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Zero resistance up to 162 K in a multiphase Tl-Ca-Ba-Cu-O system

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Zero resistance was recorded at temperatures up to 162 K for multiphase samples with nominal composition $TlCa_4Ba_3Cu_6O_x$. The compound with zero resistance at temperatures higher than 140 K could be repeatedly fabricated in a time span of about two months. The formation of the compound was found to be critically dependent on the starting stoichiometry, sintering temperature, and time as well as cooling rate. The compound was tentatively identified to be $TlCa_2Ba_3Cu_4O_x$, tetragonal in structure with $a=b=0.394$ nm and $c=3.95$ nm and of $P4/mcc$ space group by transmission electron microscopy (TEM) and electron energy dispersive spectrometry analysis. High-resolution TEM images showed that the phase is primarily of a ten-subcell structure which is consistent with a structure model with four Cu-O layers interposed between Tl-O layers.

High-temperature superconductivity has recently been discovered in the Tl-Ca-Ba-Cu-O system.[1-6] The crystal structure of a Tl-Ca-Ba-Cu-O compound in $T_c(\text{onset})=155$ K and $T_c(0)=123$ K superconducting specimens was previously characterized by transmission electron microscopy (TEM).[6,7] Convergent-beam electron diffraction (CBED) analysis established the presence of a phase with $P4/mcc$ space-group symmetry. The lattice parameters of the phase were determined to be $a=b=0.394$ nm and $c=3.95$ nm. The phase was found to consist primarily of a ten-subcell structure by both high-resolution lattice imaging and diffraction pattern analysis. A subcell is herein defined as a tetragonal cell with metal atoms occupying the corners of the cell with $a=b=0.394$ nm and c about one-tenth of the length of the tetragonal unit cell of the phase. The composition of the grains with the ten-subcell structure being predominant was measured by energy dispersive spectrometry (EDS) to be $TlCa_2Ba_3Cu_4O_x$, which is hereinafter referred to as the 1:2:3:4 phase. Polytype structures, consisting of four- and five-subcell structures were also observed. The five-subcell structure was identified to be of $P4/mmm$ space-group symmetry with $a=b=0.394$ nm and $c=1.97$ nm. Based on the $P4/mcc$ space group and the observed lattice images along the [100], [110], and [001] directions of the phase, as well as the composition ratio being 1:2:3:4, a probable structure model involving four layers of Cu-O interposed between the Tl-O layers was proposed. The sequence of cations along the c axis was suggested to be Tl-Ba-Cu-Ca-Cu-Ba-Cu-Ca-Cu-Ba-Tl.[6,7]

It was pointed out that a direct correlation between the copper-oxygen layers and the superconductivity of the material was apparent. The more copper-oxygen layers, the higher the T_c. For Tl-containing compounds, the T_c's were found to be 80, 110, and 125 K for compounds with one, two, and three Cu-O layers, respectively. It was predicted that a four-layer thallium compound would be superconducting at 150 to 160 K.[8] The 1:2:3:4 phase, which was proposed to be of a four-layer structure, was present in all samples exhibiting $T_c(\text{onset})=155$ K and $T_c(0)=123$ K, whereas it was absent in all specimens with $T_c(0)=113$ K.[7] The results strongly suggested that the phase is indeed a high-T_c superconducting phase with an exciting possibility that superconducting transition occurs at 155 K for this phase. In this Brief Report, we report possible superconductivity with zero resistance up to 162 K in a Tl-Ca-Ba-Cu-O system. The discovery was made during a deliberate attempt to fabricate superconducting compounds with more than three Cu-O layers interposed between Tl-O layers.

Appropriate amounts of high-purity $CaCO_3$, $BaCO_3$, and CuO powders were weighed stoichiometrically, ball-milled, filtered, dried, and ground in an agate mortar. Differential thermal analysis (DTA) showed that reactions of the well-mixed Ca-Ba-Cu-O powders occurred in the temperature range 920–930 °C. The results provided guidance for selecting the calcining temperature. The well-mixed oxides were, therefore, calcined at 925 °C in air for 12 h with several intermittent grindings to obtain a more homogeneous mixture of Ca-Ba-Cu-O powders. The presence of $BaCuO_2$ and CaO was found in calcined samples by x-ray diffraction. The Ca-Ba-Cu-O powders were then mixed with the appropriate amount of Tl_2O_3 to yield mixtures with nominal compositions of $TlCa_3BaCu_3O_x$, $TlCa_2Ba_3Cu_4O_x$, and $TlCa_4Ba_3Cu_6O_x$. The mixtures were ground and pressed into a cylindrical pellet, 2 mm in thickness and 8 mm in diameter, under a pressure of about 2 ton/cm^2. The pellets were then sintered in an enclosed gold crucible in flowing O_2 to alleviate possible decomposition of Tl_2O_3 to Tl_2O and O_2 for different periods of time. The annealing temperatures ranged from

