultrasonically impregnated indium metal contacts were used for soldering fine copper wire leads on pellets of 8 mm dia and 1–2 mm thickness. Temperatures were measured with a chromel–alumel thermocouple placed very near to the sample and are accurate to  $\pm 1$  K. Voltage drop across the sample, through which a dc current of 15–50 mA was passed, was measured by a nanovoltmeter (Keithley, USA, model 181).

The superconducting transition onset temperature ( $T_c^{\text{onset}}$ ) was taken as the temperature at which there is significant departure from the linear variation of the high temperature region of the resistivity ( $\rho$ ) vs. temperature ( $T$ ) plot.  $T_c^0$  is the temperature at and below which the  $\rho = 0$  as shown by zero voltage drop in the

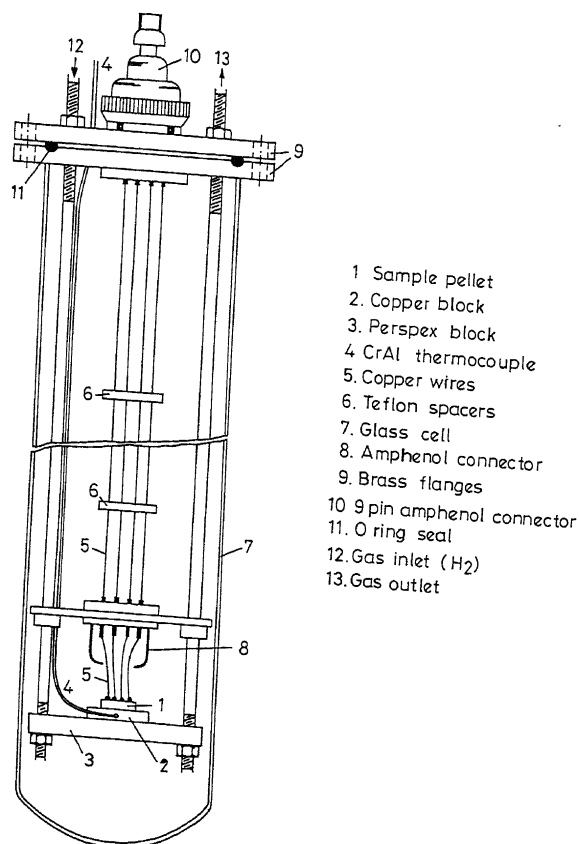


Figure 1. Schematic of four-probe d.c. electrical resistivity apparatus (range 80–300 K).

nanovoltmeter ( $< \pm 10$  nV thermal noise; also, when the polarity of the current input to the sample is changed there will be no corresponding reversal of sign of voltage in nanovoltmeter reading) for varying amounts of current passed through the sample.  $\Delta T_c$  is the width of the superconductivity transition, corresponding to the 90 and 10% drop in  $\rho$  value.

Scanning electron microscope (SEM; Cambridge Stereoscan, UK, model 180) was employed to study the surface morphology of the compounds. Both polished and etched (0.1 N HCl; 20 s) samples were examined.

### 3. Results and discussion

#### 3.1 Stability and structure

All the single additive compounds and control samples are black in colour and well-crystalline. The samples, in pellet form, are stable towards exposure to air and moisture and did not show degradation for at least 3–4 months, under ordinary conditions. However, they are usually stored in a desiccator to avoid exposure to high humidity conditions. The stability, crystallinity and phase purity of the

presently synthesised samples is ascribed to the preparative conditions employed including oxygen treatment for prolonged periods of time. The bulk density of pellets of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  alone and with the oxide additives ranges from 5.0–5.6 g/cc corresponding to 70–75% theoretical X-ray density. Oxygen estimation was not done specifically for the additive-containing  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , but from previous experiments on control samples, prepared under identical conditions, the  $\delta$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  was in the range  $0.10 \pm 0.05$ , and this corresponds to well-oxygenated samples. This is also corroborated by the powder X-ray diffraction (XRD) and superconductivity data.

