Composition dependence of superconductivity in $YBa_2(Cu_{3-x}Al_x)O_y$

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Eleven different compositions in the system $YBa_2(Cu_{3-x}Al_x)O_y (x = 0\text{–}0.3)$ have been synthesized and characterized by electrical resistivity measurements, powder X-ray diffraction, and scanning electron microscopy. The superconducting transition temperature, T_c (onset), was almost unaffected by the presence of alumina due to its limited solubility in $YBa_2Cu_3O_{7-x}$. However, $T_c(R = 0)$ gradually decreased and the resistive tails became longer with increasing Al_2O_3 concentration. This was probably due to formation of $BaAl_2O_4$ and other impurity phases from chemical decomposition of the superconducting phase by reaction with Al_2O_3.

1. Introduction

Since the discovery of high-temperature superconductivity with an onset temperature of ~93 K in the Y–Ba–Cu–O system, a number of reports have appeared studying the effects of substitution by various ions directed at the rare earth [1, 2], alkaline earth [1, 3], copper [1, 4], as well as oxygen [5, 6] sites. In our earlier studies [7, 8] on $YBa_2Cu_3O_{7-\delta}$ thick films screen printed on alumina substrates, it was found that the superconducting transition temperatures, T_c, of the films corresponding to zero resistance were much lower than that of the bulk HTS. It was suggested that this may be caused by chemical interaction of the film and the alumina substrate at the interface followed by diffusion of alumina into the film during the high-temperature sintering step. In order to verify this concept, the present investigation was undertaken where Y–Ba–Cu–O HTS materials doped with gradually increasing concentrations of alumina were prepared and characterized for their superconducting and other properties.

The objective of this study was to carry out a systematic investigation of the effect of the substitution of aluminium for copper in $YBa_2Cu_3O_{7-\delta}$ on its superconducting properties. Samples with the nominal composition $YBa_2(Cu_{3-x}Al_x)O_y$, where x was varied from 0–0.3, were synthesized by the solid-state reaction method. The resulting materials were examined by electrical resistivity measurements as a function of temperature, X-ray diffraction (XRD) and microscopy.

2. Experimental procedure

The starting materials used were Y_2O_3 (Molycorp 99.99%), $BaCO_3$ (Alfa, technical grade), CuO (Alfa, ACS grade), and Al_2O_3 (Baikowski, high-purity grade). $YBa_2Cu_3O_{7-\delta}$ powder was synthesized by the solid-state reaction method. Appropriate quantities of the powders were slurry mixed in acetone using a mortar and pestle, oven dried at ~110 °C for 2 h, and calcined at ~920 °C for 16–18 h in air in an alumina crucible. The mixture was cooled slowly, pulverized, and recalcined for 16–18 h at 920 °C. The cycle of calcining, cooling and grinding was repeated two more times resulting in a dark black powder. A master composition containing aluminium, $YBa_2Cu_2Al_1O_z$, was synthesized in a similar manner.

Aluminium-doped powders of eleven different compositions, $YBa_2(Cu_{3-x}Al_x)O_y$ (x = 0.0, 0.01, 0.02, 0.05, 0.08, 0.10, 0.12, 0.15, 0.20, 0.25, and 0.30), were prepared by mixing calculated amounts of $YBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_2Al_1O_z$ powders with a mortar and pestle, calcining for 16–18 h at ~920 °C in air in alumina crucibles, and then furnace cooling to room temperature. The resulting mixtures were reground to fine powders, uniaxially dry-pressed into ~$2.5 \times 0.5 \times 0.7$ cm^3 rectangular bars, and cold isostatically pressed at ~60 000 p.s.i (10^3 p.s.i. = 6.89 N mm^{-2}). The bars were heated at 5 °C min^{-1} to 945 °C, sintered for 10 h, cooled at ~3 °C min^{-1} to 450 °C and held for 10 h, and finally furnace cooled to room temperature. The entire sintering and annealing cycle was carried out in flowing oxygen.

A part of each sintered bar was ground to powder. Powder XRD patterns were recorded in the 2θ range 10°–90° at room temperature using a step-scan procedure (0.03°/2θ step, count time 0.4 s) on a Philips ADP-3600 automated diffractometer equipped with a crystal monochromator employing CuK_α radiation.

