SYNTHESIS, TRANSPORT, MAGNETIZATION AND STRUCTURAL CHARACTERIZATIONS OF Ti–Ca–Ba–Cu–O SPECIMENS WITH $T_0=123$ K AND $T_{\text{onset}}=155$ K

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A stable, reproducible and bulk superconductor of Ti–Ca–Ba–Cu–O (TCBCO) compound with $T_0$ above 120 K and $T_{\text{onset}}=155$ K has been prepared. Measurements of electrical and magnetic properties are reported. On the basis of the transmission electron microscopy and X-ray diffraction analyses, the predominant phase was determined to be a body-centered tetragonal structure ($a=b=0.557$ nm, $c=3.77$ nm) with a space group of I4/mcm. The composition ratios of Ti, Ca, Ba and Cu of the phase were determined by energy dispersive spectrometry to be 1:2:3:4. A probable structure model involving four layers of Cu–O interposed between Ti–O layers is proposed.

1. Introduction

The first thallium containing oxide superconductor was known in 1966 [1]. Nevertheless, it did not attract much attention until the discovery of the high-$T_c$ superconductor in the Ti–Ba–Cu–O system [2]. Recently, a record high superconducting transition temperature of 125 K for a Ti–Ca–Ba–Cu–O compound was reported [3]. It was suggested that the superconducting properties with $T_c$ values of 110 K and 125 K are associated with the superconducting phases with compositions Tl$_2$CaBa$_2$Cu$_2$O$_y$ and Tl$_2$Ca$_2$Ba$_2$Cu$_3$O$_{y-1}$, respectively [4]. However, the superconducting properties of Ti–Ca–Ba–Cu–O oxide depends sensitively on the preparation of initial composition, heat treatment, temperature and time [4,5] owing to the complexity of this five-component system. In this paper, we report the preparation of the high-$T_c$ superconducting Ti–Ca–Ba–Cu–O compound with $T_0$ above 120 K. Electrical resistivity and magnetization measurements were carried out. In addition, transmission electron microscopy (TEM) and X-ray diffraction (XRD) as well as energy dispersive spectrometry (EDS) were conducted to determine the crystal structures of the superconducting phases.

2. Experimental

Samples were prepared by first weighing appropriate amounts of high purity CaCO$_3$, BaCO$_3$, and CuO in stoichiometric proportions of Ca$_2$BaCu$_2$O$_5$, Ca$_2$Ba$_2$Cu$_3$O$_7$, and Ca$_x$BaCu$_2$O$_{4+x}$ ($x=2-4$). The constituents were ball milled, filtered, dried and ground in an agate mortar. The well-mixed powders of these oxides were then calcined at 900–950°C in air for 12 h. The final specimens were prepared by mixing the appropriate amounts of powders of Tl$_2$O$_3$ and Ca–Ba–Cu–O to yield products of nominal compositions Tl$_2$CaBa$_2$Cu$_2$O$_y$, Tl$_2$Ca$_2$Ba$_2$Cu$_3$O$_{y-1}$ or Tl–Ca$_2$BaCu$_3$O$_y$ ($x=2-4$). The mixtures were ground and pressed into a cylindrical pellet under a pressure of about 2 tons/cm$^2$ with a dimension of 8 mm × 2
mm. To alleviate the possible decomposition of Tl₂O₃ to Tl₂O and O₂ under the synthesis condition, the pellets were sintered in flowing O₂ at 880°C for 15 min and cooled to room temperature by air quenching. No further annealing was attempted.

Electrical resistivity measurements were performed by a standard AC four-probe technique. Electrical contacts were attached to the sample by fine copper wires with conductive silver paint. Magnetization data were taken in a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design). To determine the crystal structure of the sample, JEOL-2000EX and JEOL-2000FX transmission electron microscopes operating at 200 kV and an X-ray diffractometer were used. An EDAX 9100/70 energy dispersive spectrometer was employed to measure the atomic concentrations of the samples.