XRD data on the control sample and all the additive-containing samples indicated orthorhombic perovskite structure corresponding to the '123' phase. The values of lattice parameters obtained for the control sample (viz.  $a = 3.82$ ;  $b = 3.88$ ;  $c = 11.67 \text{ \AA}$ ) are in excellent agreement with those reported in the literature. In addition to the lines due to the '123' phase, lines due to impurity phases were seen in the following additive-containing  $\text{YBa}_2\text{Cu}_3\text{O}_7$ : (i) CuO peaks for the CuO-additive; composition,  $> 2 \text{ mol\%}$  (figure 2a); (ii)  $\text{Y}_2\text{BaCuO}_5$  peaks for the  $\text{Y}_2\text{O}_3$ -additive; composition  $> 3 \text{ mol\%}$ ; (iii)  $\text{BaBiO}_3$  peaks for  $\text{Bi}_2\text{O}_3$ -additive; composition  $> 4 \text{ mol\%}$  (figure 2b). No lines due to  $\text{SiO}_2$  or ZnO or  $\text{BaSiO}_3$  or  $\text{BaZnO}_2$  were seen for  $\text{SiO}_2$  and ZnO additive samples. These observations indicate that: (i) The solid solubility of CuO and  $\text{Y}_2\text{O}_3$  in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is very small; (ii)  $\text{BaBiO}_3$ , which is a perovskite (Sleight *et al* 1975), formation is energetically more favourable under the high temperature conditions and can extract Ba from  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (leaving  $\text{Y}_2\text{BaCuO}_5$  or CuO impurities in addition to the '123' phase) and thus solid solubility of Bi in '123' is small; (iii)  $\text{SiO}_2$  may form a glassy phase which is amorphous to XRD but no solid solubility of Si occurs to form a phase of the form,  $\text{YBa}_2\text{Cu}_{3-x}\text{Si}_x\text{O}_7$ ; (iv) on the other hand, Zn can be doped into '123' partly

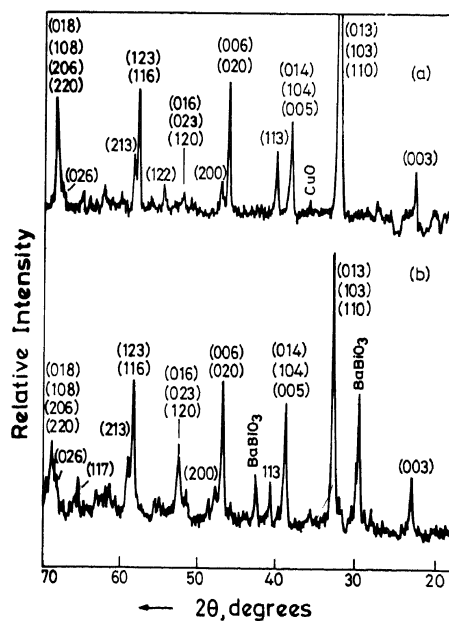


Figure 2. XRD patterns of '123' with (a) CuO–5 mol% and (b)  $\text{Bi}_2\text{O}_3$ –4 mol%.