Electrical resistivity measurements as a function of temperature were performed in the standard four-probe configuration. Silver paint was used to attach the leads, and the current density used was ~0.1 A cm^{-2}. Fracture and polished surfaces of the specimens were observed in a Jeol JSM-840A scanning electron microscope (SEM). X-ray dot mapping of various elements was carried out using a Kevex Delta class analyser.

3. Results and discussion

Although resistivity data only around T_c will be reported, the resistivity of all samples was measured from room temperature to temperatures below T_c. The temperature dependence of electrical resistivity normalized to its value at 100 K for some typical compositions is shown in Fig. 1. All the samples exhibited metallic behaviour in the normal state as seen from the R versus T curves in Fig. 1. All the compositions were superconducting. The values of transition temperature, T_c (onset), T_c ($R = 0$), and the transition width (10%–90%), ΔT_c, for various compositions are listed in Table I. Variations in T_c and ΔT_c as a function of x are presented in Figs 2 and 3, respectively. The undoped superconductor has a T_c (onset) of 91 K, T_c ($R = 0$) of 89.5 K, and ΔT_c of 1.4 K. The T_c (onset) of the doped samples is $\sim 91 \pm 0.8$ indicating no effect of aluminium substitution as borne out by statistical analysis. However, T_c ($R = 0$) systematically decreases with increase in aluminium concentration (to 60.9 K for $x = 0.3$). Also, the resistive tails become larger and the transition width gradually broadens with increase in x (Fig. 3). This is probably due to an increase in the fraction of the nonsuperconducting phases. Our T_c ($R = 0$) values for $x = 0.05$ and 0.10 compositions are in good agreement with the results of Siegrist *et al.* [9]

The powder XRD spectra of some typical compositions are given in Fig. 4. An analysis of the peak positions and intensities shows that the parent undoped compound has an orthorhombic structure with lattice parameters, $a = 0.3827$ nm $b = 0.3885$ nm, and $c = 1.1679$ nm, in good agreement with the values given in the literature [10]. The aluminium-doped materials preserve the basic orthorhombic structure, though some modifications in the diffraction patterns

