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Single-Crystal Structure of $NdBa_2Cu_3O_{6.88}$ Superconductor with a Tetragonal Unit Cell

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We report here the growth and single-crystal X-ray structure analysis of $NdBa_2Cu_3O_{6.88}$ with a tetragonal unit cell and a superconducting transition temperature of 63 K. Both *a* and *b* edge centers are partially occupied.

INTRODUCTION

The superconducting properties as well as the crystal structure of the rare earth superconductors $ABa_2Cu_3O_{7-y}$ (A = Y, Sm, Eu, Nd, Gd, Dy, Dy, Ho, Er, Tm, and Yb) are now well studied (1–4). X-ray powder diffraction studies of $Nd_{1-x}Ba_{2-x}Cu_3O_{7-y}$ have revealed that the orthorhombic distortion decreases as x increases and the system goes to the tetragonal phase at $x > 0.2$ (5–8). The T_c is also found to decrease as x increases. However, a detailed structural study of the system with A = Nd has not been carried out. Earlier, it was reported that the superconducting systems $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ce_xCuO_4$ exist in two different crystal structures (9). In view of this and to elucidate the structural similarities between $NdBa_2Cu_3O_7$ and $YBa_2Cu_3O_7$, we have carried out a single-crystal structural analysis for $NdBa_2Cu_3O_7$. The results are presented here.

EXPERIMENTAL

Single crystals of $NdBa_2Cu_3O_{6.88}$ were grown by the melt growth technique. Appropriate stoichiometric mixtures of high-purity Nd_2O_3, $BaCO_3$, and CuO powders were prepared. The mixed powder was pelletized, placed in an alumina crucible, and calcined in air at 940°C for 10 hr. Then the furnace was allowed to cool slowly to room temperature. The calcined sample was reground, pelletized, fired again at 1000°C for 24 hr, and then allowed to cool to room temperature. No crystals were observed in the crucible. For $YBa_2Cu_3O_7$, it has been reported in the literature (10) that the crystals were grown around 980°C. The above procedure was repeated for furnace temperatures of 1050 and 1080°C. No crystals were found at any of these temperatures. However, when the sample was fired at 1100°C in air for 30 min and slowly cooled to room temperature, it was found that a large number of fine single crystals had grown in the crucible. The crystals were separated from the alumina crucible using a needle. They had average approximate dimensions of $60 \times 400 \times 400$ μm.

Alternating current susceptibility measurements were carried out for the crystals, and the transition temperature was found to be 63 K, which is shown in Fig. 1. The Meissner transition curve is somewhat broad. This might be due to the presence of other closely related phases in the flux. Whether microtwined orthorhombic domains are present in the specimen could not be ascertained. A crystal was cut to approximately $60 \times 100 \times 100$ μm to reduce absorption effects and was mounted on an Enraf–Nonius four-circle single-crystal X-ray diffractometer. Graphite-monochromatized Mo$K\alpha$ radiation was used for the diffraction. Twenty-five reflections with $30° < 2\theta < 40°$ were collected through the random search routine. All 25 reflections from the random search were indexed, showing that the specimen mounted was a single crystal and belonged to a single phase. The least-squares refined values of the tetragonal unit cell were $a = 3.911(1)$ Å, $b = 3.913(2)$ Å, $c = 11.725(2)$ Å.

Intensity data were collected for one hemisphere ($h = 0, 4$; $k = \pm 4$; $l = \pm 14$). A total of 704 reflections with $4° < 2\theta < 60°$ were recorded and psi-scan absorption correction was applied to the data using the program Molen (11).

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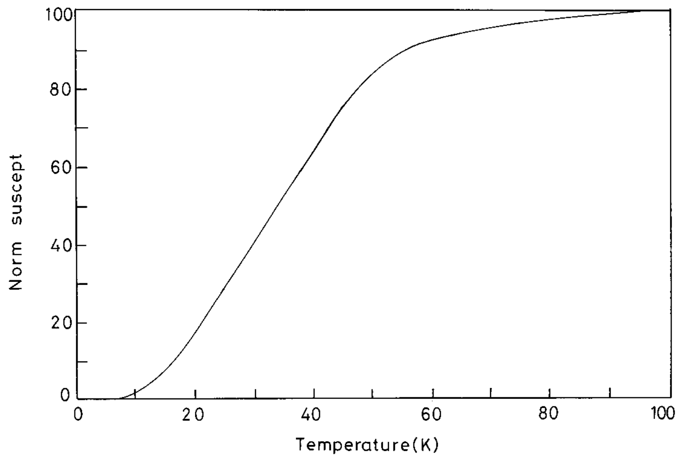

FIG. 1. Measurements of temperature vs ac susceptibility.

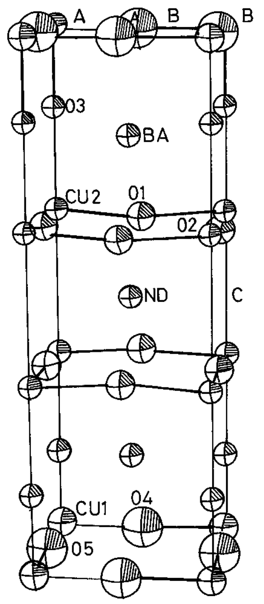

FIG. 2. Crystal structure of $NdBa_2Cu_3O_{6.88}$.