3. Results and discussion

For samples with nominal compositions of Tl₂CaBa₂Cu₂O₈, Tl₂Ca₂Ba₂Cu₃O₉, and TlCa₂Ba-Cu₃O₇, superconducting zero resistance temperatures were found to be about 113 K. For TlCa₃BaCu₃O₇, (x= 3, 4) samples, zero resistance was achieved at 123 K and a small kink was evident at 155 K. The reproducible kink in the resistivity curves above Tc (R = 0) indicates possible existence of disconnected grains in the samples with higher superconducting transition temperatures. Electrical resistivity data normalized to the value at 300 K of the above samples are shown in fig. 1.

Figure 2 presents the temperature dependence of the DC magnetization measured in an applied magnetic field of 50 Oe between 10 and 350 K for samples with nominal starting composition TlCa₃BaCu₃O₇. A sharp transition into the superconducting state occurs at 120 K, in excellent agreement with the transport data shown in fig. 1(b). A rough estimate by neglecting any correction concerning the geometric demagnetization effects of the irregular shaped sample and the superconducting grain size effect, a Meissner effect of 16% of -1/(4π) for the initial, rapid change in magnetization from Tc to 90 K was obtained. The percentage of flux exclusion increases as the temperature is decreased.

Structural analysis by X-ray diffraction of the sample with the nominal starting composition of Tl₂CaBa₂Cu₂O₈ and Tl₂Ca₂Ba₂Cu₃O₉, or TlCa₂BaCu₃O₇, indicated they were dominated by the so-called 2122 and 2223 phases, respectively, in agreement with those reported previously [6–10]. These phases were also reported to be associated with a Tc value of about 110 K.

A new structure was identified in samples prepared with the nominal starting composition of TlCa₃BaCu₃O₇, which exhibited a T0 at 123 K and a T0, sets at 155 K as described above. EDS measurements showed that the sintered samples (TlCa₃BaCu₃O₇), were mainly of a composition ratio of Tl, Ca, Ba and Cu varying from 1:2:3:4 to 1:2:3:4. Two mirror planes and one four-fold axis were found.
in the convergent beam electron diffraction (CBED) pattern along the [001] direction of the grain with the composition ratio of 1:2:3:4 as shown in fig. 3. This pattern reveals a 4mm symmetry in the diffraction group and the corresponding point groups are either 4mm or 4/mm. Careful examination of CBED patterns along the [100] and [310] directions indicated that they are of 2mm symmetry. It is therefore concluded that the structure is of the 4/mmm point group. Combined with the analyses of electron diffraction patterns along [100], [110], [001] and [310] directions, the space group was determined to be I4/mcm. The lattice parameters of the tetragonal phase were determined to be \( a = b = 0.557 \text{ nm} \) and \( c = 3.77 \text{ nm} \). High resolution lattice images of the 1:2:3:4 phase along the [110] direction, shown in fig. 4, clearly demonstrate that the phase is primarily of ten-subcell structure. It is to be noted that a strong (1 TO) diffraction spot is evident in the [110] pattern for the 1:2:3:4 phase, whereas it is forbidden for the so-called 2:2:2:3 phase. A probable structure model involving four layers of Cu–O is proposed. The sequence of cations along the c axis is suggested to be Tl–Ba–Cu–Ca–Cu–Ba–Cu–Ca–Cu–Ba–Tl. Polytypes of the phase with four- as well as with five-subcell structures were observed. The four-subcell structure is thought to correspond to the phase with the composition ratio 1:2:2:3 determined by EDS. The details of the structural analysis will be published elsewhere [11].

In summary, sintering of TlCa\(_{x}\)Ba\(_{2}\)Cu\(_{3}\)O\(_y\) (\( x = 3, 4 \)) at 880°C for a short time in O\(_2\) ambient followed by air quench results in the formation of a superconducting phase with zero resistance around 123 K and \( T_{\text{onset}} \) at 155 K. Bulk superconductivity above 120 K is reflected in the DC magnetization data. Based on the TEM and XRD analyses, the predominant phase was found to be a body-centered tetragonal structure \( (a = b = 0.557 \text{ nm}, c = 3.77 \text{ nm}) \) with a space group of I4/mcm. As determined by EDS, the composition ratio of Tl, Ca, Ba, Cu for the phase is 1:2:3:4. A probable structure model involving four-layers of Cu–O interposed between Tl–O layers is proposed.

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**References**


