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Crystallographic phases and transport properties in the superconducting Tm-Ba-Cu-O compound system

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The Tm-Ba-Cu-O compound system becomes a superconductor at a critical temperature T_c, measured at the midpoint of the resistive transition, of 92 K. From x-ray diffraction techniques, the material seems to be composed of two phases. The dominating (opaque) phase ($\gtrsim 94\%$ in weight) is the superconducting $TmBa_2Cu_3O_{6+x}$ oxide (isostructural with superconducting oxygen-deficient $YBa_2Cu_3O_{6+x}$), which crystallizes in the orthorhombic *Pmmm* space group with $a = 3.819(2)$, $b = 3.889(2)$, $c = 11.669(7)$ Å, and $D_c = 7.21(1)$ g cm^{-3}. The other (green) phase is the semiconducting Tm_2BaCuO_5 oxide [space group *Pbnm* or $Pbn2_1$; $a = 7.079(8)$, $b = 12.09(1)$, $c = 5.633(2)$ Å, and $D_c = 8.53(2)$ g cm^{-3}] isostructural with the series of L_2BaCuO_5 (L = Y, Sm, Eu, Gd, Dy, Ho, Er, Yb) oxides.

The discovery by Bednorz and Müller[1] of a superconducting transition at about 30 K in $La_{2-x}Ba_xCuO_{4-y}$ has been followed by the quest for even higher-T_c systems. This search has met with success, and superconductivity in the 90-K range has been found in the multiphase metallic oxide Y-Ba-Cu-O system[2-6] and in single-phase $ABa_2Cu_3O_{6+x}$ (A = Y, La, Nd, Sm, Eu, Gd, Ho, Er, and Lu) oxides.[7] Critical temperatures above 77 K have also been reported in superconducting cuprate perovskites generically represented by $M_3Cu_3O_x$ [$M_3 = Ba_2L$, $BaCaL$, $Ba_2(L_{1-y},Sc_y)$, $Ba_2(Q_{1-y}R_y)$, and $(Ba_{2-y},Sr_y)L$ with L, Q, and R = Y, Eu, and La].[8] In a recent article, superconductivity at 155 K in a multiphase fluorinated Y-Ba-Cu-O compound system with nominal composition $YBa_2Cu_3F_2O_y$ has been announced.[9] We report hereby the preparation and crystallographic characterization of a Tm-Ba-Cu-O oxide system which superconducts at about 90 K, the identification of the superconducting phase, and the transport properties of the compound.

The Tm-Ba-Cu-O compound system was prepared with nominal composition represented by $Tm_1Ba_2Cu_3O_{6+x}$ through solid-state reaction of appropriate amounts of finely ground and mixed Tm_2O_3, CuO, and $BaCO_3$ (all 99.9% pure) in a platinum crucible at 950 °C, under flowing oxygen for 15 h. The resulting material was cooled and pulverized. At this point two different procedures were applied respectively to two portions of the powder (samples A and B). Sample A was reheated under the same conditions as above and removed from the furnace for regrinding several times during 6 h of firing. The reacted product was again pulverized after cooling and pressed into disks of 13 mm in diameter and 1 mm in thickness. The disks were sintered in a flux of O_2 at 950 °C for 40 h and then allowed to cool down slowly to room temperature. The same sequence of treatments was followed for sample B, but now the material was not reground during 15 h of the initial firing and the pellets were sintered for 12 h. Indium leads were attached to the disks with silver paste contacts. The standard four-probe technique was used for the resistivity (ρ) measurements. Temperature was measured (with an accuracy of ±0.5 K) using a copper-constantan thermocouple. X-ray diffraction data were obtained at room temperature from the pressed pellets (whose diffraction patterns exhibited orientational effects) and from powder samples obtained by grinding pieces of them. The data were collected using a Philips PW 1380/01 powder diffractometer with Ni-