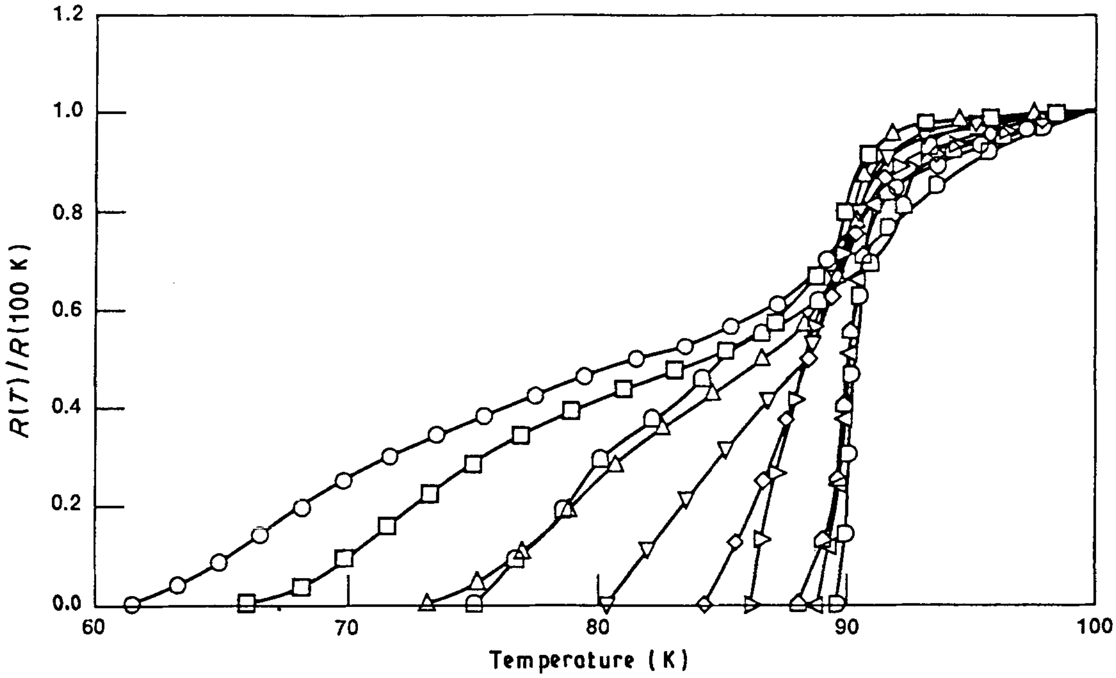

Figure 1 Temperature dependence of normalized resistance of $YBa_2(Cu_{3-x}Al_x)O_y$ superconductor doped with various Al^{3+} concentrations. x = (○) 0.30, (□) 0.25, (△) 0.20, (◻) 0.15, (▽) 0.12, (◇) 0.10, (▷) 0.08, (◻) 0.05, (◁) 0.02, (◻) 0.01, 00

TABLE I Lattice parameters, transition temperatures, and transition widths of superconducting $YBa_2(Cu_{3-x}Al_x)O_y$ compounds doped with various Al^{3+} concentrations

X	Lattice parameters			Transition temp.		ΔT_c (10%–90%) (K)
	a (nm)	b (nm)	c (nm)	T_c (onset) (K)	T_c ($R = 0$) (K)	
0.0	0.3827	0.3885	1.1679	91.0	89.5	1.4
0.01	0.3824	0.3887	1.167	91.0	89.5	1.8
0.02	0.3837	0.3892	1.168	91.2	88.7	2.0
0.05	0.3828	0.388	1.166	90.7	88.2	4.0
0.08	0.3839	0.388	1.169	90.8	86.2	4.1
0.10	0.3833	0.3862	1.166	90.2	84.3	5.1
0.12	0.3837	0.3882	1.1673	90.2	80.2	8.6
0.15	0.3852	0.3869	1.1676	93.2	73.9	16
0.20	0.3829	0.3877	1.167	91.3	73.0	14
0.25	0.386	0.388	1.164	91.0	65.8	20.4
0.30	3.83	3.90	1.166	91.8	60.9	25.6

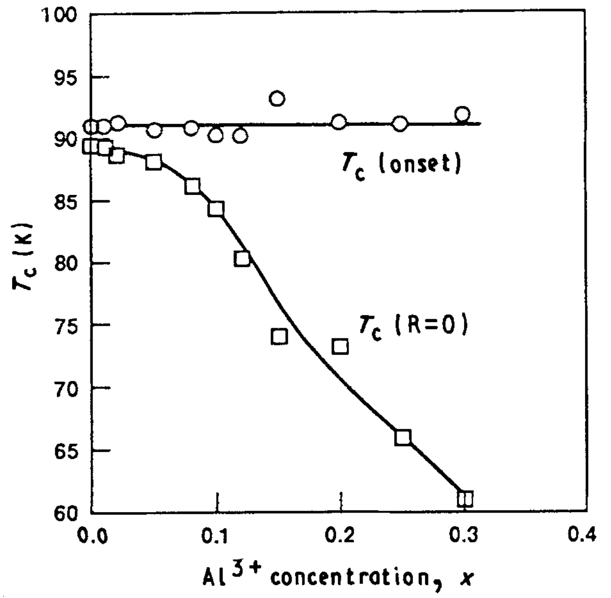

Figure 2 Variations in transition temperatures, T_c (onset) and T_c ($R = 0$), of $YBa_2(Cu_{3-x}Al_x)O_y$ superconductor as a function of Al^{3+} dopant concentration.

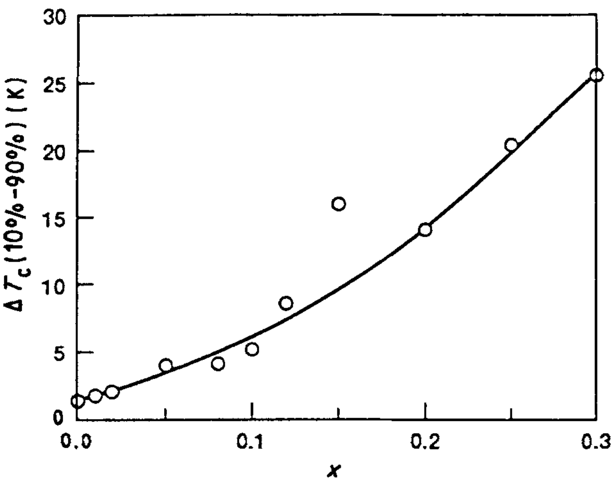

Figure 3 Influence of Al^{3+} dopant concentration on the transition width of $YBa_2(Cu_{3-x}Al_x)O_y$ superconductor.

