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LETTERS TO THE EDITOR

The Variation of Microstructure for the $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ Phase with T_c of 119 and 127 K

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We report the synthesis, superconducting properties, X-ray diffraction, and microstructure of the $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ phase having T_c of 119 K (an as-synthesized sample) and 127 K (a vacuum-annealed sample). The electron diffraction and [010] bright field image of the 119-K phase indicate a nearly perfect periodicity along the *c*-axis of $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$. In contrast, the 127-K phase exhibits a significant change in microstructure, where intergrowth defects of $Tl_2Ba_2Cu_3Cu_4O_{12-\delta}$ and $Tl_2Ba_2Ca_2Cu_3O_{9-\delta}$ are observed for this vacuum-annealed sample. These kinds of intergrowth defects arising from the unavoidable loss of thallium during the high-temperature (750°C), extended vacuum annealing (10 days) and the resulting oxygen nonstoichiometry appear to play an important role in the enhancement of T_c from 119 to 127 K. © 1992 Academic Press, Inc.

1. Introduction

Soon after the discovery of superconductivity in the Tl-based compounds by Sheng and Hermann in 1988 (*1*, *2*), Parkin *et al.* (*3*) have improved the T_c up to 125 K of $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ (Tl-2223); this system exhibits the highest T_c yet found of any family of superconducting cuprates discovered to date. Due to the natural volatility of thallium, the synthesis of single phase Tl-2223 material with a consistently high T_c is difficult to obtain. However, such major problems have recently been overcome in two important areas. First, Kikuchi *et al.* (*4*) and Liu *et al.* (*5*, *6*) have synthesized a mono-

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phasic Tl-2223 phase by using the compositions $Tl_{2-x}Ba_2Ca_{2+x}Cu_3O_{10-\delta}$ ($0.2 \leq x \leq 0.4$), reflecting substitution of the Ca ions into the Tl sites. Secondly, a small, but reproducible increase in T_c above 125 K has been reported for the Tl-2223 phase subjected to extended vacuum annealing at temperatures around 700 ~ 800°C (*7–9*). In related developments, Martin *et al.* (*10*) and Maignan *et al.* (*11*) have found that both the superconductivity and microstructure of the $Tl_2Ba_2CaCu_2O_{8+\delta}$ and $Tl_2Ba_2CuO_{6+\delta}$ phases were greatly affected by high-temperature (≥400°C) annealing. These authors (*10, 11*) also observed a splitting of the crystal and a surface decomposition resulting in an amorphous surface layer.

Because of the obvious importance in determining which microscopic characteristics favor superconductivity at these highest temperatures, we have studied the superconductivity and microstructure of the Tl-2223 phase both before and after vacuum annealing.

2. Experimental

High-purity powders of Tl_2O_3, BaO_2, CaO, and CuO were weighed in the appropriate proportions to constitute the nominal composition of $Tl_{1.6}Ba_2Ca_{2.4}Cu_3O_{10-\delta}$. The powders were then mixed using a mortar and pestle and pressed into a pellet (10 mm in diameter and 3 mm in thickness) under a pressure of 5 ton/cm^2. The pellets were wrapped in gold foil (to prevent loss of thallium at elevated temperatures) and sintered at 910°C for 3 hr in oxygen. After sintering, the furnace was cooled to room temperature at a rate of 5°C/min. One of the as-synthesized pellets was then wrapped in gold foil, encapsulated in an evacuated quartz tube (oxygen pressure ~10^{-4} Torr), and annealed at 750°C for 10 days.

The magnetic properties of the samples were measured (field cooled) in an applied magnetic field of 10 G using a Quantum Design (MPMS) SQUID magnetometer. The powder X-ray diffraction (XRD) spectra were obtained from a Philips diffractometer (CuK_α radiation) by step scanning over an angular range of $10° \leq 2\theta \leq 100°$, in increments of 0.02° (2θ). Lattice constants were determined with the refinement program DBW 3.2 (*12*). The electron diffraction and lattice fringes studies were performed with a JEM-120CX electron microscope fitted with a side goniometer (±60°). The crystallites of the samples were dispersed, without any mechanical crushing of the sample, in alcohol and deposited on a holey carbon film.

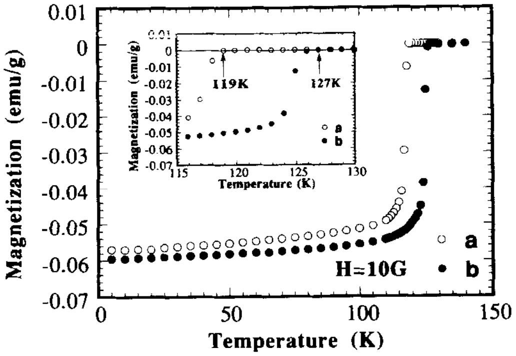

FIG. 1. Temperature dependence of the field cooled (10 G) magnetization of the (a) as-synthesized and (b) vacuum-annealed samples with the nominal composition of $Tl_{1.6}Ba_2Ca_{2.4}Cu_3O_{10-\delta}$. The inset provides greater detail of the magnetization of the samples over the temperature range 115 ~ 130 K.