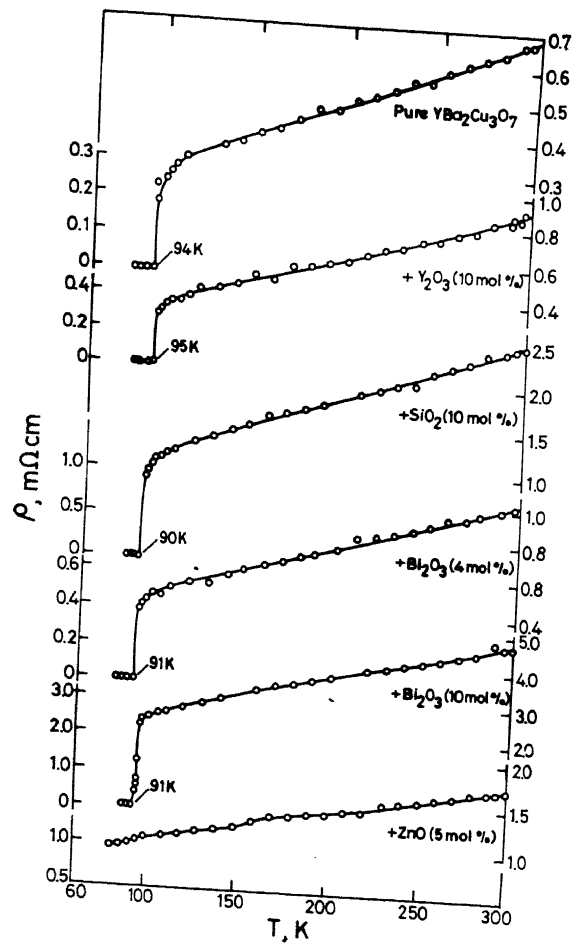
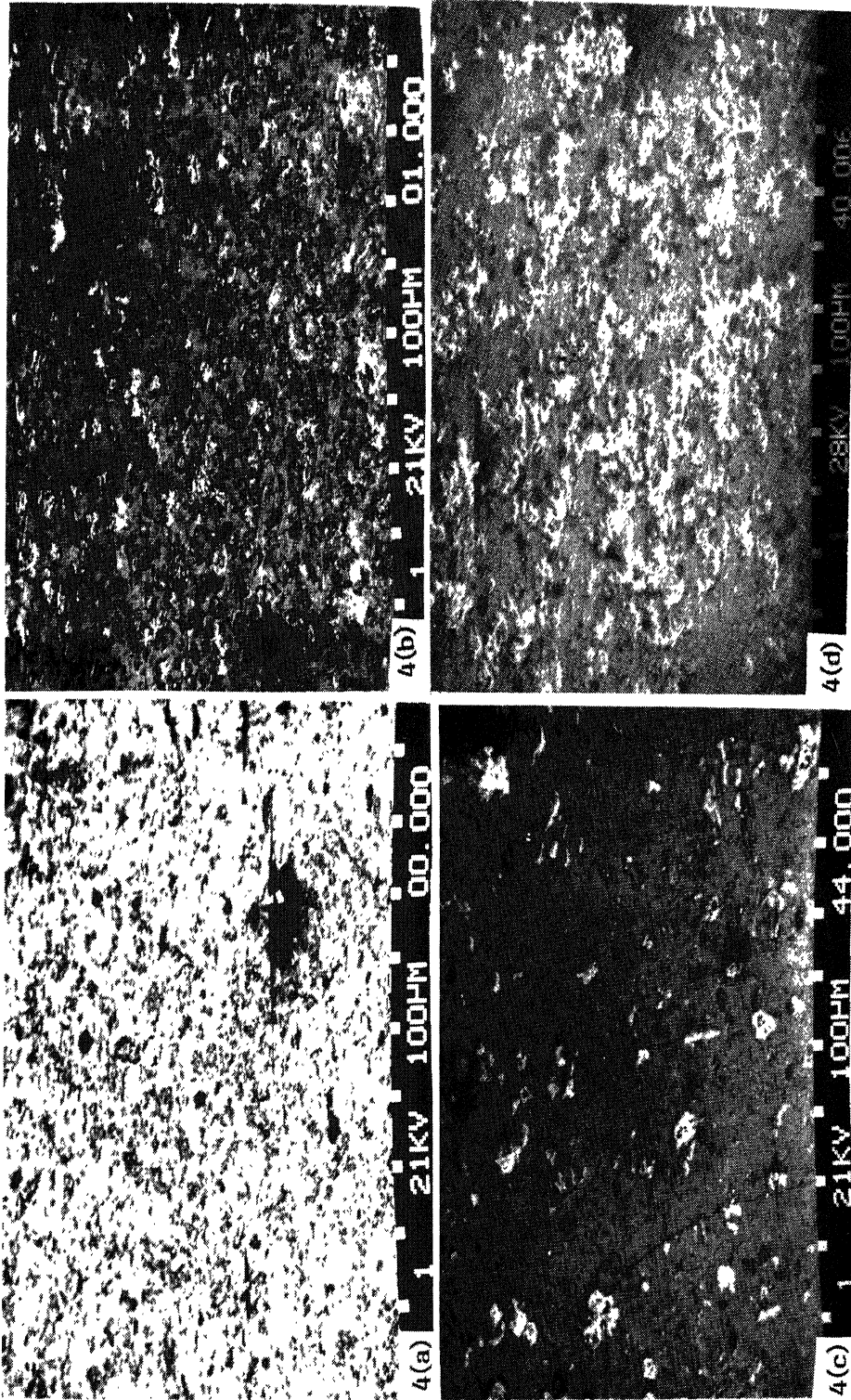