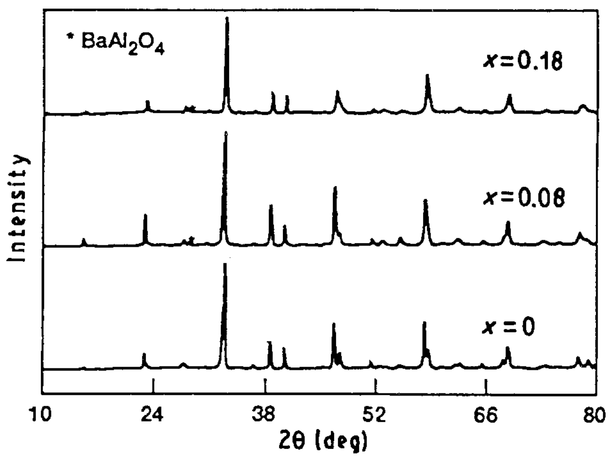

Figure 4 Typical powder X-ray diffraction spectra of $YBa_2(Cu_{3-x}Al_x)O_y$ superconducting compounds of three different compositions.

are observed. Values of lattice parameters calculated on the basis of an orthorhombic unit cell for various compositions are given in Table I. Diffraction peaks for $BaAl_2O_4$ are also present in XRD patterns of samples having ~3% or higher substitution of aluminium for copper ($x \geqslant 0.08$). The following chemical reaction has been proposed [11] between $YBa_2Cu_3O_7$ and Al_2O_3 in the sintered powder form at an annealing temperature of 945 °C in oxygen

$$4YBa_2Cu_3O_7 + 6Al_2O_3 \rightarrow$$

$$2Y_2BaCuO_5 + 10CuO + 6BaAl_2O_4 + O_2 \quad (1)$$

However, formation of Y_2BaCuO_5 and CuO phases was not detected by XRD in the present study.

Scanning electron micrographs taken from the polished and fracture surfaces of HTS specimens of different compositions are presented in Figs 5 and 6, respectively. Pores, a few micrometres in size, are present indicating the samples are not fully dense.

The SEM images and the X-ray dot maps of various constituent elements taken on the polished surfaces of the HTS samples with $x = 0.1$ and 0.2 are presented in Figs 7 and 8, respectively. The distribution of aluminium as well as of all other elements is seen to be uniform throughout the specimen (Fig. 7) with $x = 0.1$. However, in the HTS with higher aluminium content, $x = 0.2$ (Fig. 8), a large grain rich in copper but deficient in barium and yttrium is present. A few small particles rich in aluminium or yttrium are also detected.

Studies of the effects of various substituents on superconductivity of $YBa_2Cu_3O_7$ have been reported [1–6]. Most of the elements, other than rare earths, which substitute into the cuprate perovskite lattice reduce the superconducting onset temperature. In the present study the T_c (onset) was almost unaffected by the substitution of copper by aluminium. This is in agreement with the findings of Yan *et al.* [1] that the presence of alumina did not have any significant effect on the T_c of $YBa_2Cu_3O_7$. However, from XRD, the heavily doped materials showed [1] the presence of appreciable amounts of second phases. The material

