

Synthesis of single-domain superconductor $\text{TmBa}_2\text{Cu}_{3-x}\text{O}_{7-y}$ and its atomic structure

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A method of obtaining single-domain crystals of the superconductors $\text{TmBa}_2\text{Cu}_{3-x}\text{O}_{7-y}$ with $T_c = 90\text{--}92$ K and a transition width of 1 K has been developed. The atomic structure of a single-domain sample of $\text{TmBa}_2\text{Cu}_{2.972}\text{O}_{6.89}$ has been studied and the structure of this sample has been compared with the structure of Y superconductors.

High-quality single crystals, which are free from twins and which are formed as a result of a ferroelastic phase transition from a high-temperature tetragonal phase to a low-temperature orthorhombic phase are essential for high-precision analysis of the physical properties of high- T_c superconductors of the 1-2-3 type. Twinning depends to

a large extent on the conditions under which the single crystals are synthesized. A suitable choice of these conditions makes it possible to grow crystals with large domains or single-domain samples. The quality of such single-domain crystals is generally better than that of samples whose single-domain state is obtained by thermomechanical means.¹

The single-domain crystals of $\text{TmBa}_2\text{Cu}_{3-x}\text{O}_{7-y}$ were grown by the solution-melt method for a nonstoichiometric melt of a quasi-ternary system² $\text{Tm}_2\text{O}_3\text{-BaO-CuO}(\text{Cu}_2\text{O})$. The best results were obtained when we used melts of 3 mole% of Tm_2O_3 , 30 mole% of BaO, and 67 mole% of CuO. The samples were crystallized in air in corundum crucibles 5–10 ml in volume. The size of the crystals was 1–3 mm after they were mechanically extracted from the solidified mass. The domain structure was studied under an optical polarizing microscope and by x-ray structural analysis. The temperature of the transition to the superconducting state was determined from the temperature dependence of the magnetization using a vibration magnetometer and from the temperature dependence of the resistance, which was measured by the four-probe method. The manner in which the crystals were cooled after being grown was found to have a considerable effect on the superconducting properties, the degree of orthorhombic lattice distortion, and the domain structure of the sample. The critical temperature of the crystals was $T_c = 90\text{--}92\text{ K}$ and the width of the transition to the superconducting state was less than 1 K without additional annealing in oxygen when they were cooled in the temperature interval 825–525 K at a rate of 2–4 deg/h. Such

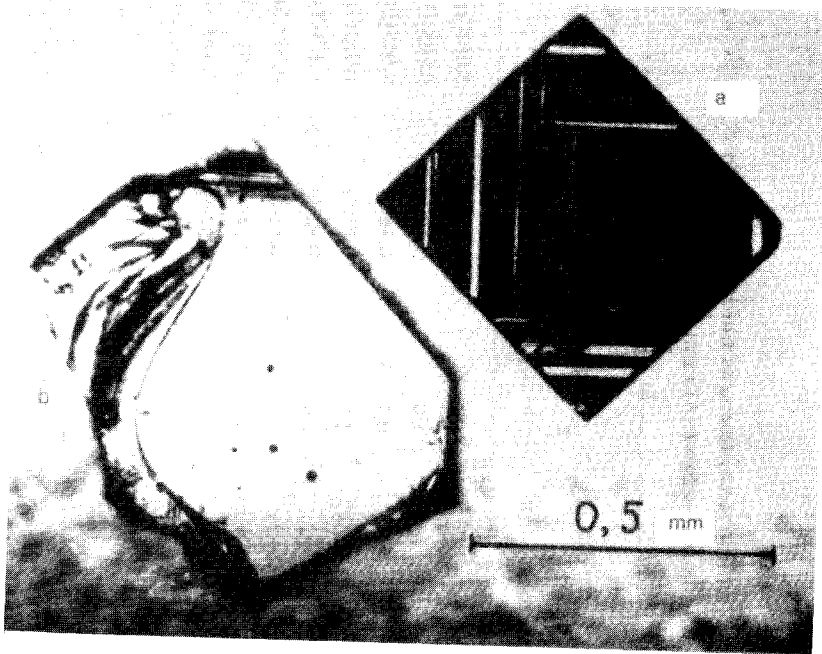


FIG. 1. The $\text{TmBa}_2\text{Cu}_{3-x}\text{O}_{7-y}$ crystals in a reflected polarized light in crossed Nicol prisms. (a) Poly-domain sample and (b) single-domain sample.