3. Results and Discussion

In Fig. 1 we show the temperature dependence of the field-cooled (10 G) magnetization of a (a) as-synthesized and (b) vacuum-annealed samples with the nominal composition of $Tl_{1.6}Ba_2Ca_{2.4}Cu_3O_{10-\delta}$. The onset temperatures of diamagnetism of the as-synthesized and vacuum-annealed samples appeared at 119 and 127 K, respectively (see inset, Fig. 1). Moreover, the

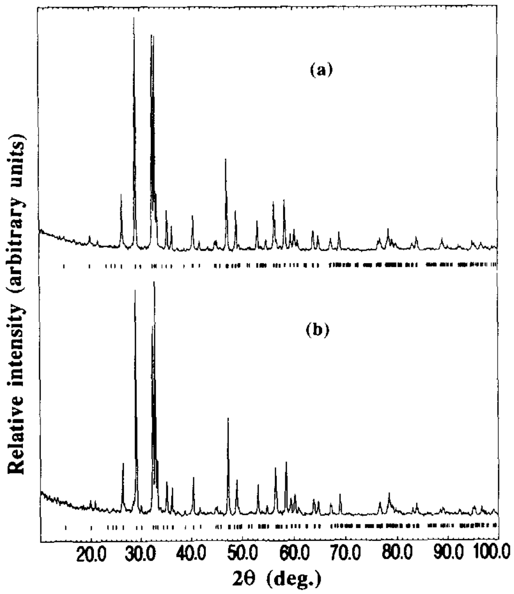

FIG. 2. XRD patterns of the (a) as-synthesized and (b) vacuum-annealed samples with the nominal composition of $Tl_{1.6}Ba_2Ca_{2.4}Cu_3O_{10-\delta}$. Computed Bragg angles derived from the $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ phase are symbolized by marks.

superconducting volume fractions for samples before (Fig. 1a) and after (Fig. 1b) vacuum annealing remain approximately constant (~50% at 5 K of full diamagnetism), which reveals that the T_c of the as-synthesized can be effectively enhanced without detriment to the bulk superconducting effect.

In Fig. 2 we show the XRD patterns of the (a) as-synthesized and (b) vacuum-annealed samples with the nominal composition of $Tl_{1.6}Ba_2Ca_{2.4}Cu_3O_{10-\delta}$. Almost all of the XRD peaks in the as-synthesised sample (Fig. 2a) could be indexed to the Tl-2223 phase having a tetragonal unit cell (*I4/mmm*) with lattice constants of a = 3.8522(2) Å and c = 35.628(2) Å. The computed Bragg angles derived from the $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ phase having these lattice parameters are also given in Fig. 2. Following the vacuum annealing process, the XRD pattern of the sample (Fig. 2b) was superficially very similar to that of as-synthesized sample; however, a careful examination of the patterns revealed a slight contraction of the a lattice constant (3.8493(2) Å) and a small enlargement of the c lattice constant (35.701(2) Å) for the annealed sample.

The microstructure of the as-synthesized and vacuum-annealed samples was systematically investigated by electron diffraction in order to test for homogeneity and crystallinity of the phase. The electron microscopy observations were performed on about 20 crystallites for each sample.

(*a*) *The As-Synthesized Sample* (T_c = *119 K*)

The investigation of numerous crystals and the reconstruction of the reciprocal space attest to the homogeneity of the sample. The particles are well crystallized and the electron diffraction patterns exhibit sharp reflections; such a sample of [010] electron diffraction pattern is shown in Fig. 3a ($h\ 0\ l: h + l = 2n$ in agreement with the I-type space group of the Tl-2223 structure). The corresponding bright field images give evidence of a very regular, periodic stacking of the layers along the c-axes; in fact, very few intergrowth defects are observed, less than five events per crystal. One example from such a crystal is shown in Fig. 3b; only two defective members (as indicated by the arrow in Fig. 3b) $TlBa_2Ca_2Cu_3O_{9-\delta}$ (Tl-1223) appear in a regular matrix.

(*b*) *The Vacuum-Annealed Sample* (T_c = *127 K*)

The electron microscopy study of the vacuum-annealed samples show that the crystals exhibit a lamellar morphology resulting from a "splitting" of the crystal, similar to that reported earlier for the annealed $Tl_2Ba_2CaCu_2O_8$ (Tl-2212) and $Tl_2Ba_2CuO_6$ (Tl-2201) samples (*10, 11*). Moreover, amorphous areas are frequently observed on the

