Journal of Alloys and Compounds, 177 (1991) 279–284
JAL 0061

Structural and superconducting properties of $YBa_2Cu_{3-x}Al_xO_{6+\delta}$ $(0 \leqslant x \leqslant 0.20)$

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(Received June 17, 1991)

Abstract

A series of $YBa_2Cu_{3-x}Al_xO_{6+\delta}$ $(0 \leqslant x \leqslant 0.20)$ samples are prepared and their morphology and structural properties are investigated by scanning electron microscopy energy-dispersive X-ray analysis and X-ray diffraction techniques. Superconducting parameters are obtained from the a.c. magnetic susceptibility and critical current density measurements. Transformation to a tetragonal phase occurs for $x \geqslant 0.2$ and T_c decreases strongly relative to the orthorhombic phase. A few degrees decrease of T_c upon tetragonal phase transformation is consistent with the importance of Cu(2) planes for the superconductivity in these oxides.

1. Introduction

Trivalent iron, cobalt, aluminium and gallium and divalent nickel and zinc have been substituted on the copper sites in YBCO and the effect of substitution on the structure and superconductivity has been investigated intensively [1–6]. All the trivalent substitutions cause an orthorhombic-to-tetragonal phase transformation near 3–5% concentration. Unlike the oxygen-deficient tetragonal phase which is non-superconducting the substituted tetragonal phase has a T_c which remains above liquid nitrogen temperature and the depression of T_c is typically 2–5 K per atom per cent of the substitution. There are two inequivalent Cu(1) chain and Cu(2) plane sites in YBCO and the superconductivity is interpreted by the substitutional occupancy of Cu(1) or Cu(2) sites. Substitution of aluminium on yttrium sites shows a gradual change in the lattice parameters and T_c [7]. Neutron diffraction investigation of aluminium-substituted YBCO shows that aluminium occupies the Cu(1) chain sites [8]. Van Dover *et al.* [9] observed that a single crystal of composition $YBa_2Cu_{2.90}Al_{0.10}O_{6+\delta}$ where $\delta \approx 1$ with aluminium on the Cu(1) sites has a tetragonal phase with a superconducting transition of 84 K. A strong decrease in the upper critical field and normal state resistivity of the tetragonal phase compared with the orthorhombic phase

0925-8388/91/$3.50

was observed and this decrease was explained by a twofold change in the Fermi surface area of the tetragonal phase. The effects of aluminium substitution at the Cu(1) sites in the polycrystalline YBCO on the structure, microstructure, superconductivity, a.c. magnetic susceptibility and the critical current density are reported in the present paper.

2. Experimental details

A series of oxides of compositions $YBa_2Cu_{3-x}Al_xO_{6+\delta}$ $(0<x<0.20)$ were prepared by mixing and grinding the Y_2O_3, $BaCo_3$, CuO and $Al(NO_3)_3$ powders and calcining at 960 °C for 24 h. Pellets of about 3 mm thickness were pressed out of the calcined powder and sintered at 900 °C for 18 h and 500 °C for 5 h in flowing oxygen at atmospheric pressure and cooled to room temperature at a cooling rate of 1°C min^{-1}. The lattice parameters were calculated from the X-ray diffraction patterns taken on powdered samples at room temperature. Microstructure and the distributions of elements were investigated by optical microscopy, scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDXA) techniques. The superconducting transition temperatures were determined and the superconducting behaviour was investigated from the temperature dependence of the zero-field magnetic susceptibility $\chi_{a.c.}(T)=\chi'(T)+i\chi''(T)$. An a.c. mutual inductance bridge technique with $f=36$ Hz and $Ih_{a.c.}I=40$ uT was used to monitor both χ' and χ'' as a function of temperature and T_c was determined from the onset of the diamagnetic transition in $\chi'(T)$. The critical current density measurements were made using four-terminal transport measurement techniques. The E field criterion of 50 uV cm^{-1} was used for the critical current density calculation.

3. Results and discussion

The X-ray diffraction patterns of the sintered pellets show different orders of texturing. The lattice parameters were calculated from the X-ray diffraction patterns of the powdered samples. The oxides of compositions $YBa_2Cu_{2.95}Al_{0.05}O_{6+\delta}$ and $YBa_2Cu_{2.90}Al_{0.10}O_{6+\delta}$ are orthorhombic whereas $YBa_2Cu_{2.80}Al_{0.20}O_{6+\delta}$ is of tetragonal phase.