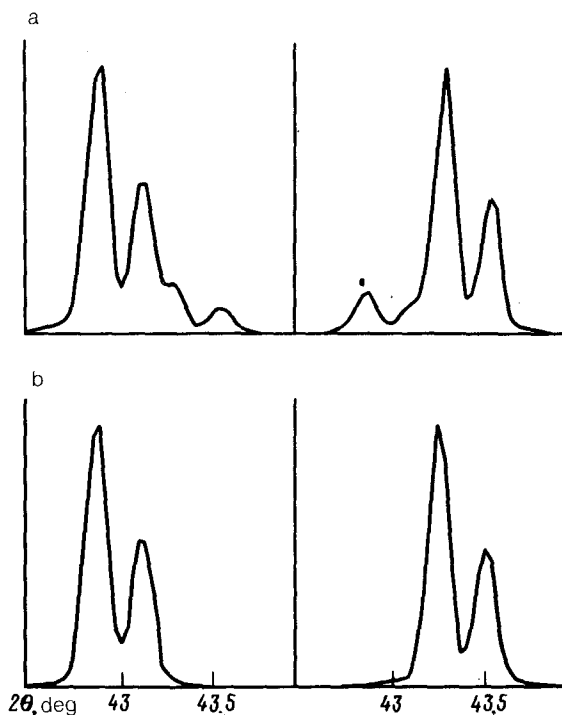


FIG. 2. Profiles of x-ray diffraction 040 and 400 reflections of (a) twinned $\text{TmBa}_2\text{Cu}_{3-x}\text{O}_{7-y}$ crystals and (b) single-domain crystals.

crystals have larger domains. Samples with sections of up to 0.5 mm, in which there is generally no twinning, are encountered rather frequently.³ The nearly single-domain individual crystals were up to 1 mm in size. Figure 1 reproduces photomicrographs of polydomain and single-domain samples. For comparison, we synthesized and then analyzed two series of crystals which differed only in the rates at which they were cooled: 2 and 8 deg/h. On the basis of a 2D scanning of x-ray diffraction $h00$ reflections we found that the angular width ($\Delta\omega$) of the reflections in the crystals of the first and second series is 0.2° and 1.0° , respectively. The volume of the second twinning component in this case was no greater than 2–3% in the first crystals, while it reached 15–20% in the second crystals. The 2θ profiles of the x-ray diffraction 400 and 040 reflections of the crystals of the first and second series are shown in Fig. 2.

The complete x-ray structural analysis of the atomic structure of the crystals $\text{TmBa}_2\text{Cu}_{3-x}\text{O}_{7-y}$ was carried out using a specially selected thin single-crystal wafer $142 \times 136 \times 14 \mu\text{m}$ in size. The integral intensities of the diffraction reflections were measured on a computer-controlled four-circle x-ray RED-4 diffractometer (Mo K_α radiation, a graphite monochromator, ω scanning at rates of 0.5–8.0 deg/min, $\sin \theta / \lambda \leq 0.85 \text{ \AA}^{-1}$). A total of 2271 reflections were measured in the reciprocal-space limitation hemisphere. After averaging the intensities which are equivalent in the Laue mmm reflection symmetry ($R_{av} = 2.5\%$) we obtained an array consisting of 547 inde-

TABLE I. Positions and coordinates of atoms, population, thermal parameters $B_{\text{equiv}} (\text{\AA}^2)$, and semiaxes of thermal vibrations (\AA) along the a , b , and c directions.

Atom	n	x/a	y/b	z/c	q	B_{equiv}	TVE semiaxes		
							a	b	c
Tm	1	1/2	1/2	1/2	1.0	0.33(1)	0.063(1)	0.065(1)	0.067(1)
Ba	2	1/2	1/2	0.18466(1)	1.0	0.50(1)	0.085(1)	0.075(1)	0.079(1)
Cu(1)	1	0	0	0	0.972(3)	0.46(1)	0.087(2)	0.077(2)	0.065(2)
Cu(2)	2	0	0	0.35669(4)	1.0	0.37(1)	0.055(1)	0.057(1)	0.089(1)
(O1)	2	0	0	0.1588(2)	1.0	0.82(4)	0.121(5)	0.106(5)	0.076(5)
(O2)	2	1/2	0	0.3796(2)	1.0	0.61(3)	0.067(6)	0.089(5)	0.105(5)
(O3)	2	0	1/2	0.3795(2)	1.0	0.54(3)	0.087(5)	0.065(6)	0.095(6)
(O4)	1	0	1/2	0	0.89(1)	0.94(8)	0.145(8)	0.062(12)	0.103(9)

pendent reflections with the intensities $I > 3\sigma(I)$. The correction for the x-ray absorption of the sample was introduced by numerical integration. The atomic structure was refined by the method of least squares in an all-matrix version. The extinction was taken into account in accordance with Becker-Koppens formalism. The basic model used for refining the structure was taken from Ref. 4. All the calculations were carried out using the Prometheus program package.⁵ The factors ultimately responsible for the discrepancy between the experimental structure amplitude moduli and those calculated from a model are $R = 1.23$ and $R_w = 1.61\%$ for 33 refined parameters and 547 independent experimental diffraction reflections which were used in refining the values.

