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Superconductivity Studies on Tl–*M*–Ba–Cu–O (*M* = Ce, Th, Pr, Tb, Pb, and Te) System[1]

K. A. THOMAS, U. V. VARADARAJU, AND G. V. SUBBA RAO

Materials Science Research Centre, Indian Institute of Technology, Madras 600 036, India

AND C. V. TOMY AND S. K. MALIK

Tata Institute of Fundamental Research, Bombay 400 005, India

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Superconductivity with a $T_{c,\mathrm{zero}}$ at 75 ± 1 K has been observed in Tl–M–Ba–Cu–O (M = Ce, Th) system for a starting nominal composition of $Tl_{2.2}M_1Ba_2Cu_3O_y$. X-ray data show that the compounds are multiphasic with the 2201 phase as the predominant one which is responsible for superconductivity. Lower T_c values are noted for M = Pr and Tb. Only metallic behavior is observed for pure $Tl_2Ba_2Cu_1O_y$ and M = Pb or (Pb + Sb) or Te containing phases down to 15 K. © 1990 Academic Press, Inc.

Introduction

The discovery of superconductivity in the Tl–Ba–Cu–O system has generated a lot of research activity in thallium-based cuprates. This resulted in the synthesis and characterization of a series of phases having the general formula $Tl_mBa_2Ca_{n-1}Cu_nO_{m+2(n+1)}$ (m = 1 or 2; n = 1–4) and the property of high temperature superconductivity (HTSC) (*1–5*). The compound $Tl_2Ba_2Ca_2Cu_3O_{10}$ (2223) possesses the highest known transition temperature (T_c) of 125 K. The crystal structures of these phases are layer-type with tetragonal symmetry (*4, 5*).

The phase with m = 2 and n = 1, viz., $Tl_2Ba_2Cu_1O_6$ (2201) is a very interesting compound in that it does not contain calcium and the single CuO_2 plane is sandwiched between the BaO layers with the sequence, TlO–BaO–CuO_2–BaO–TlO. In this respect, it resembles the single layer Tl cuprate $TlBa_2CuO_{4.5}$ (1201) and La_2CuO_4, which have the layer sequence, TlO–BaO–CuO_2–BaO and LaO–CuO_2–LaO, respectively. The compound 2201 is relatively easy to prepare and has a tetragonal structure with a fairly large c lattice parameter (a = 3.866 Å; c = 23.24 Å) due to the fact that it is a bilayer thallium cuprate. An orthorhombically distorted structure ($a_o \approx b_o \approx \sqrt{2}a_t$; $c_o \approx c_t$) can also exist (*6, 7*). The compound is metallic with low resistivity. The superconducting properties, how-

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ever, are at variance and, in the literature, T_c values ranging from 0 to 80 K have been reported (*4–8*). Details of preparative conditions, which will affect the oxygen stoichiometry (i.e., y in $Tl_2Ba_2CuO_{6-y}$) are assumed to be responsible for the above variations in the reported T_c. Recent studies by Shimakawa *et al.* (*7*) indicate that a $T_{c,zero}$ (zero resistance) of 53 and 50 K respectively are exhibited by both the tetragonal and the orthorhombic polymorphs of 2201 and a decrease in the value of oxygen content (Δy) of 0.037 can induce superconductivity in a nonsuperconducting phase. The 2201 phase, similar to the other thallium cuprates, is amenable to chemical substitutions at Tl and Ba sites. In addition, several meta or unstable phases can be stabilized by suitable substitution. Thus, Ku and Wu (*8*) report a $T_{c,zero}$ of 50 K in $Tl_2Ba_{2-x}La_xCuO_{6+y}$, x = 0.2. It is now known that many of the HTSCs including the thallium cuprates are near the metal-insulator phase boundary and superconductivity is induced with T_c increasing smoothly from 0 K near the metal-insulator phase boundary to a maximum value *inside* the metallic region. The phase boundary can be reached either by changes in the oxygen stoichiometry and/or by chemical substitutions.

