Aluminum substitution in $Ba_2YCu_3O_7$

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We have investigated the effect of aluminum incorporation on the structure and superconducting transition temperature of single crystals of high-T_c cuprate perovskite superconductors. The use of alumina crucibles for crystal growth results in incorporation of aluminum to varying extents in crystals of composition $Ba_2YCu_{3-x}Al_xO_7$, $x=0-0.22$. We have performed x-ray studies on several crystals to determine structural effects of Al incorporation. We find that aluminum substitutes only for copper atoms in the chains. Superconducting transition temperatures T_c determined by dc diamagnetic susceptibility measurements change only slightly, to ~ 80 K for $x=0.1$, then drop sharply with higher aluminum concentrations. Results are discussed in relation to the importance of the Cu—O chains and oxygen stoichiometry to superconductivity in $Ba_2YCu_3O_7$.

I. INTRODUCTION

The discovery of high-temperature superconductivity in barium yttrium cuprate, $Ba_2YCu_3O_7$,[1,2] has prompted intense research activity aimed at determining the properties, structure, and mechanism for superconductivity in this material. Systematic substitution of impurity atoms and determination of substituent effects on properties such as superconducting transition temperatures provides a way to probe superconductivity in $Ba_2YCu_3O_7$. In addition, ceramic processing variables such as densification and microstructure are often controlled by dopant incorporation[3] which may lead to unexpected changes in the behavior of the superconductor. Also, interfacial reactions between thin films and substrates can have important effects on the behavior of the film. In superconducting intermetallic alloys, impurities typically have a detrimental effect on superconductivity by introducing scattering centers which disrupt current-carrying Cooper pairs. Some studies of the effects of impurities on superconductivity in ceramic samples of cuprate perovskites have recently been reported.[4-7] Most impurity atoms other than rare earths which substitute into the $Ba_2YCu_3O_7$ lattice drastically reduce onset temperatures. Aluminum incorporation was studied in ceramic samples of $Ba_2YCu_3O_7$ and was found to suppress T_c by ~ 6 K/at.% and to shift the crystal symmetry from orthorhombic to tetragonal.[6,7] However, the location of the substituent atom in the structure is difficult to determine in ceramic samples, and the presence of a small amount of impurity phase, particularly if of poor crystallinity, is difficult to determine.

Recently, large single crystals of $Ba_2YCu_3O_7$ were grown from barium cuprate–copper oxide partially melting mixtures.[8] Some degree of contamination or doping of crystals resulted from most materials used as crucibles to contain the melts. Crystals grown in alumina crucibles have superconducting transition temperatures as high as ~ 90 K upon oxygen annealing, although some crystals are highly contaminated with aluminum leading to lowered transition temperature. We have examined a series of single-crystal samples of $Ba_2YCu_3O_7$ crystals grown in alumina crucibles and annealed under constant conditions to determine the site upon which aluminum substitutes and the effect of aluminum on superconductivity in $Ba_2YCu_3O_7$.

II. EXPERIMENT

Single crystals of $Ba_2YCu_3O_{7-x}$ and $Ba_2SmCu_3O_{7-x}$ were grown from partially melting mixtures of rare-earth oxide, barium carbonate, and copper oxide contained in alumina crucibles.[8] Crystals grew as platelets with dimensions up to $4\times4\times0.1$ mm^3. Crystals were annealed in O_2 at 500 °C for >12 h to maximize the oxygen content of the lattice. For x-ray studies, smaller crystals, usually $0.06\times0.06\times0.01$ mm^3, were chosen. Cell constants of these crystals were measured on a NONIUS CAD4 κ-axis diffractometer driven by the NRCCAD program package.[9] Absolute 2θ values of at least twenty reflections in the range of 50–65° were used to determine cell constants. X-ray intensities from several crystals were collected and the atomic positions were determined using the NRCVAX structure package.[10] As-grown crystals are tetragonal in contrast to the oxygen-annealed crystals which have orthorhombic symmetry. Due to twinning in the a-b plane, the annealed orthohombic crystals show a pseudotetragonal symmetry. Depsite the twinning, structural data can be obtained from these crystals.[11,12] The mosaic structure of the crystals increases upon O_2 annealing, resulting in large standard deviations in measured lattice parameters. Orthorhombic lattice constants can also be measured by centering on the maximum peak height of each reflection as the peaks from the different twin orientations are sufficiently separated. A S.H.E. superconducting quantum interference device (SQUID) magnetometer was used to measure dc magnetic susceptibility of individual crystals at low fields. Aluminum contents were determined by semiquantitative x-ray energy-dispersive analysis (EDXA) measured at several points on