The lattice parameters are listed in Table 1 and the plot of the lattice parameters as a function of aluminium concentration is also shown in Fig. 1. It should be noted that the single crystal of composition $YBa_2Cu_{2.90}Al_{0.10}O_{6+\delta}$ where $\delta\approx1$ already transforms to a tetragonal phase [9] whereas the polycrystalline material remains orthorhombic and an orthorhombic-to-tetragonal phase transformation occurs for the aluminium concentrations above $x=0.10$. The SEM investigation and EDXA imaging of the aluminium-substituted oxides show that aluminium is homogeneously distributed in the grains. Figures 2(a) and 2(b) show the scanning electron micrograph and EDXA imaging of aluminium for $YBa_2Cu_{2.80}Al_{0.20}O_{6+\delta}$.

TABLE 1

Lattice and superconducting parameters of $YBa_2Cu_{3-x}Al_xO_{6+\delta}(0 \leqslant x \leqslant 0.2)$

Oxide	Lattice parameters (Å)	$T_{c,\ onset}$ (K)	$T_{c,\ mid}$ (K)	T_c (K)	J_c[a] (A cm^{-2})
$YBa_2Cu_3O_{6+\delta}$	$a=3.812\pm0.001$	95	91	2	
	$b=3.860\pm0.005$	91.5		2	
	$c=11.646\pm0.004$				
$YBa_2Cu_{2.95}Al_{0.05}O_{6+\delta}$	$a=3.819\pm0.001$	92	89.5	6	5.2
	$b=3.866\pm0.006$				
	$c=11.650\pm0.005$				
$YBa_2Cu_{2.90}Al_{0.10}O_{6+\delta}$	$a=3.825\pm0.002$	93	92	2	3.8
	$b=3.872\pm0.006$				
	$c=11.678\pm0.005$				
$YBa_2Cu_{2.80}Al_{0.2}O_{6+\delta}$	$a=3.858\pm0.005$	84	81	7	1.2
	$b=3.874\pm0.021$				
	$c=11.649\pm0.012$				

[a]Zero magnetic field, 77 K.

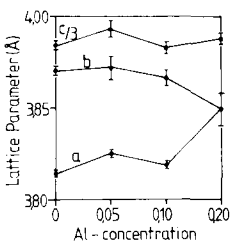
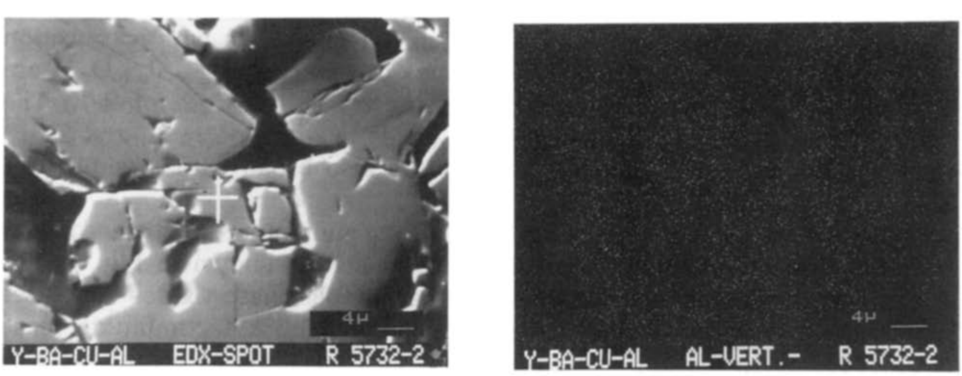


Fig. 1. Lattice parameter as a function of aluminium concentration in $YBa_2Cu_{3-x}Al_xO_{6+\delta}$.



(a) (b)

Fig. 2. (a) Scanning electron micrograph and (b) EDXA imaging of aluminium for $YBa_2Cu_{2.80}Al_{0.20}O_{6+\delta}$.

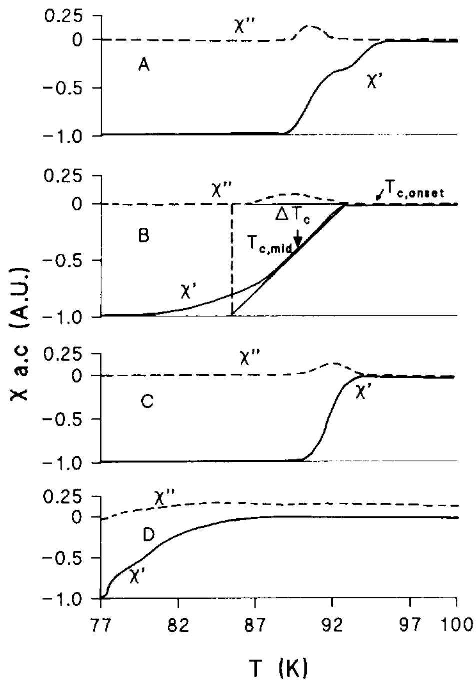


Fig. 3. A.c. magnetic susceptibility as a function of temperature for YBCO and aluminium-substituted oxides: curves A, $YBa_2Cu_3O_{6+\delta}$; curves B, $YBa_2Cu_{2.95}Al_{0.05}O_{6+\delta}$; curves C, $YBa_2Cu_{2.90}Al_{0.10}O_{6+\delta}$; curves D, $YBa_2Cu_{2.80}Al_{0.20}O_{6+\delta}$.