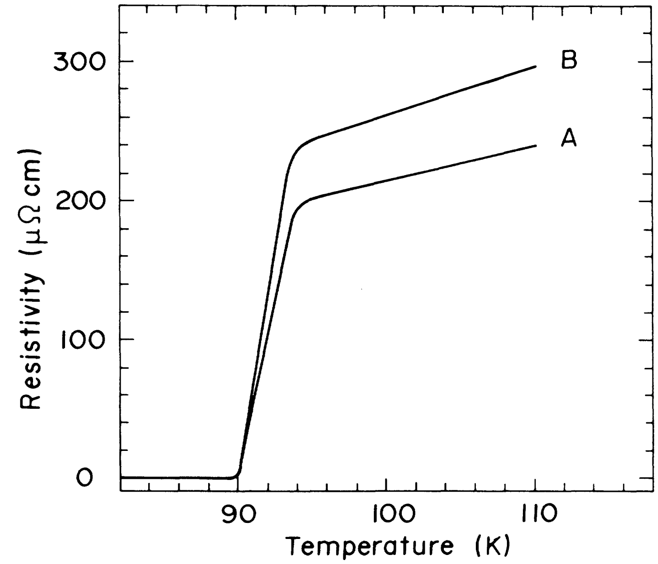

FIG. 1. Resistivity vs temperature for samples A and B. Current density was 1 A cm^{-2}.

filtered Cu $K\alpha$ radiation. The theoretical x-ray diffraction patterns shown below were computed with the program LAZY PULVERIX.[10]

The resistivity data for samples A and B from 110 K to below T_c are shown in Fig. 1. The onset temperature of the resistive transition occurs at 94 K, and the point of "zero resistance" at 90 K. The critical temperature was defined at the midpoint value $T_c = 92$ K. The larger resistivity of sample B at the onset temperature and above, as compared with sample A, is in part due to the different procedures followed in the synthesis of the samples and to the presence of traces of a semiconducting phase with concentration in the first sample higher than in the second one (see below).

The powder x-ray diffraction spectrum of sample A is shown in Fig. 2. The relevant part of the spectrum corresponding to sample B is depicted in the inset of Fig. 3. Within the sensitivity of the method, sample A is almost single phase with small traces (about 1% in weight) of a second crystal phase. Sample B contains a slightly larger proportion of this second compound (about 6%). In both samples the dominant phase turned out to be the high-T_c superconducting $TmBa_2Cu_3O_{6+x}$ oxide (black) while the other one is a semiconducting Tm_2BaCuO_5 oxide (green). The x-ray diffraction data of this compound (prepared as described by Michel and Raveau[11] for a series of related oxides) are shown in Fig. 3.

From geometric x-ray diffraction information, the superconducting crystal phase seems to belong to the orthorhombic system with $a = 3.819(2)$, $b = 3.889(2)$, and $c = 11.699(7)$ Å. Relative peak intensities in the x-ray diffraction pattern show that (as expected) the $TmBa_2Cu_3O_{6+x}$ oxide is basically isostructural with $YBa_2Cu_3O_{6+x}$.[12-15] This can be appreciated in Fig. 2 where the observed x-ray diffraction pattern of the superconducting phase is compared with the calculated one obtained employing the above refined unit-cell constants and the atomic fractional coordinates and isotropic thermal parameters for $YBa_2Cu_3O_{6.8}$ (space group $Pmmm$) reported in Ref. 15.