TABLE I. Aluminum concentrations, lattice parameters, and superconducting transition temperature for $Ba_2YCu_{3-x}Al_xO_7$ samples. The estimated standard deviations (in brackets) refer to the last digit printed.

x (Al)	a	b	c	T_c
0	3.851(3)	3.851(3)	11.672(9)	92
0.05[a]	3.835(5)	3.884(5)	11.688(9)	88
0.10[a]	3.844(2)	3.8947(3)	11.657(5)	75
0.11	3.847(4)	3.851(3)	11.659(8)	82
0.12	3.855(3)	3.859(3)	11.684(8)	51
0.13	3.843(3)	3.859(2)	11.667(4)	45
0.135	3.856(2)	3.860(2)	11.674(4)	45
0.18	3.854(2)	3.856(2)	11.668(3)	20
0.22	3.854(2)	3.861(2)	11.672(4)	< 4.2

[a]Ceramic samples.

each crystal compared to barium, yttrium, and copper signals. An absolute measure of aluminum content was obtained from the occupation parameter refinement on one crystal. Aluminum substitution levels in the crystals studied range from $x=0$ to 0.22 for $Ba_2YCu_{3-x}Al_xO_7$. One samarium sample of composition $Ba_2SmCu_{2.79}Al_{0.21}O_7$ was also studied. Table I gives lattice parameters, superconducting transition temperatures, and aluminum contents for a series of oxygen-annealed $Ba_2YCu_{3-x}Al_xO_7$ crystals and ceramic samples.

III. RESULTS AND DISCUSSION

Crystals grown from alumina crucibles exhibit a wide range of T_c's. Even after annealing for extended periods, samples were found to have T_c's that ranged from 0 to ~90 K. Auger and EDXA spectroscopies indicated the presence of varying amounts of aluminum in the crystals. Results of the single crystal x-ray diffraction indicate that

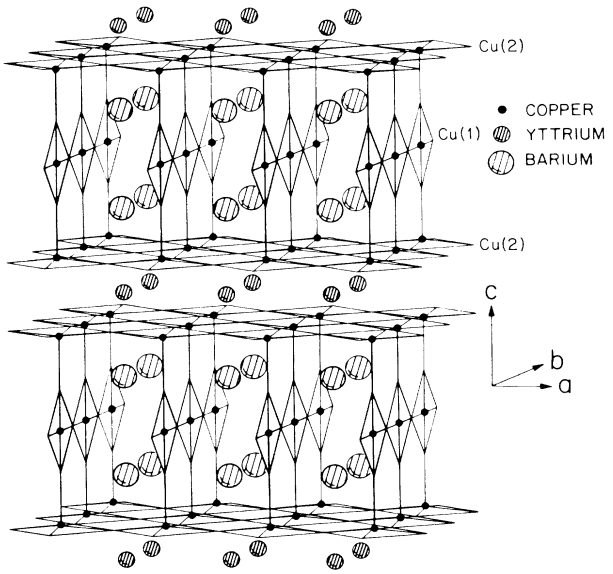

FIG. 1. Crystal structure of $Ba_2YCu_3O_7$.

TABLE II. Crystallographic data for $Ba_2YCu_{2.78}Al_{0.22}O_{6.4}$, tetragonal lattice (as grown), space group $P4/mmm$. $a=3.8637(2)$ Å, $c=11.7231(7)$ Å, $Z=1$. 673 reflections measured, 382 unique, $R_F=0.046$.