Recently Wang *et al.* (*9*) reported a reproducible 90 K superconductivity ($T_{c,zero}$ = 80–83 K) in thallium cuprates with the nominal starting composition, $Tl_{2.2}Ba_2Ce_1Cu_3O_y$. It is interesting to note that compositions with Ce >or< 1.0 were found to give a lower T_c (< 20 K). The phase responsible for HTSC has not been clearly identified by Wang *et al.* but they found X-ray lines due to 2201 phase in addition to lines from the impurity phases (CuO and $BaCeO_3$). It is possible that the *proper* 2201 phase gets stabilized by the substitution of Tl^{3+} by Ce^{4+} and also the metal-insulator phase boundary is suitably shifted by the optimum concentration of Ce (and thus the oxygen content (y)) to give rise to HTSC. With this in view, we have taken up a study of the system M–Tl–Ba–Cu–O with M = Ce, Th, Pr, Tb, Pb, and Te. Our results show that a reproducible $T_{c,zero}$ of 75 ± 1 K attributable to the 2201 phase can be obtained for $M_{1.0}$ = Ce and Th. However, Pr and Tb produce a lower T_c whereas Pb, Te, and the combination ($Pb_{0.5}$ + $Sb_{0.5}$) as well as the pure 2201 phase do not show a T_c above 15 K, though all the phases show metallic behavior.

Experimental

The compounds were prepared using high purity Tl_2O_3 (Cerac, UK: 99.99%), $BaCO_3$ (Cerac, UK: 99.9%), CeO_2 (IRE, India: 99.99%), ThO_2 (Fluka: 99.9%), Sb_2O_3 (Ventron: 99.99%), PbO_2 (BDH: 99.9%), TeO_2 (Aldrich: 99.9%), and CuO (Cerac: 99.99%). PrO_2 and TbO_2 were prepared by the solvolytic disproportionation of Pr_6O_{11} (IRE: 99.99%) and Tb_4O_7 (IRE: 99.99%) in acid solutions and characterized by X-ray diffraction (*10*). A master composition of $Ba_2Cu_3O_y$ was prepared using $BaCO_3$ and CuO by heating at 900°C in air for a minimum of 48 hr with several intermittent grindings and heatings. Appropriate amounts of Tl_2O_3 and MO_2 (or Sb_2O_3) were then added to give a nominal composition, $Tl_{2.2}MBa_2Cu_3O_y$. The mixture is then thoroughly ground and pressed into pellets (8 mm diameter, 1–2 mm thick) which are introduced into a preheated tubular furnace (870–900°C) with the oxygen flow. The heating time was 3–5 min. The samples were then pulled out of the hot zone of the furnace and allowed to cool to room temperature by furnace shutoff maintaining the flow of oxygen.

In the Th_x–Tl–Ba–Cu–O system, compounds with x = 0.0, 0.25, 0.50, and 0.75 have also been prepared. Pure $Tl_2Ba_2CuO_6$ (2201) phase has also been prepared starting from Tl_2O_3, $2BaO_2$ (Cerac: 99.99%), and CuO (using similar heat-treatment conditions but without recourse to the master composition). Powder X-ray diffraction

(XRD; Philips unit, Cu$K\alpha$ radiation, Ni filter) has been employed for the phase identification. The lattice parameters were calculated by least-squares (LSQ) fitting of high angle lines using a computer program. Theoretical XRD patterns with the intensities were generated using the Lazypulverix program for comparison with the observed ones. Four probe dc electrical resistivity measurements were made from room temperature down to 68 K using an indigenously fabricated setup with liquid N_2 or a closed cycle CTI Model 21C He refrigerator down to 15 K. Magnetization measurements were done on select samples using a Quantum Design Model 1822 MPMS SQUID magnetometer.

Results and Discussion

a. Structure and Stability

The samples are well-crystalline, black, and are stable under atmospheric conditions. For phases with M = Th, we notice slight melting of the samples under the preparative conditions presently employed, especially when $0.25 < x < 1.0$. The XRD patterns of all $Tl_{2.2}MBa_2Cu_3O_y$ phases revealed that they are multiphasic. When M = Ce and Th, the major phase could be indexed as 2201 ($Tl_2Ba_2CuO_6$) and CuO was always the impurity phase. In addition $BaCeO_3$ and ThO_2 respectively were also observed as the other impurity phases (Fig. 1). Wang *et al.* (*9*) also noted $BaCeO_3$ and CuO impurity phases in their studies. In the $Tl_{2.2}Th_xBa_2Cu_3O_y$ series of compounds we noted a decrease in the intensity of the ThO_2 lines as x decreases from 1.0 to 0.25. On the other hand, when M = Pr and Tb, the major phase lines correspond to 1212 type and not the 2201 type structure. When M = Pb, unequivocal indexing of the XRD patterns was not possible.