880 to 990 °C. The samples were then cooled by furnace cooling (3–5 °C/min), controlled cooling (18 °C/h) or cooling in air. DTA was conducted with a Du Pont Instruments 1090B thermal analyzer. A standard four-point probe was used for electrical resistance measurement. Electrical contacts to the samples were made by fine copper wires attached to the samples with a conductive silver paint. The temperature was recorded with a calibrated platinum resistor close to the sample. Resistances of some of the samples were also measured by the van der Pauw technique. The average values of voltages and currents across the two adjacent terminals were obtained by switching the electrical leads to minimize the shape effect. The detection limit for zero resistance was 10^{-6} Ω. In order to clarify possible effects of the cooling rate on the phase transition, the temperature measurement was also calibrated with known 90-K Y-Ba-Cu-O, 80- and 110-K Bi-Sr-Ca-Cu-O, and 123-K Tl-Ca-Ba-Cu-O compounds. In all instances, a temperature difference of less than 3 K was found for zero resistance between samples subjected to slow and fast cooling. The slow and fast cooling herein refer to cooling from room temperature to about 100 K in about 1 h and 15 min, respectively. Magnetization data were taken in an automatic superconducting quantum interference device (SQUID) magnetometer (quantum design); x-ray diffraction (XRD) analysis was performed by a Philips x-ray diffractometer. JEOL-2000EX and JEOL-2000FX transmission electron microscopes operating at 200 kV were used. An EDAX 9100/70 energy dispersive spectrometer (EDS) was used to measure the atomic concentrations of the samples. Quantitative analysis was performed using standard techniques with concentration-absorption-fluorescence (ZAF) correction factors from the EDAX 9100 program developed by EDAX laboratories.[9]

Zero resistance up to 162 K was recorded for samples with nominal composition $TlCa_4Ba_3Cu_6O_x$, annealed at 970 °C for 4.5 min followed by furnace cooling. In samples annealed at 990 °C for 4.5 min followed by furnace cooling, zero resistance was achieved at 152 K. Electrical resistance versus temperature curves for selected samples are plotted in Fig. 1. The temperatures at which zero resistance was recorded for these samples are listed in Table I. The results demonstrated that zero resistance at temperatures higher than 130 K was repeatedly observed for many samples. However, efforts to obtain evidence of magnetic susceptibility above 123 K were not successful. The absence of the Meissner effect is probably related to the filamentary nature of the compound. Some samples were found to be stable against repeated electrical measurements. Zero resistance at temperatures above 130 K could be repeated up to one week. Others lost zero resistance above 140 K following subsequent handling. The exact cause for the instability of some of the samples is yet to be clarified. As the samples were subjected to slow cooling during electrical measurement, zero resistance was recorded at about 120 K in contrast to the zero-resistance temperatures higher than 140 K measured with fast cooling. Since a similar cooling rate effect was not found for 90 K Y-Ba-Cu-O, 80- and 110-K Bi-Sr-Ca-Cu-O and 123-K Tl-Ca-Ba-Cu-O compounds, in the absence of Meissner effect, it is conjectured that a phase transition occurred at temperatures higher than the highest superconducting temperature (125 K) reported previously.