Atom	x	y	z	B_{iso} (Å^2)	Occupancy
Ba	$\frac{1}{2}$	$\frac{1}{2}$	0.19016(8)	0.95(2)	
Y	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.54(4)	
Cu(1)	0	0	0	0.92(7)	0.78(3)
Al	0	0	0	0.92(7)	0.22(3)
Cu(2)	0	0	0.3587(2)	0.62(4)	
O(1)	0	0	0.155(1)	1.7(3)	
O(2)	$\frac{1}{2}$	0	0.3797(7)	0.83(2)	
O(3)	0	$\frac{1}{2}$	0	0.9(8)	0.21(3)

aluminum substitutes for copper on only one site, that of Cu(1) in the Cu–O chains. Initial refinement of the structure of the twinned crystals as pseudotetragonal in space group $P4/mmm$ showed reduced electron density at the Cu(1) site of the structure illustrated in Fig. 1. A subsequent refinement which assumes that the electron density at this site arises from full occupancy of the site, but by both copper and aluminum atoms, yields a significant improvement in the refinement (from $R=0.058$ to 0.046 for the yttrium sample with $x=0.22$) and provides a determination of the amount of aluminum present on this site. Structural refinements on three crystals were carried out. Crystal data for two yttrium samples (one of which was annealed in oxygen) and one samarium sample are given in Tables II, III, and IV.

Superconductivity in individual crystals was determined from measurements of the dc susceptibility. The T_c correlates with the aluminum content of the crystals as shown in Fig. 2. Surprisingly, the compound tolerates a relatively high concentration of Al on the Cu–O chains while transition temperatures remain high. We find that T_c

TABLE III. Crystallographic data for $Ba_2YCu_{2.89}Al_{0.11}O_7$, orthorhombic (pseudotetragonal, O_2 annealed) lattice, space group $Pmmm$. $a=3.851(2)$ Å, $b=3.859(2)$ Å, $c=11.677(4)$ Å, $Z=1$. 762 reflections measured, 277 unique, $R_F=0.076$. The estimated standard deviations (in brackets) refer to the last digit printed.

Atom	x	y	z	B_{iso} (Å^2)	Occupancy
Ba	$\frac{1}{2}$	$\frac{1}{2}$	0.1868(2)	0.89(6)	
Y	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.50(11)	
Cu(1)	0	0	0	0.97(17)	0.89(4)
Al	0	0	0	0.97(17)	0.11(4)
Cu(2)	0	0	0.3571(4)	0.52(10)	
O(1)	0	0	0.158(3)	1.8(8)	
O(2a)	$\frac{1}{2}$	0	0.378(2)	0.7(6)	
O(2b)	0	$\frac{1}{2}$	0.378(2)	0.7(6)	
O(3)	0	$\frac{1}{2}$	0	1.0(2)	

TABLE IV. Crystallographic data for $Ba_2SmCu_{2.79}Al_{0.21}O_{6.5}$, tetragonal lattice (as grown), space group $P4/mmm$. $a=3.8789(4)$ Å, $c=11.494(1)$ Å, $Z=1$. 2208 reflections measured, 276 unique, $R_F=0.056$. The estimated standard deviations (in brackets) refer to the last digit printed.

Atom	x	y	z	B_{iso} (Å^2)	Occupancy
Ba	$\frac{1}{2}$	$\frac{1}{2}$	0.1851(1)	1.24(4)	
Sm	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.53(5)	
Cu(1)	0	0	0	2.9(3)	0.79(3)
Al	0	0	0	2.9(3)	0.21(3)
Cu(2)	0	0	0.3521(2)	0.57(5)	
O(1)	0	0	0.156(3)	6.6(2)	
O(2)	$\frac{1}{2}$	0	0.373(1)	0.9(3)	
O(3)	$\frac{1}{2}$	0	0	2.4(40)	

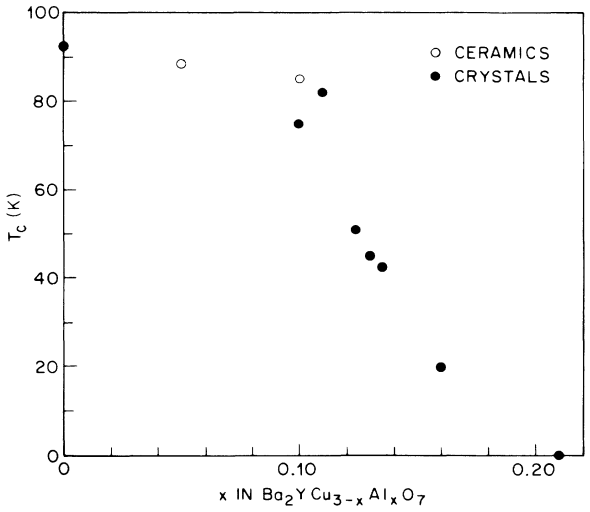

FIG. 2. Superconducting onset temperatures as a function of aluminum content in $Ba_2YCu_{3-x}Al_xO_7$ samples.

drops gradually to ~80 K for 0.1 Al, then decreases sharply with increasing Al concentration. Additionally, we find that the transition width increases with increasing Al content which may reflect microscopic inhomogeneity.