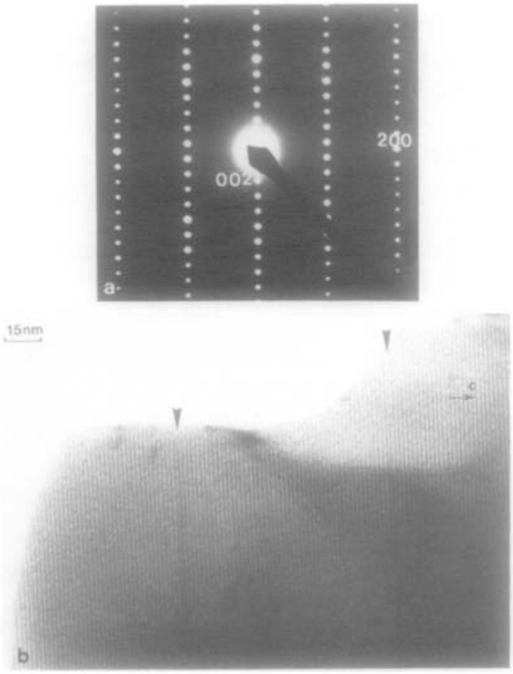

FIG. 3. [010] (a) Electron diffraction and (b) bright field image of the as-synthesized sample: a highly regular stacking of the layers is observed along the c-axis. Black arrows indicate the presence of Tl-1223 defective members; this is a rare phenomenon in the sample.

crystal edges. The electron diffraction patterns exhibit, in a quite systematical way, diffuse streaks and/or extra reflections along the c-axis. A typical example is shown in Fig. 4, where the superposition of two systems of reflections is clearly observed. The first one (as shown by the small white arrow in Fig. 4) corresponds to a c-parameter close to 36 Å and $h + l = 2n$ as the condition of reflection. The second one (as illustrated by white triangles in Fig. 4) corresponds to a c-parameter close to 15.5 Å and no condition of reflection. Such electron diffraction patterns are consistent with the coexistence, in the matrix, of Tl-2223 and Tl-1223 members (respectively), in aleatory sequences. The bright field images confirm the existence of numerous defective members. Two examples are shown in Fig. 5. The first image (Fig. 5a) shows the presence of $Tl_2Ba_2Ca_3Cu_4O_{12-\delta}$ (Tl-2234) members (as indicated by black triangles in Fig. 5a) in a quite regular (about one every eleven Tl-2223 members); one Tl-1223 member is also observed (as shown by the white triangle in Fig. 5a). The second image (Fig. 5b) shows the intergrowth of Tl-2223 and Tl-1223 members (some of these are labelled by a curled arrow) in a highly irregular manner. Both members, Tl-2234 and Tl-1223, correspond to thallium-poor compositions with regard to the nominal composition of our samples. As previously reported (*10*), the annealing of thallium cuprates at high temperature ($T > 400°C$) almost invariably involve thallium loss from the sample. The present study shows that thallium and oxygen nonstoichiometry, resulting from such extended annealing, appear to be accommodated in the matrix through the formation of intergrowth defects. Indeed, the weight loss of ~5%, corresponding to the contributions from thallium and oxygen, was discovered in our vacuum-annealed sample as compared to the as-synthesized sample (*9*). This result indicates that the thallium

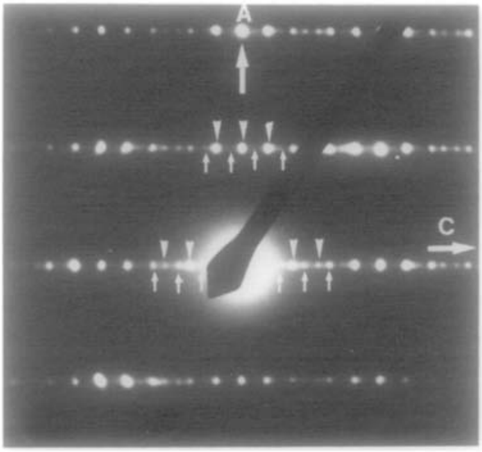

FIG. 4. [010] Electron pattern of the vacuum-annealed samples exhibiting a superposition of two systems. The small arrows indicate a Tl-2223 system and the white triangles a Tl-1223 system.

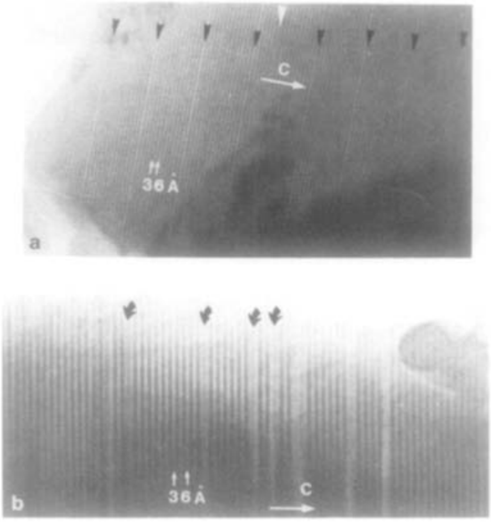

FIG. 5. Bright field images of the annealed sample where (a) Tl-2234 defective members (black arrows) arise in a quite regular way in the Tl-2223 matrix and (b) numerous Tl-1223 defective members are intergrown in an aleatory way with the Tl-2223 members.

loss from the rock-salt layers of the vacuum-annealed sample may play a very important role in the development of intergrowth and that both oxygen nonstoichiometry and these intergrowth defects are crucial to the increase of T_c's from 119 to 127 K.

Acknowledgments

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