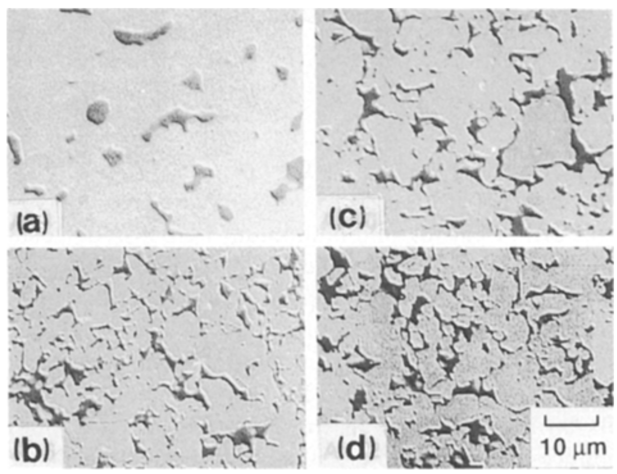

Figure 5 Scanning electron micrographs taken from the polished surfaces of $YBa_2(Cu_{3-x}Al_x)O_y$ superconductors having different aluminium contents: (a) $x = 0.05$, Al-4, (b) $x = 0.1$, Al-6; (c) $x = 0.2$, Al-10; and (d) $x = 0.3$, Al-12.

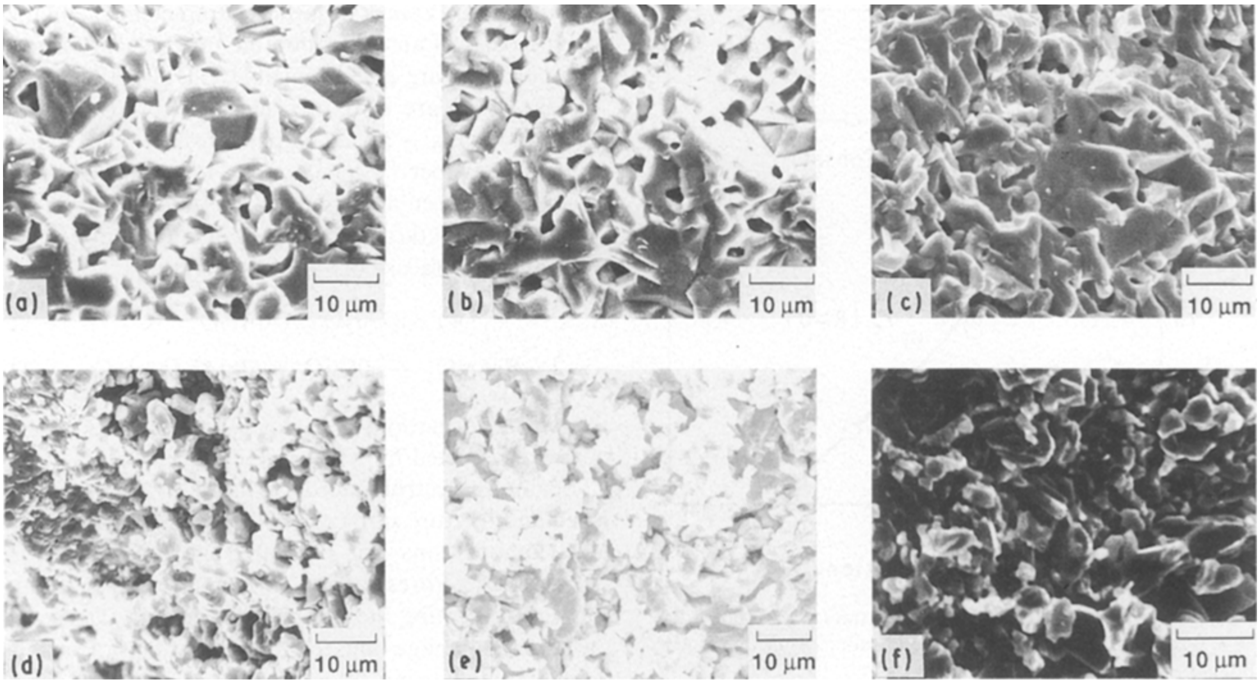

Figure 6 Scanning electron micrographs of fracture surfaces of $YBa_2(Cu_{3-x}Al_x)O_y$ compounds of different compositions. (a) $x = 0.01$, (b) $x = 0.05$, (c) $x = 0.08$, (d) $x = 0.10$, (e) $x = 0.12$, (f) $x = 0.30$.