For comparison with the single-crystal samples, we prepared ceramic samples with part of the copper replaced by aluminum. Single-phase samples were difficult to prepare, although several single-phase samples with low aluminum levels were obtained. The others showed a strong tendency to form the insulating Y_2BaCuO_5 phase. Lattice parameters and superconducting transition temperatures for these ceramic samples are included in Table I. Lattice parameters are in agreement with the single-crystal data and other reported data.[6] All ceramic samples, including the multiphase ones, showed the trend towards a tetragonal metric symmetry, indicating that they incorporated aluminum.

One view of the fully oxygenated $Ba_2YCu_3O_7$ structure considers chain copper atoms, Cu(1), as formally Cu^{3+} in a nearly square planar coordination sphere. Al prefers an octahedral oxygen coordination which is possible at the Cu(1) site only if oxygen is added to adjacent $(\frac{1}{2},0,0)$ sites. The presence of aluminum in the lattice thus leads to increased crosslinking of Cu—O chains and a more tetragonal symmetry of the crystals. Higher aluminum levels in the crystals are evidenced by slightly shortened c axes as a consequence of the shorter Al—O distance relative to the Cu—O distance along c. The decrease in c due to Al incorporation is, however, much less than that resulting from oxygen loss to form $Ba_2YCu_3O_6$ ($c=11.819$ Å).[13] The preference of aluminum for an octahedral environment could alter the oxygen content of the material. Indeed, occupation of oxygen sites along both a and b could lead to oxygen stoichiometries in excess of $x=7.0$ in samples with significant aluminum substitutional doping levels. The structural refinement on the oxygen-annealed crystal, however, refines to $x=7.0$. Other transition-metal ions that prefer octahedral environments might also be expected to substitute on the Cu(1) site.

Microtwinning in the a-b plane is a ubiquitous feature of these materials whose structural nature and impact on physical properties is not known. At a twin boundary, the Cu(1) atoms along (110) must be symmetrical in the a-b plane. In has been suggested that this symmetry can arise from oxygen loss along the b axis so that the local geometry is similar to that of $Ba_2YCu_3O_6$.[14] Octahedral aluminum atoms would also provide a locally symmetric environment that could act as twinning centers. For the substitutional levels considered in this study, a lower limit to the domain size can be calculated assuming aluminum is found only at the twin boundaries and that twin boundaries are due only to the presence of aluminum atoms. The calculation leads to a domain size 20 Å in diameter in the a-b plane for $x=0.22$.

Implications of Al substitution to thin-film growth are clear. Thin films grown on Al_2O_3 substrates are likely to incorporate Al during the annealing process which typically requires heating above 900 °C. The superconducting properties of the film are therefore likely to be impaired, at least for very thin films. Indeed, reactions between sapphire substrates and $Ba_2YCu_3O_7$ thin films have been reported.[15] Film thickness together with the annealing procedure thus determines whether a T_c of 90 K can be reached in films on sapphire substrates.

In summary, aluminum has been found to substitute for copper in the Cu—O chains and provides further evidence of the crucial nature of the chains to superconductivity in the cuprate perovskites. The suppression of onset temperatures at higher aluminum concentrations may reflect disruption of conduction paths along the infinite Cu—O chains by the Al impurities. However, the T_c suppression is seen only after a threshold aluminum concentration of ~0.1 is reached. Aluminum incorporation may affect the oxygen content of crystals, and T_c's have been shown to be sensitive to the oxygen content of the lattice.[13] Detailed measurements of oxygen uptake in single crystals of $Ba_2YCu_3O_7$ as a function of aluminum content may provide clues to the behavior of aluminum substituted samples.

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