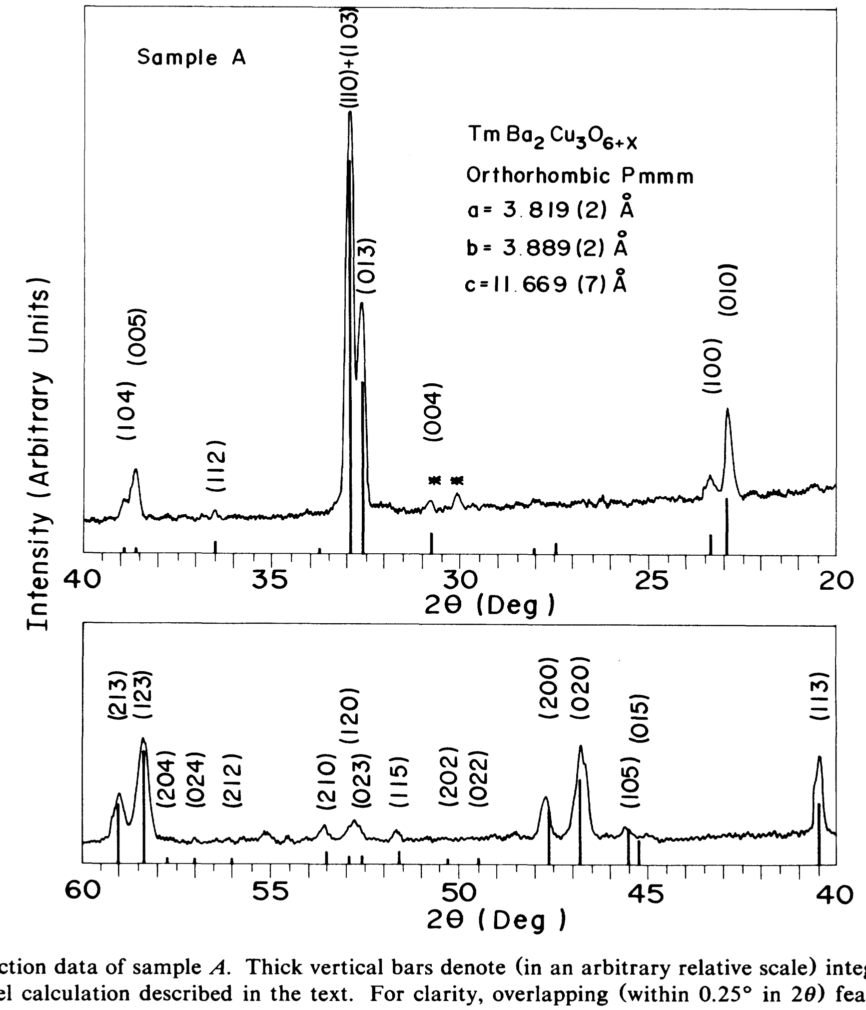

FIG. 2. X-ray diffraction data of sample A. Thick vertical bars denote (in an arbitrary relative scale) integrated x-ray diffraction intensities for the model calculation described in the text. For clarity, overlapping (within 0.25° in 2θ) features in the theoretical spectrum have been labeled by the Miller index of the strongest reflection contributing to the line. The two contributors to the strongest line in the spectrum (at $2\theta = 32.86°$) have practically the same intensity. Starred peaks at 30.71 and 32.12° have contributions from the (211) and (131) reflections, respectively, corresponding to traces (about 1% in weight) of semiconducting Tm_2BaCuO_5 oxide in the sample.