Figure 3. Resistivity versus temperature plots of pure and additive ( $\text{Y}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{ZnO}$ )-containing  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , showing superconductivity transitions ( $\text{ZnO}$  exception).

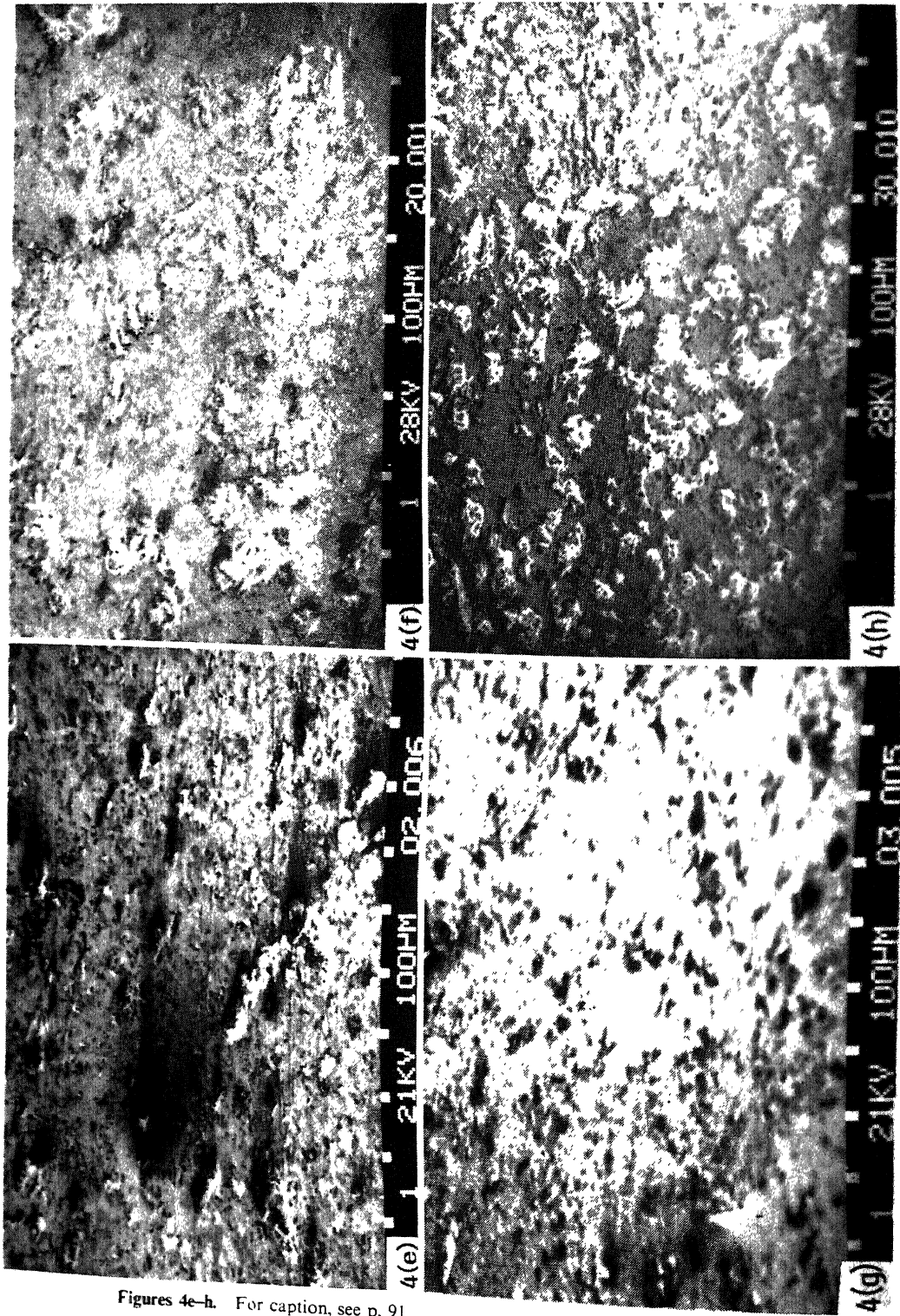
Table 1. Resistivity and superconductivity data on pure and oxide-additive  $\text{YBa}_2\text{Cu}_3\text{O}_7$  phases.