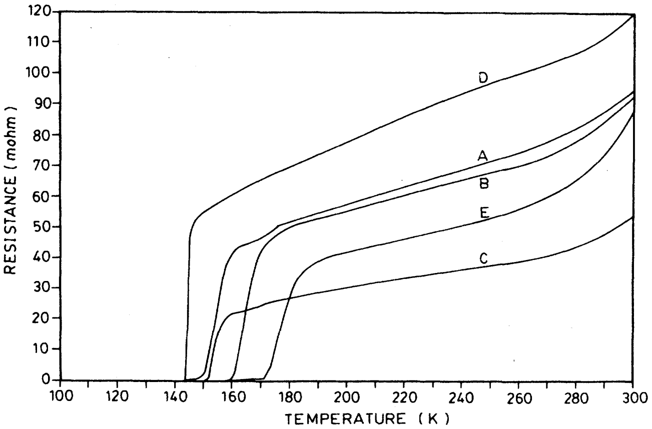

FIG. 1. Electrical resistance vs temperature curves for selected samples. The designation of samples is listed in Table I.

None of the samples prepared with starting compositions $TlCa_3BaCu_3O_x$ and $TlCa_2Ba_3Cu_4O_x$ exhibited zero

TABLE I. Temperatures at which the fabricated samples showed zero resistance. The samples that were used for the electron microscopy analysis are marked by an asterisk (furnace cooled).

Sample number	File number	Sintering condition	Zero resistance
	*L*58	950 °C, 4.5 min	122
	*L*108	965 °C, 4.5 min	134
	*L*131	965 °C, 10 min	132
	*L*56*F*	970 °C, 4.5 min	130
	*L*55*F*	970 °C, 4.5 min	133
	*L*55*B*	970 °C, 4.5 min	134
A	*L*54*	970 °C, 4.5 min	146
B	*L*56*B*	970 °C, 4.5 min	160
E	*L*71*B*	970 °C, 4.5 min	162
	*L*72-2*	970 °C, 4.5 min	140
	*L*79−1*F*	970 °C, 4.5 min	132
	*L*100	970 °C, 4.5 min	138
	*L*108*	970 °C, 4.5 min	134
	*L*110	970 °C, 4.5 min	140
	*L*113	970 °C, 4.5 min	140
	*L*126	970 °C, 4.5 min	133
	*L*135	975 °C, 10 min	135
	*L*136	975 °C, 10 min	137
	*L*140*	980 °C, 10 min	158
	*L*141	980 °C, 10 min	135
	*L*142	980 °C, 10 min	156
	*L*143	980 °C, 10 min	137
	*L*144	985 °C, 10 min	146
	*L*145	985 °C, 10 min	133
D	*L*64*C*	990 °C, 4.5 min	142
C	*L*64*B*	990 °C, 4.5 min	152

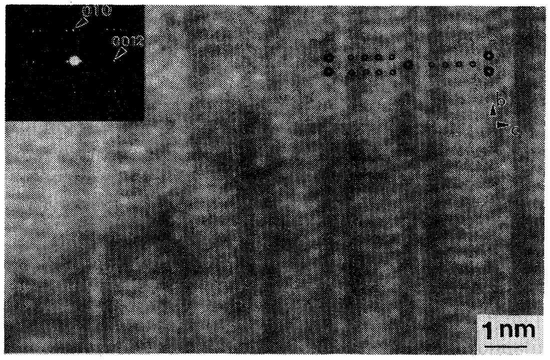

FIG. 2. High-resolution (HR) lattice image showing the ten-subcell structure of the 1:2:3:4 phase along [100] direction. Inset, [100] diffraction pattern.

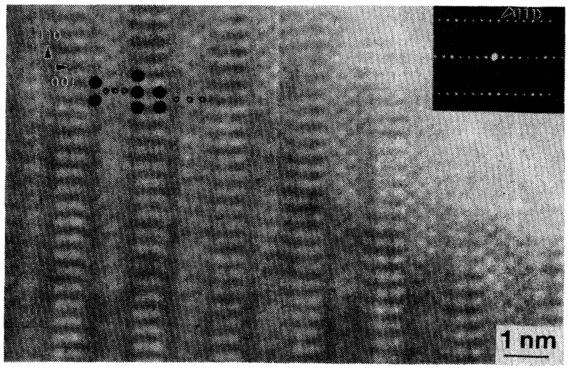

FIG. 3. HR image of a 2:2:2:3 phase along [100] direction. Inset, [100] diffraction pattern.

resistance at temperatures above 123 K. Annealing at temperatures lower than 950 °C, air quenching and slow cooling (18 °C/h) were found to be detrimental to the superconducting properties of the $TlCa_4Ba_3Cu_6O_x$ samples. Annealing time was also found to strongly affect the superconducting properties of various samples. As a rule, sintering of samples with an overall composition always failed to produce a large amount of the phase with the same composition.