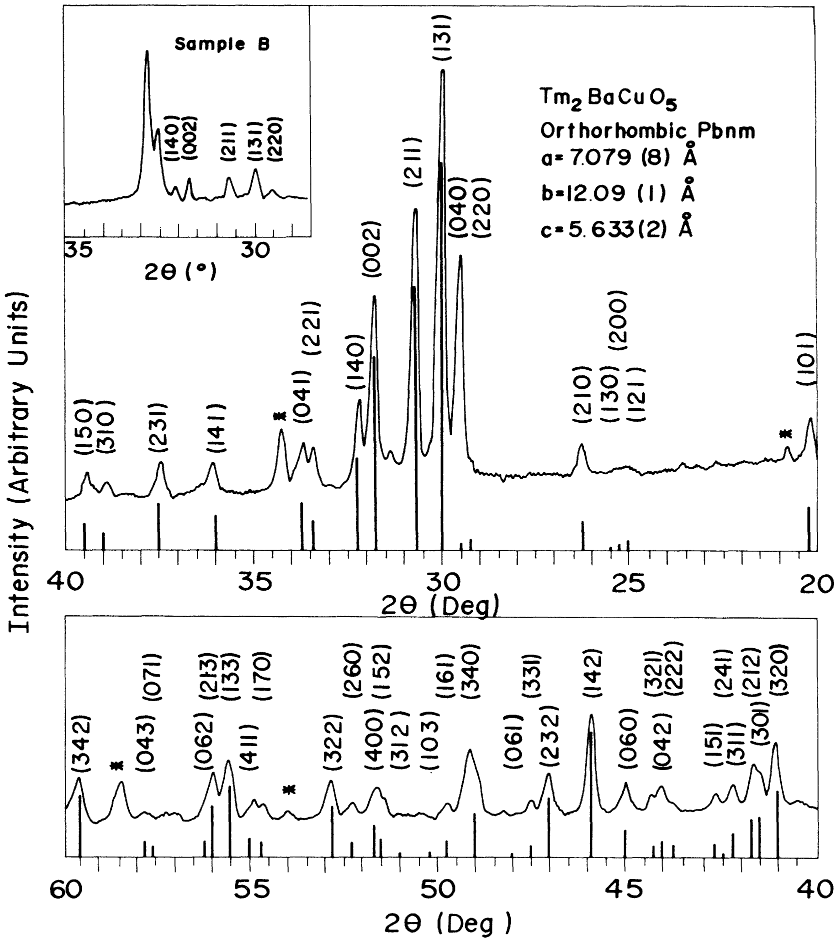

FIG. 3. Experimental and calculated x-ray diffraction spectra of Tm_2BaCuO_5. The peak at about 29.6° has contribution from unreacted Tm_2O_3. Starred features have not been identified. Inset: x-ray diffraction data of sample *B* for scattering angle in the range 28.5°–35°. The strongest two peaks at 32.6° and 32.9° correspond, respectively, to the (013) and (110)+(103) reflections of the dominating, superconducting $TmBa_2Cu_3O_{6+x}$ phase, while the indexed lines correspond to a 6% in weight of semiconducting Tm_2BaCuO_5 oxide in the mixture.

The presence of the semiconducting Tm_2BaCuO_5 crystal in the Tm-Ba-Cu-O system was inferred by analogy with the related case of the Y-Ba-Cu-O mixtures where, together with the superconducting $YBa_2Cu_3O_{6+x}$ phase, there is also present the semiconducting Y_2BaCuO_5 compound.[13] Tm_2BaCuO_5 was assumed to be isostructural with the series of orthorhombic L_2BaCuO_5 (L = Y, Sm, Eu, Gd, Dy, Ho, Er, Yb) oxides crystallographically described in Ref. 11. As these crystals exhibit a strong linear correlation between the unit-cell dimensions and the lanthanide ionic radius (r), approximated unit-cell parameters $a=7.08$, $b=12.09$, and $c=5.63$ Å for the thulium compound were estimated from the linear regressions curves $a_i=\alpha_i+\beta_i r$ ($i=1,2,3$) with $\alpha_1=5.25(6)$ Å, $\beta_1=2.10(7)$; $\alpha_2=9.24(9)$ Å, $\beta_2=3.28(9)$; $\alpha_3=4.37(5)$ Å, $\beta_3=1.44(6)$ determined by least-squares fit to the data in Ref. 11. These unit-cell dimensions were refined employing x-ray diffraction data from polycrystalline Tm_2BaCuO_5 (see Fig. 3) to the following final values: $a=7.079(8)$, $b=12.09(1)$, and $c=5.633(2)$ Å. The above procedure may be useful as a first step in the crystallographic detection and characterization of still unreported L_2BaCuO_5 (L = lanthanide) phases which could eventually be formed in other multiphase L-Ba-Cu-O superconducting systems.[16]

As described for the case of the $TmBa_2Cu_3O_{6+x}$ crystal, in Fig. 3 the powder x-ray diffraction data of the Tm_2BaCuO_5 oxide is compared with the corresponding computed x-ray diffraction spectra obtained employing the atomic fractional coordinates and isotropic thermal parameters (assuming space-group symmetry *Pbnm*) of the isostructural Y_2BaCuO_5 compound reported in Ref. 11. Further refinement of the molecular structure of both the superconducting and semiconducting crystals is in progress.

In summary, we have prepared the Tm-Ba-Cu-O compound system which superconducts above 90 K and characterized crystallographically the dominant, superconducting phase as the $TmBa_2Cu_3O_{6+x}$ oxide and a second phase in the system as the semiconducting Tm_2BaCuO_5 compound. The T_c value for $TmBa_2Cu_3O_{6+x}$ oxide is about the same (within ±5%) as for other members of the isostructural lanthanide-containing series,[7] hence confirming in this oxide the reported relative lack of sensitivity of T_c to the replacement of the trivalent rare-earth ion in the lattice.

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[16] In Table I of Ref. 5, the unidentified x-ray diffraction peaks for $Y_{2-x}Ba_xCuO_{4-y}$, $x=0.25$ at 2θ equal to 29.86°, 31.64°, 31.98°, 38.79°, 40.76°, and 45.62° actually correspond respectively to the (131), (002), (140), (150)+(240), (320)+(202), and (142) reflections of the Y_2BaCuO_5 component in the multiphase system. The (211) reflection of Y_2BaCuO_5, which is second only to (131) in intensity and should appear at about 30.5° in the x-ray diffraction spectra of Fig. 1 in this article, overlaps with a peak due to the $Y_2Cu_2O_5$ component at about the same scattering angle.