The unit cell parameters of the test sample are $a = 3.814(1)$, $b = 3.876(1)$, $c = 11.673(3)$ Å, and the crystals have a $Pmmm$ group symmetry. Table I lists the coordinates of the basal atoms of the structure, position multiplicity n , atomic occupation of the crystallographic sites q , equivalent (isotropic) characteristics of the thermal motion of atoms B_{equiv} , and the semiaxes of the thermal-vibration ellipsoids (TVE), which take into account the anisotropy of the thermal vibrations of the basal atoms. Using the filling factors q obtained by us, we can write the refined chemical formula of the test sample $\text{TmBa}_2\text{Cu}_{2.972}\text{O}_{6.89}$. The copper deficiency corresponds to the Cu(1) site. The Cu(2) atoms occupy 100% of their crystallographic sites. By analogy, only the O(4) site is oxygen deficient, i.e., it belongs to the Cu(1)-O(4)-Cu(1)-O(4) chains and does not involve the Cu(2) atomic layers and the O atoms which are associated with these copper atoms. The following circumstance should be taken into account in the analysis of the defect content of the structure with respect to the Cu(1) atoms. A chemical analysis showed that crystals grown in corundum crucibles typically have up to 2% Al atoms. We did not chemically analyze the single crystal $\sim 3 \times 10^{-4}$ mm³ in volume which we studied. To fully compensate for the Cu(1) atomic deficiency, while retaining the x-ray scattering power at the experimental level, however, this site must be filled with Cu atoms at the 95% statistical level and with Al atoms at the 5% statistical level. A comparison of these estimates shows that copper deficiency of the structure at the Cu(1) site is a real deficiency. The accuracy of our x-ray diffraction experiment is not good enough yet to allow us to independently locate $\sim 2\%$ of Al impurity atoms in the structure.

An important difference between our structure data for $\text{TmBa}_2\text{Cu}_{2.972}\text{O}_{6.89}$ and the results of experimental studies of $\text{TmBa}_2\text{Cu}_{2.94}\text{O}_{6.82}$ crystals (Ref. 6) is that in Ref. 6 the filling of the (1/200) site with the O(5) atoms was set at the 10% level. We have found the O atoms at this site to be absent in this case. The accuracy of this assertion is characterized by a standard deviation of σ in the electron density distribution equal to 1% filling of the site with O atoms. The O(5) atoms may appear in the orthorhombic structure for two reasons. The first is that a small fraction (by volume) of the second twinning component may be present in the nearly single-domain sample. Such a possibility was suggested in Ref. 6. In our case we can cite another reason which is linked with the Al impurity atoms, whose ion radius is much smaller than that of copper. An Al atom at the (000) site may arrange an octahedral environment consisting of O atoms, which is characteristic for this atom. Considerably more precise structural analysis is necessary to experimentally solve these problems.

A comparison of the structure data on the single-domain crystal of $\text{TmBa}_2\text{Cu}_{2.972}\text{O}_{6.89}$ and the results of experimental studies of the compound $\text{YBa}_2\text{Cu}_{2.94}\text{O}_{6.82}$ (Ref. 6) and $\text{YBa}_2\text{Cu}_3\text{O}_{6.93}$ (Ref. 7) should first consider the systematic decrease of the atomic spacing of Tm–O compared with that of Y–O. The first values of the atomic spacing are 2.394 Å and 2.370 Å, and the second values are 2.406 Å and 2.382 Å (Ref. 7), 2.405 Å and 2.386 Å (Ref. 6). Making the Tm polyhedron smaller than the Y polyhedra reduces in our structure the atomic spacing of Cu(2)–Cu(2) to 3.346 Å compared with 3.401 Å in Ref. 7 and 3.368 Å in Ref. 6, reduces the atomic spacing of Tm–Cu(2) to 3.192 Å compared with 3.211 Å for Y–Cu(2) in Ref. 7 and 3.207 Å in Ref. 6, and reduces the atomic spacing of Tm–Ba atoms to 3.681 Å compared with 3.696 Å for Y–Ba in Ref. 7 and 3.689 Å in Ref. 6. The reduction of atomic spacing reduces the size of the unit cell of the Tm compound: $a = 3.814$, $b = 3.876$, $c = 11.673$ Å, in comparison with the Y crystals: $a = 3.836$, $b = 3.883$, $c = 11.686$ Å (Ref. 6) and $a = 3.8166$, $b = 3.8852$, $c = 11.6901$ Å (Ref. 7). Against the background of these correlating changes of the Tm compound we see an increase in the atomic spacing of Ba–Ba to 4.311 Å compared with 4.298 Å in Ref. 7 and 4.308 Å in Ref. 6 and an increase in the atomic spacing of Cu(1)–Cu(2) to 4.164 Å compared with 4.144 Å in Ref. 7 and 4.159 Å in Ref. 6. A replacement of Y atoms by Tm atoms changes minimally the atomic spacing of Cu(1)–O and Cu(2)–O in the structures, except for Cu(2)–O(1). The last atomic spacing characterizes the weakest link, the chemical link (the Jahn–Teller effect), and clearly is highly unstable.

The very narrow temperature transition to the superconducting state with $T_c = 90\text{--}92$ K observed in single-domain crystals of $\text{TmBa}_2\text{Cu}_{3-x}\text{O}_{7-y}$ can be attributed to the fact that upon transition from Y compound to Tm compound the copper-oxygen layer in the structure of the latter compound remains the most stable layer in terms of the atomic spacing, and hence in terms of the chemical bonds.

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