Figure 3 shows the real χ' and imaginary χ'' parts of the complex a.c. magnetic susceptibility $\chi_{a.c.}$ as a function of temperature for the YBCO and aluminium-substituted oxides. The superconducting parameters $T_{c,\ onset}$, $T_{c,\ mid}$ and the transition width ΔT_c were determined from the χ' and χ'' plots and the values are listed in Table 1. The $YBa_2Cu_3O_{6+\delta}$ shows two superconducting transitions with onset values of 95 and 91.5 K, each having a transition width of 2 K. The $T_{c,\ mid}$ value is 91 K. $YBa_2Cu_{2.95}Al_{0.05}O_{6+\delta}$ shows $T_{c,\ onset}$ and $T_{c,\ mid}$ values at 92 K and 89.5 K respectively with a transition width of 6 K. The $T_{c,\ onset}$ and $T_{c,\ mid}$ values of the $YBa_2Cu_{2.90}Al_{0.10}O_{6+\delta}$ are 93 and 92 K with a sharp superconducting transition width of 2 K. The oxide $YBa_2Cu_{2.80}Al_{0.20}O_{6+\delta}$ of tetragonal phase has lower $T_{c,\ onset}$ and $T_{c,\ mid}$ values of 84 and 81 K and the transition is also broad with a width of 7 K.

The critical current density J_c (77 K) of the aluminium-substituted YBCO as a function of externally applied magnetic field is shown in Fig. 4. The J_c value of the aluminium-substituted orthorhombic phase oxides decreases rapidly upon application of an external magnetic field. A maximum decrease of J_c occurs with the application of about 10 Gauss and at higher fields J_c remains practically constant. The zero-field J_c values at 77 K of the orthorhombic phase $YBa_2Cu_{2.95}Al_{0.05}O_{6+\delta}$ and $YBa_2Cu_{2.90}Al_{0.10}O_{6+\delta}$ are 5.2 A cm^{-2}

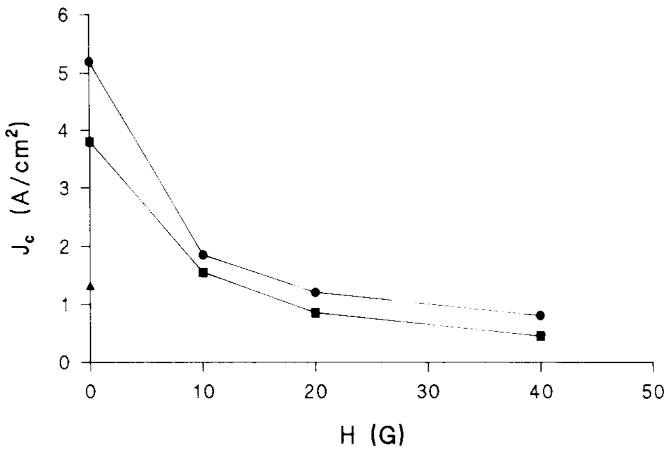


Fig. 4. Critical current density J_c (A cm^{-2}) as a function of magnetic field for $YBa_2Cu_{3-x}Al_xO_{6+\delta}$ for $x=0.05$ (●), $x=0.10$ (■) and $x=0.20$ (▲).

and 3.8 A cm^{-2} respectively as also listed in Table 1 whereas the zero-field J_c value is reduced to 1.2 A cm^{-2} for the tetragonal phase. The upper critical field slope H'_{c211} was also found to decrease from 5 for the orthorhombic $YBa_2Cu_3O_{6+\delta}$ to 1.3 for the single-crystal tetragonal phase $YBa_2Cu_{2.90}Al_{0.1}O_{6+\delta}$ [9].

The X-ray, SEM and EDXA investigations show that aluminium is homogeneously distributed in the grains and does not precipitate at the intergrain boundaries. Aluminium occupies the Cu(1) chain sites in YBCO and does not improve the weak link behaviour as is also seen from the χ'' behaviour. The transformation to a tetragonal phase and a few degrees decrease of T_c of the $YBa_2Cu_{2.80}Al_{0.20}O_{6+\delta}$ is consistent with the importance of Cu(2) planes for the superconductivity. A strong decrease of the critical current density with aluminium substitution is observed for the tetragonal phase relative to the orthorhombic YBCO.

Acknowledgment

One of the authors (H.R.K.) thanks the Bundesministerium für Forschung und Technologie for partial support of this work under Grant 13N56990.

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