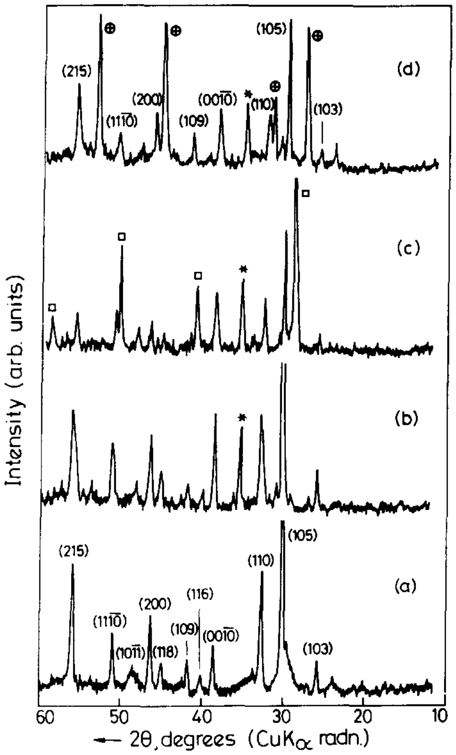

FIG. 1. Powder X-ray diffraction patterns of the phases with nominal compositions in the Tl–M–Ba–Cu–O system: (a) $Tl_2Ba_2Cu_1O_y$, (b) $Tl_{2.2}Ba_2Cu_3O_y$, (c) $Tl_{2.2}CeBa_2Cu_3O_y$, (d) $Tl_{2.2}ThBa_2Cu_3O_y$. The patterns can be indexed as the $Tl_2Ba_2CuO_y$ (2201) phases with minor impurity phases. (Impurity lines due to *, CuO; □, $BaCeO_3$; ⊕, ThO_2.)

The composition $Tl_{2.2}Ba_2Cu_3O_y$ also gave $Tl_2Ba_2Cu_1O_6$ (2201) as the major phase with CuO as impurity whereas $Tl_2Ba_2CuO_6$ prepared from Tl_2O_3, BaO_2, and CuO (nominal 2201) formed a single phase material (Fig. 1). The tetragonal lattice parameters presently obtained by LSQ fitting of (*hkl*) lines are a = 3.87 Å and c = 23.21 Å and are in good agreement with those reported in the literature (*5*).

b. Electrical and Superconducting Properties

All the phases in the system Tl–M–Ba–Cu–O including the pure 2201 phase were found to be metallic with low room temperature resistivities ($\rho_{300\ K}$ =

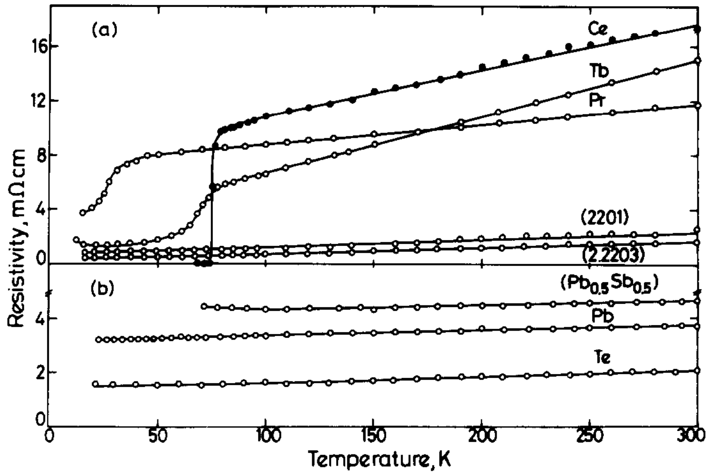

FIG. 2. Resistivity vs temperature plots for the phases with nominal composition, $Tl_{2.2}M_1Ba_2Cu_3O_y$; (a) M = Ce, Pr, and Tb; (b) M = Pb, Te and $(Sb_{0.5}Pb_{0.5})$. Data on nominal $Tl_{2.2}Ba_2Cu_3O_y$ and $Tl_2Ba_2CuO_6$ also included (a). As can be seen, the phase with M = Ce exhibits HTSC.