The 1:2:3:4 phase was detected in samples with zero resistance at above 140 K and examined by TEM. An example is shown in Fig. 2. $BaCuO_2$ was detected by both TEM and XRD in all sintered $TlCa_4Ba_3Cu_6O_x$ samples. The structure of the 1:2:3:4 phase is distinctly different from the so-called 2:2:2:3 phase observed in samples exhibiting $T_c(0)$ at about 110 K.[3,4,10–14] The 2:2:2:3 phase was detected by both electron diffraction and EDS in samples prepared under different conditions which will be described in detail elsewhere.[15] A high-resolution image of the structure of the 2:2:2:3 phase along the [100] direction is shown in Fig. 3. Based on the $P4/mcc$ space group and the observed lattice images along [100], [110], and [001] directions of the phase as well as the composition ratio being 1:2:3:4, a probable structure model involving four layers of Cu-O was proposed. The sequence of cations along the c axis is suggested to be Tl-Ba-Cu-Ca-Cu-Ba-Cu-Ca-Cu-Ba-Tl. The schematical diagrams of the probable structures of 1:2:3:4 and 1:2:2:3 phases are highlighted in Figs. 2 and 3, respectively. The diagrams were drawn with the assumption that the dark dots correspond to metal atoms. We note that identification of exact positions of metal atoms by lattice imagings requires extensive image simulation with known electrical-optical and specimen parameters. However, by a comparison of the lattice images of 1:2:3:4 and 2:2:2:3 compounds, layers with the heavy Tl atoms could be identified since the 2:2:2:3 compound was well characterized previously.[11]

As described earlier, it was predicted that a four-layer thallium compound would be superconducting at 150 to 160 K.[8] In this context, the 1:2:3:4 phase, which was proposed to be of a four-layer structure and found in all samples exhibiting T_c-zero above 140 K, is likely to be the phase responsible for zero resistance at such high temperatures.

In summary, zero resistance up to 162 K was observed in multiphase samples with nominal composition $TlCa_4Ba_3Cu_6O_x$. The compound with zero resistance higher than 140 K could be repeatedly fabricated. The formation of the high-T_c superconducting compound was found to be critically dependent on the starting stoichiometry, sintering temperature, and time as well as cooling rate. The compound was tentatively identified to be $TlCa_2Ba_3Cu_4O_x$, tetragonal in structure with $a=b=0.394$ nm and $c=3.95$ nm and of $P4/mcc$ space group by TEM and EDS analysis. High-resolution TEM images showed that the phase is primarily of a ten-subcell structure which is consistent with a structure model with four Cu-O layers interposed between Tl-O layers.

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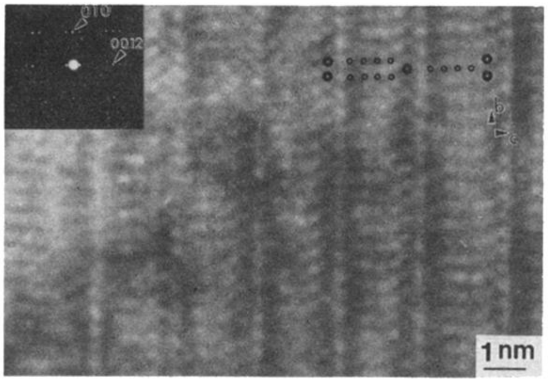

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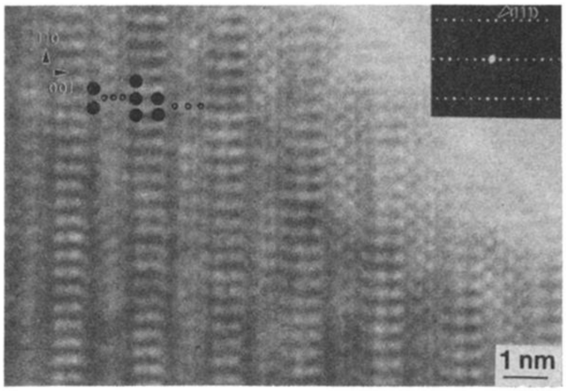

FIG. 3. HR image of a 2:2:2:3 phase along [100] direction. Inset, [100] diffraction pattern.