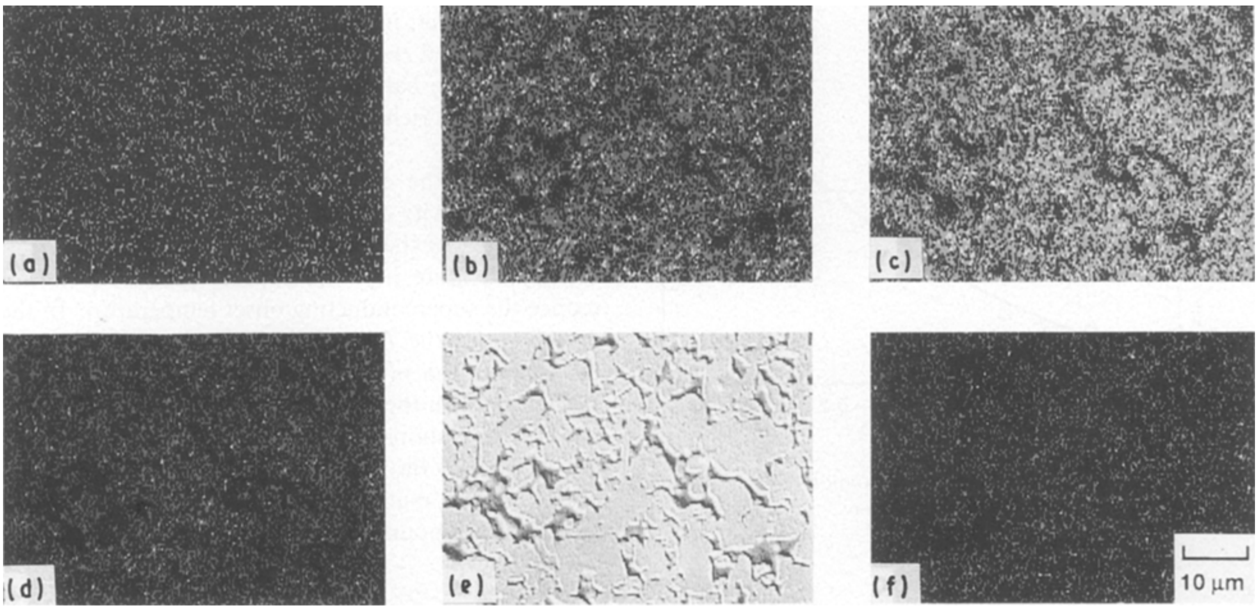

Figure 7 SEM image and X-ray dot maps of different constituent elements taken from the polished surface of the $YBa_2Cu_{2.9}Al_{0.1}O_y$ superconductor. (a) Al, (b) Ba, (c) Y, (d) Cu, (e) IM, (f) O.

doped with 23.1 mol % $AlO_{1.5}$ ($x = 0.273$) was found to contain 4% $BaAl_2O_4$. Grains having high concentrations of barium and aluminium were also detected by SEM and EDAX. The amount of $BaAl_2O_4$ increased and another impurity phase, Y_2BaCuO_5, formed at higher concentrations of $AlO_{1.5}$. These results show that alumina doping does not affect the superconductivity of the $YBa_2Cu_3O_{7-\delta}$ phase due to its limited solubility in the HTS. However, it does induce decomposition of the superconducting phase by leaching out some components of the HTS. In another study [12], substitution of aluminum in $YBa_2Cu_3O_7$ ceramic samples was found to suppress T_c by ~ 6 K/at % and to shift the crystal symmetry from orthorhombic to tetragonal. The effects of aluminium doping on properties of single crystals of $YBa_2(Cu_{3-x}Al_x)O_7$ ($x = 0$–0.22) compositions have also been studied [9]. Aluminium substitutes for copper in the Cu–O chains only, whereas the CuO_2 planes remain unperturbed. The T_c, determined from d.c. diamagnetic susceptibility measurements, changed from 92 K for $x = 0.0$ to ~ 80 K for $x = 0.1$, and then dropped sharply for higher x. Single-phase polycrystalline ceramic samples could be prepared [9] for only low aluminium content.