1–35 mΩ cm). Superconductivity is encountered for M = Ce, Th, Pr, and Tb. The Ce-containing phase showed a $T_{c,zero}$ value of 74 K (Fig. 2a) which is less than that reported (80–83 K) by Wang *et al.* (*9*). The Th-containing phase, presently synthesized for the first time, showed a $T_{c,zero}$ of 75 K (Fig. 3). The $T_{c,onset}$ values are ~80 and ~90 K respectively for M = Ce and Th phases.

Superconductivity is also shown for x = 0.25, 0.50, and 0.75 in the $Tl_{2.2}Th_xBa_2Cu_3O_y$ system. Even though the $T_{c,onset}$ (taken as the temperature at which significant departure fron the linear ρ-T behavior is noted)

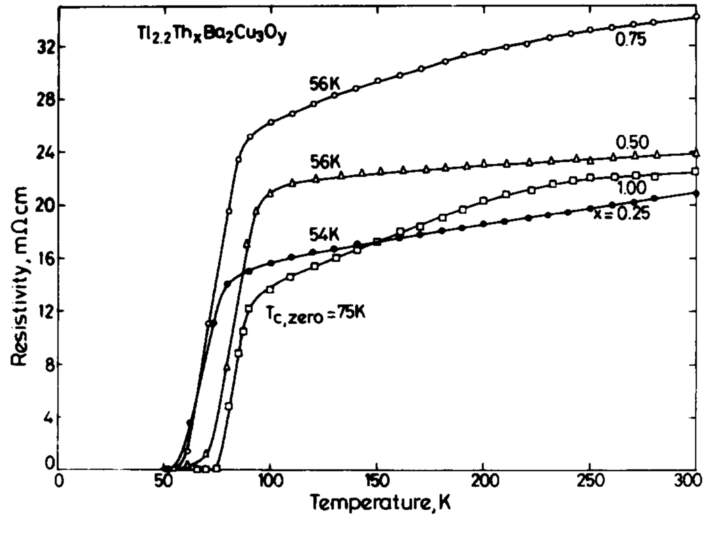

FIG. 3. Resistivity vs temperature plots for $Tl_{2.2}Th_xBa_2Cu_3O_y$ showing superconductivity for $x \geq 0.25$. Values of x and $T_{c,zero}$ are indicated.

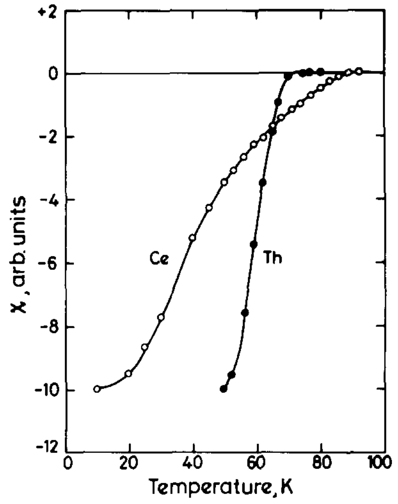

FIG. 4. Magnetic susceptibility (arbitrary units) vs temperature plots for the phases with nominal compositions $Tl_{2.2}MBa_2Cu_3O_y$; M = Ce and Th showing superconducting transitions.

values are in the 75–100 K region, the $T_{c,zero}$ values are lower. It is interesting, however, that $T_{c,zero}$ values are clustered in a narrow range (54–56 K) for $x < 0.75$ (Fig. 3). This behavior is similar to that noted by Wang *et al.* (*9*) for the $Tl_{2.2}Ce_xBa_2Cu_3O_y$ system ($x \leq 1.0$) and conclusively establish that a nominal concentration of $M_{1.0}$ (M = Ce or Th) is necessary to stabilize the 80 K superconductor.