Additives (mol%)	$\text{YBa}_2\text{Cu}_3\text{O}_7$	$T_c$ onset (K)	$T_c^0$ (K)	$\Delta T_c$ (K)	$\rho_{300\text{K}}$ ( $\text{m}\Omega \text{ cm}$ )	$\rho_{110\text{K}}$ ( $\text{m}\Omega \text{ cm}$ )	$(1/\rho_{300\text{K}})(d\rho/dT)$ (range 140–240 K)
Pure		105	94	3	0.69	0.21	2.9
$\text{Y}_2\text{O}_3$	(5)	110	94	5	1.23	0.63	2.6
	(10)	105	95	4	0.90	0.36	3.11
$\text{SiO}_2$	(5)	110	94	7.5	1.28	0.61	2.66
	(10)	115	90	12	2.50	1.22	2.52
$\text{Bi}_2\text{O}_3$	(4)	96	90	2	1.03	0.50	2.72
	(10)	100	91	3	4.80	2.60	2.4
$\text{CuO}$	(5)	100	92	2	0.74	0.30	3.11
$\text{ZnO}$	(5)	—	—	—	1.73	1.10	1.97



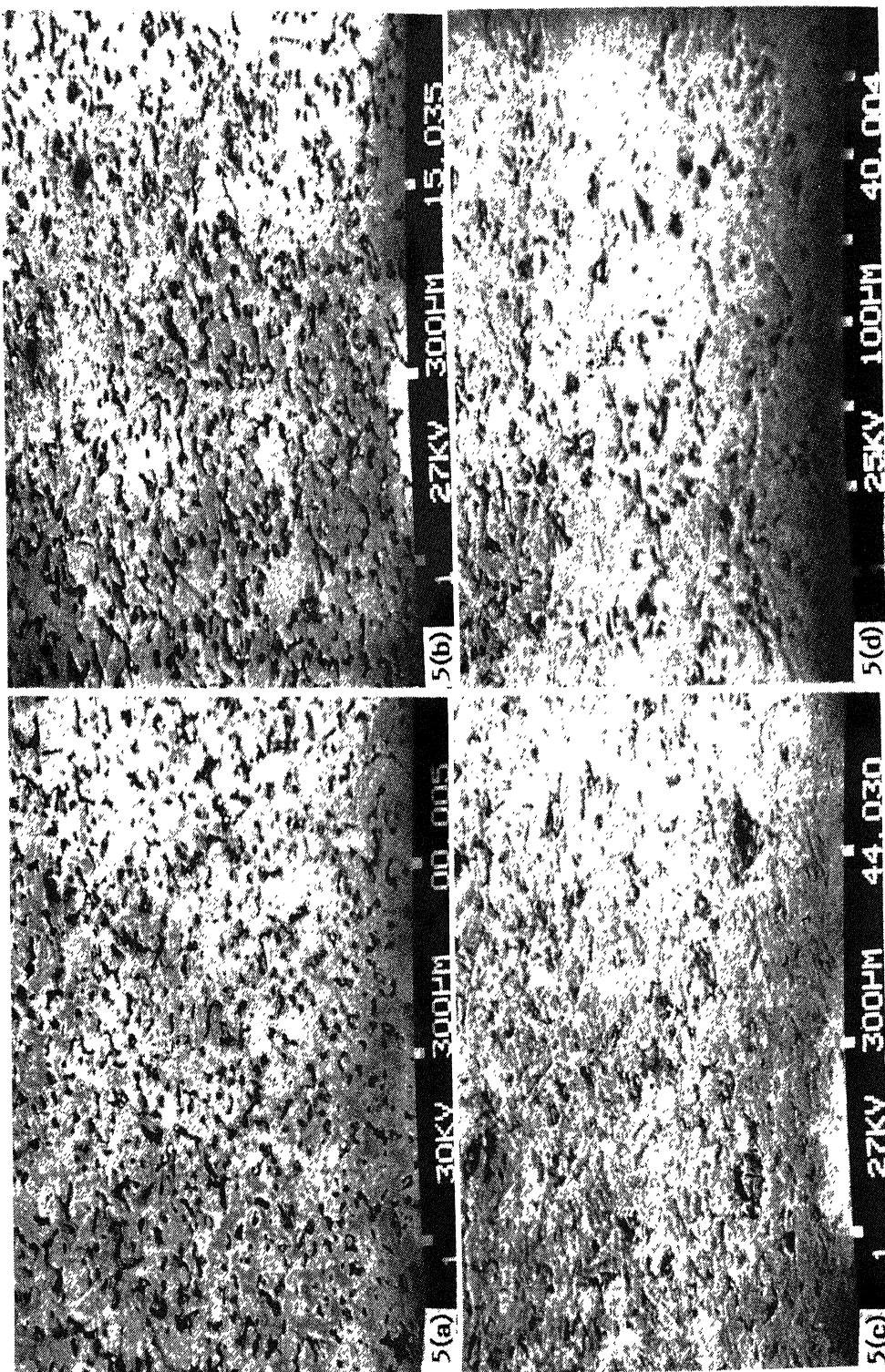
Figures 4a-d. For caption, see p. 91.