In the case of polycrystalline $YBa_2(Cu_{3-x}Al_x)O_y$, it has been shown [9, 13, 14] that aluminium substitutes at the Cu–O_1 chain sites resulting in a slow decrease in

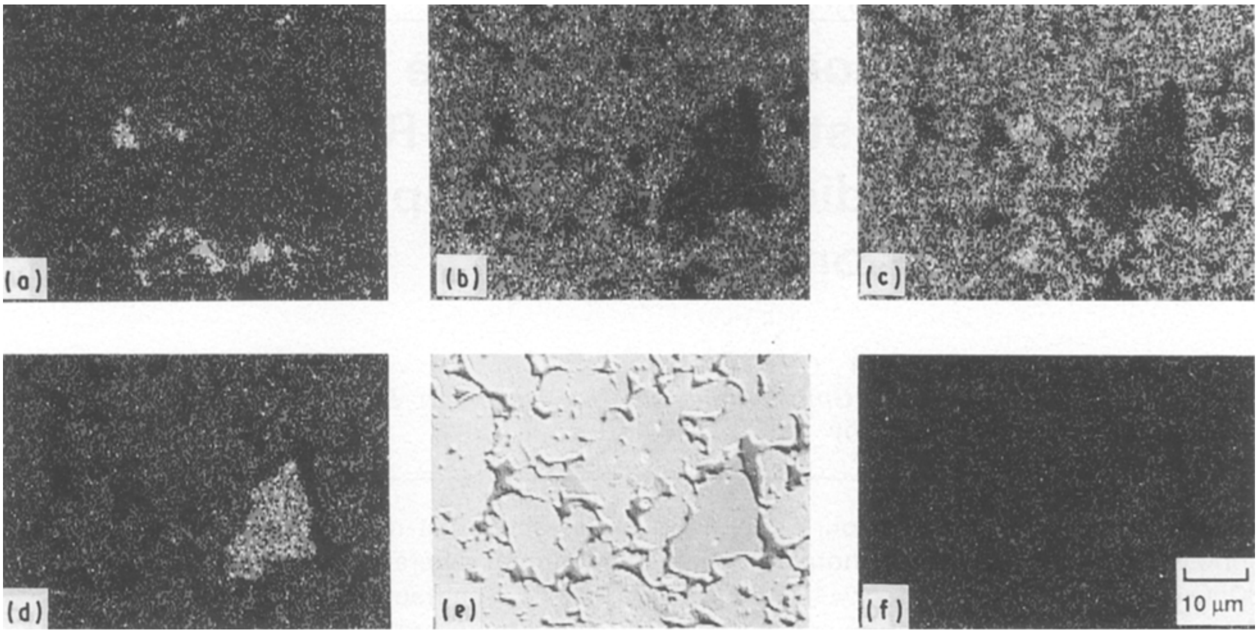

Figure 8 SEM image and X-ray dot maps of various elements taken from the polished surface of the $YBa_2Cu_{2.8}Al_{0.2}O_y$ superconductor. (a–f) as in Fig. 7.

T_c. Also the structure changes from orthorhombic to tetragonal for $x > 0.1$. For these materials it is known [13, 15] that doping at the Cu(2) site by ions such as Zn^{2+} and Ni^{2+}, is most effective in reducing the T_c, whereas doping at the Cu(I) sites by ions such as Al^{3+}, Ga^{3+}, Fe^{3+} and Co^{3+}, is most effective in promoting the orthogonal to tetragonal structure transformation. In these chemically complex materials, charge selectivity may control [15] the site selectivity.

4. Conclusion

Materials of nominal composition $YBa_2(Cu_{3-x}Al_x)O_y$ ($x =$ 0–0.3) have been prepared and characterized by electrical resistivity measurements, X-ray diffraction and microscopy. The temperature corresponding to the onset of superconducting transition was unaffected by the presence of alumina due to its limited solubility in the HTS phase. However, the resistive tails became longer and T_c ($R = 0$) decreased with increase in the dopant concentration probably due to the formation of $BaAl_2O_4$ and other impurity phases from chemical reaction between HTS and alumina.

$YBa_2Cu_3O_{7-\delta}$ reacts chemically with alumina. Interfacial diffusion barrier coatings need to be developed for successful use of alumina as a substrate material for HTS films in order to circumvent its chemical reaction with the $YBa_2Cu_3O_{7-\delta}$ superconductor.

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