RESULTS AND DISCUSSION

Inspection of the data after absorption correction showed ($I_{hkl} = I_{\bar{h}kl} = I_{h\bar{k}l} = I_{hk\bar{l}}$) the existence of, at least, orthorhombic symmetry. No systemic absences were observed. The space group *Pmmm* was assigned tentatively. Two hundred and sixteen unique data were obtained after merging of equivalent reflections. The structure was solved by direct methods using the SHELEX 86 computer program (12), which gave the heavy atom positions unambiguously. Successive refinements, followed by computation of Fourier difference maps, using SHELEX 93 (13), gave the positions of all oxygens. Site occupancy factors of all atoms were refined and it was found that except for O(4) and O(5), there was very little variation from the crystallographically acceptable full occupancy, while O(4) and O(5) atoms refined to almost 36 and 52% occupancy of the respective sites. However, the oxygen content could not be estimated experimentally. Table 1 shows the fractional coordinates, site occupancies, and thermal parameters of all atoms in the asymmetric unit. The structure is refined to an R factor (based on F_o) of 5.2%. The quantity minimized is $KW(I_o - I_c)$, where I and K stand for the intensity and scale factors, respectively, and

$$W = 1/[(\sigma(F_o^2)^2) + (0.037P)^2 + 0.31P],$$

where

$$P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3.$$

However, whether Nd is present in the Ba site or Ba is present in the Nd site could not be ascertained through the respective site-occupancy refinements, as both elements have nearly the same scattering power.

The unit cell of the title compound is shown in Fig. 2. There are two inequivalent Cu sites, represented by Cu(1)

TABLE 1
Fractional Atomic Coordinates and Thermal Parameters for $NdBa_2Cu_3O_{6.88}$

Atom	x	y	z	s.o.f	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	0.0000	0.0000	0.0000	0.12500	0.0444(36)	0.0361(27)	0.0331(5)	0.0000	0.0000	0.0000
Cu(2)	0.0000	0.0000	0.3518(3)	0.25000	0.0077(19)	0.0036(15)	0.0052(23)	0.0000	0.0000	0.0000
Nd	0.5000	0.5000	0.5000	0.12500	0.0081(12)	0.0044(10)	0.0063(15)	0.0000	0.0000	0.0000
Ba	0.5000	0.5000	0.1869(2)	0.25000	0.0152(12)	0.0114(10)	0.0117(16)	0.0000	0.0000	0.0000
O(1)	0.5000	0.0000	0.3697(17)	0.25000	0.0108(76)	0.0103(67)	0.0096(9)	0.0000	0.0000	0.0000
O(2)	0.0000	0.5000	0.3702(16)	0.25000	0.0152(78)	0.0061(59)	0.0077(8)	0.0000	0.0000	0.0000
O(3)	0.0000	0.0000	0.1563(17)	0.2500	0.0583(76)	0.0461(12)	0.037(2)	0.0000	0.0000	0.0000
O(4)	0.5000	0.0000	0.0000	0.04549	0.0248(21)					
O(5)	0.0000	0.5000	0.0000	0.06466	0.0425(19)					

TABLE 2
Interatomic Distances for $NdBa_2Cu_3O_{6.88}$ and $YBa_2Cu_3O_7$

$NdBa_2Cu_3O_{6.88}$		$YBa_2Cu_3O_7$	
Bond	Distance (Å)	Bond	Distance (Å)
Nd–O(1)	2.482(12)	Y–O(1)	2.418(15)
Nd–O(2)	2.478(12)	Y–O(2)	2.399(15)
Ba–O(1)	2.902(15)	Ba–O(1)	2.980(19)
Ba–O(2)	2.905(15)	Ba–O(2)	2.948(19)
Ba–O(3)	2.789(3)	Ba–O(3)	2.750
Ba–O(4)	2.938(2)	Ba–O(4)	Vacant
Ba–O(5)	2.938(2)	Ba–O(5)	2.891
Cu(2)–O(1)	1.967(2)	Cu(2)–O(1)	1.929(3)
Cu(2)–O(2)	1.968(2)	Cu(2)–O(2)	1.961(3)
Cu(2)–O(3)	2.292(21)	Cu(2)–O(3)	2.341(28)
Cu(1)–O(3)	1.833(20)	Cu(1)–O(3)	1.834(27)
Cu(1)–O(4)	1.956	Cu(1)–O(4)	Vacant
Cu(1)–O(5)	1.956	Cu(1)–O(5)	1.947(5)

and Cu(2), and five different kinds of oxygen atoms, O(1) to O(5), present in the structure. In the basal plane of the unit cell, both *a* and *b* centers are partially occupied by oxygen. The Cu(1) atoms have six-fold oxygen coordination when the *a* and *b* edge centers are simultaneously occupied. There exist linked O(4)–Cu(1)–O(4)–Cu(1) linear chains along the *a* axis and O(5)–Cu(1)–O(5)–Cu(1) linear chains along the *b* axis. Throughout the refinement procedure Cu(1) had a much higher temperature factor than Cu(2), which indicates either that the Cu(1) position is partially disordered or that it has a large thermal motion. The Cu(2) atoms are 5-coordinated with respect to oxygen. Cu(2) atoms are slightly buckled out of the square plane formed by O(1) and O(2) atoms. The deviation of Cu(2) from the O(1), O(2) square plane is 0.213 Å. The variation of the interatomic distances of $NdBa_2Cu_3O_{6.88}$ from the reported values of $YBa_2Cu_3O_7$ (14) is given in Table 2.

In summary, we have grown and solved the crystal structure for the 63 K superconductor $NdBa_2Cu_3O_{6.88}$. From the results it can be seen that the structure satisfies *P*4/*mmm* symmetry. Except for the tetragonal symmetry (with superconducting transition), the structure of $NdBa_2Cu_3O_{6.88}$ is essentially that of $YBa_2Cu_3O_7$. The salient features which may indicate minor differences from the structure of $YBa_2Cu_3O_7$ have been presented. The structure factor table is deposited with NAPS.

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