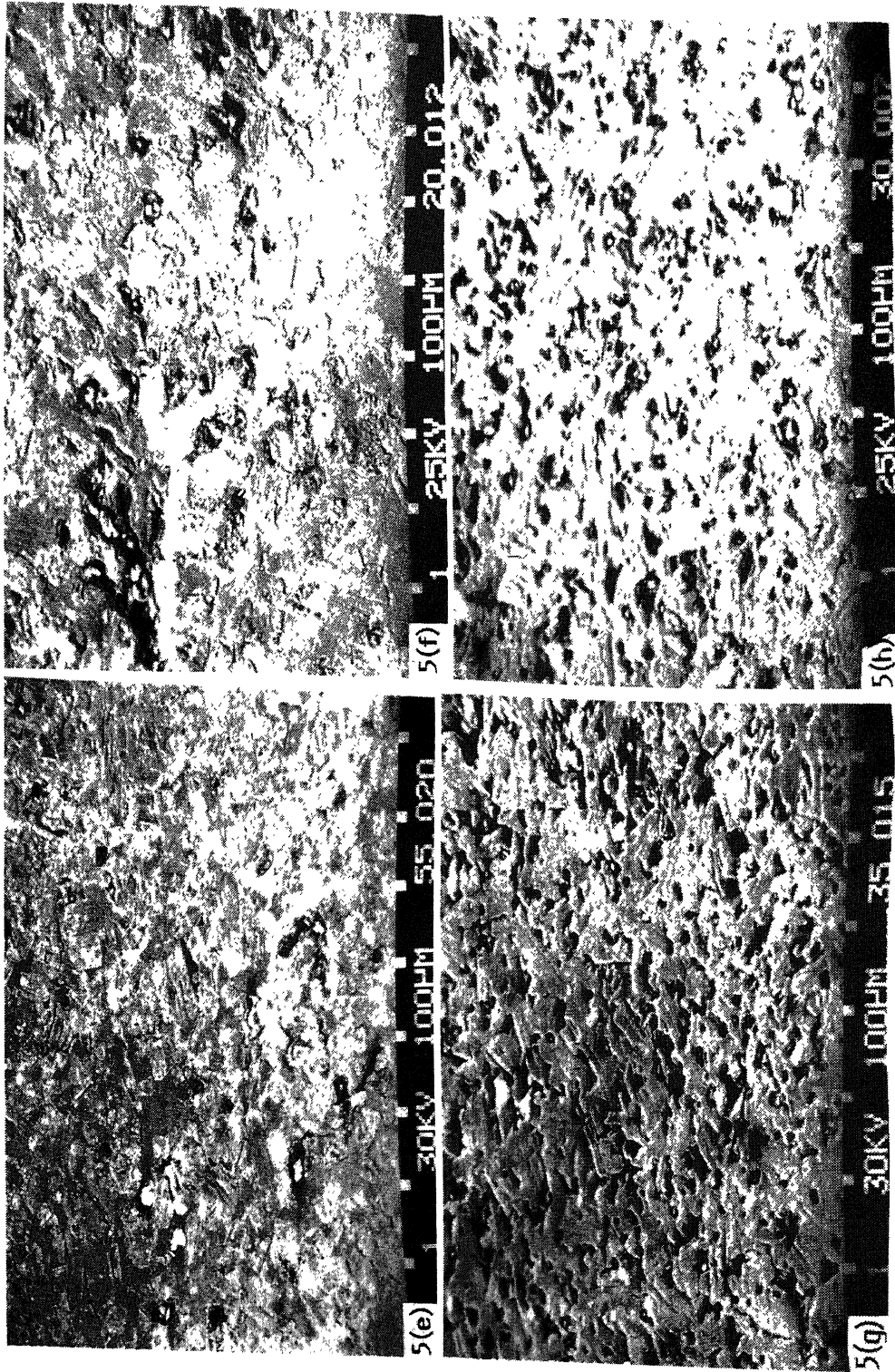


Figures 4e-h. For caption, see p. 91.





Figures 5a-d. For caption, see p. 91.



Figures 5e-f. For caption, see p. 91.

replacing copper and thereby produce changes in the physical properties. The latter finding is consistent with the observations by others in the literature (Dunlap *et al* 1987; Xiao *et al* 1987; Krishnan *et al* 1988; Narasimha Rao *et al* 1988). However, there are no significant changes in the lattice parameters of the parent  $\text{YBa}_2\text{Cu}_3\text{O}_7$  in all the above cases. Though Jarvinen *et al* (1988) did not specifically mention the formation of a  $\text{BaBiO}_3$  phase in their experiments on the  $\text{Bi}_2\text{O}_3$  additive to  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , since it is stated that the solid solubility is small with  $\text{Bi}_2\text{O}_3$ , it can be safely presumed that  $\text{BaBiO}_3$  existed as an impurity in their phases.

The coil (quick) test for superconductivity has been performed on all the additive containing compounds in addition to the control (pure)  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . Since the samples (and the coils) are dipped in liquid  $\text{N}_2$ , no temperature variation is possible but the test indicates whether the compounds are superconducting or not at and above 77 K. Tests have shown that with the exception of ZnO-containing phase, all the other additive compounds including the control  $\text{YBa}_2\text{Cu}_3\text{O}_7$  are superconducting at and above 77 K. This reiterates the statement made earlier that the solid solubility of the additives CuO,  $\text{Y}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{SiO}_2$  in the parent  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is small and that the basic features of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  are retained. However, it was noted that for the same quantity of the samples tested ( $\sim 100$ – $200$  mg) by the coil test, the superconductivity signal strength was relatively small in 10 mol%  $\text{Bi}_2\text{O}_3$  and  $\text{SiO}_2$  containing samples, as compared to the control sample of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . The fact that the 5 mol% ZnO containing  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is not superconducting at 77 K indicates that either  $T_c$  is below 77 K or is destroyed completely. Earlier studies have shown that when Cu is substituted by 5 mol% Zn, the  $T_c$  is lowered below 60 K (Dunlap *et al* 1987; Xiao *et al* 1987; Krishnan *et al* 1989; Narasimha Rao *et al* 1988).

To check on the stability of the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and additive containing phases, the coil test was carried out, on samples that have been stored without any precautions, after a month. The superconducting signal strength was unchanged in the control and  $\text{Y}_2\text{O}_3$ -containing (in the range 1–10%)  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , while there was only marginal decrease (by about 5–10%) in the CuO-,  $\text{Bi}_2\text{O}_3$ - and  $\text{SiO}_2$ -containing material.

Four-probe d.c. electrical resistivity ( $\rho$ ) data of pure and additive-containing  $\text{YBa}_2\text{Cu}_3\text{O}_7$  in the range 85–300 K indicated metallic behaviour with  $\rho_{300\text{K}}$  in the range 0.3–2.0 milliohm cm. The  $\rho$ -T data in the range 140–300 K can be fitted into an equation of the form  $\rho = A + BT$  where  $A$  and  $B$  are constants. Transition to a superconducting state was observed in all the phases except where ZnO was the additive. The latter phase remained metallic in the range 83–300 K (figure 3 and table 1). The  $T_c^0$  values are in the range  $92 \pm 2$  in all the compounds indicating

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**Figure 4.** Surface morphology by SEM of polished specimens of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and with additives ( $100\times$ ). (a) Pure  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ; (b) CuO–5 mol%; (c)  $\text{Bi}_2\text{O}_3$ –4 mol%; (d)  $\text{Bi}_2\text{O}_3$ –10 mol%; (e)  $\text{SiO}_2$ –5 mol%; (f)  $\text{SiO}_2$ –10 mol%; (g)  $\text{Y}_2\text{O}_3$ –5 mol%; (h)  $\text{Y}_2\text{O}_3$ –10 mol%.

**Figure 5.** Surface morphology by SEM of polished and etched (0.1 N HCl for 20 s) specimens of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and with additives ( $100\times$ ). (a) Pure  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ; (b) CuO–5 mol%; (c)  $\text{Bi}_2\text{O}_3$ –4 mol%; (d)  $\text{Bi}_2\text{O}_3$ –10 mol%; (e) ZnO–5 mol%; (f)  $\text{SiO}_2$ –10 mol%; (g)  $\text{Y}_2\text{O}_3$ –5 mol%; (h)  $\text{Y}_2\text{O}_3$ –10 mol%.

negligible effect of the oxide additives on the inherent superconducting behaviour of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . It is of specific interest to note that 10%  $\text{SiO}_2$  addition does not affect the  $T_c$ . It is worthwhile studying higher concentrations of  $\text{SiO}_2$  to see whether a glass-ceramic composition can be obtained which still retains the high  $T_c$  behaviour.

SEM studies on pure and additive-containing  $\text{YBa}_2\text{Cu}_3\text{O}_7$  have been made on polished, and polished and etched samples. Etching by 0.1 N HCl gave rise to a white layer (not easily seen with the naked eye but visible on SEM) indicating, perhaps, the formation of a  $\text{Y}_2\text{O}_3$  layer. However, as can be seen in figures 4 and 5, the surface morphology can easily be discerned.  $\text{Bi}_2\text{O}_3$  and  $\text{SiO}_2$  additives improve the grain size and their interconnectivity compared to the ones containing CuO or  $\text{Y}_2\text{O}_3$ . Increasing the  $\text{Bi}_2\text{O}_3$  content has a beneficial effect but as is known from XRD, higher concentrations yield an increasing second phase ( $\text{BaBiO}_3$ ). Perhaps, it is worthwhile studying the effect of  $\text{BaBiO}_3$  addition to  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

#### 4. Summary and conclusions

Effect of five oxide additives on the superconductivity behaviour of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  has been studied. Except for ZnO which produces a decrease in  $T_c$  (to below 77 K), the oxides CuO,  $\text{Y}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{SiO}_2$ , up to a concentration of 10 mol%, do not affect the high temperature superconductivity of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . Solid solubility of the above four oxides in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is limited (very small) as indicated by the X-ray data where impurity phases are formed with an increase in the content of the oxide additive.  $\text{Bi}_2\text{O}_3$  and  $\text{SiO}_2$  act as good sintering aids to  $\text{YBa}_2\text{Cu}_3\text{O}_7$  giving rise to larger grain size and better interconnectivity of the grains. The latter should aid in increasing the critical current density ( $J_c$ ) of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  in bulk form.

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