Magnetic susceptibility studies done on $Tl_{2.2}MBa_2Cu_3O_y$ (M = Ce and Th) phases show that the superconductivity is bulk in nature (Fig. 4). The T_c value of 75 K (M = Th) determined from the temperature of diamagnetic onset agrees excellently with the $T_{c,zero}$ obtained by ρ-T measurements. For M = Ce, the T_c value of 85 K from χ-T data is larger than the $T_{c,zero}$ (74 K) from ρ-T data but compares well with that reported by Wang *et al.* (*9*). We also note that the transition with M = Ce is broader compared to that with M = Th.

The 2201 phases obtained from nominal compositions $Tl_{2.2}Ba_2Cu_3O_y$ and $Tl_2Ba_2CuO_6$ (see Experimental) were found to be only metallic and no superconductivity was encountered down to 15 K, the lowest temperature reached with our set up. Our findings are in agreement with those of several workers in the literature (*4, 7, 8, 11*). For the phases with M = Pr and Tb a clear drop in resistivity was noted at 35 and 75 K respectively indicating the onset of superconductivity (Fig. 2a). However, zero resistance has not been observed down to 15 K. For M = Pb, ($Pb_{0.5}Sb_{0.5}$) and Te in the $Tl_{2.2}MBa_2Cu_3O_y$ system, an almost temperature-independent resistivity behavior is noticed with no superconducting transition down to 15 K (Fig. 2b).

The room temperature resistivities of the phases which show superconductivity were found to be three–five times larger than nonsuperconducting but metallic phases, including the pure 2201 phase. This indicates the approach toward the metal-to-insulator phase boundary in the M-substituted compounds. However, the role of Ce and Th ions in the stabilization of HTSC phase is not clear. Also the importance of a nominal composition of $M_{1.0}$ is intriguing even though XRD clearly reveals that only part of Ce or Th is entering into the lattice, possibly at the Tl site. It is not clear whether doping by M ion is directly producing a decrease in charge carrier concentration (approaching insulator or semiconductor behavior) or indirectly affecting the oxygen stoichiometry in the $Tl_2Ba_2Cu_1O_{6+y}$ phase. Studies by Rao *et al.* (*12*) and Parise *et al.* (*13*) clearly showed that Pb substitutes at the Tl site as Pb ion in (Tl, Pb)–Sr–Ca–Cu–O systems. Wang *et al.* (*9*) mentioned that their preliminary Seebeck data indicate an n-type behavior for the $Tl_{2.2}Ce_1Ba_2Cu_3O_y$ phase indicating that these are electron superconductors.

As mentioned earlier in the case of Pr- and Tb-containing phases the major phase appears to be 1212 from XRD studies. In such a case, the phase should exhibit semiconductor behavior (*14*). However, it is possible that a second phase exists similar to that reported by Bourgault *et al.* (*15*) wherein partial substitution at the Tl and Sr sites simultaneously has been suggested with the composition $Tl_{1-x}Pr_xSr_{2-y}$ Pr_y-CuO_z. It is further suggested that Pr enters the lattice as Pr^{4+} at the Tl site and as Pr^{3+} at the Sr site. In the present case similar substitution at the Tl and Ba sites (instead of Sr) may be taking place. The observed metallic behavior and onset of superconductivity could be due to such a phase (the T_c value reported for the Sr compound is 30 K from χ-T measurements (*15*)).

Detailed Seebeck and Hall data will indeed throw light on the nature of the Ce- and Th-containing phases and HTSC. These studies are underway.

Conclusions

Our results show that superconductivity with $T_{c,zero}$ of 75 ± 1 K can be achieved in a starting nominal composition of the system $Tl_{2.2}M_1Ba_2Cu_3O_y$, for M = Ce and Th, but not when M = Pb or Te under the preparative conditions presently employed. Nominal $M_{1.0}$ is necessary to stabilize the 75 K phase and the $T_{c,zero}$ decreases to 54 K when M = Th and $x \leq 0.75$. Phases where M = Pr and Tb also exhibit a drop in resistivity below 70 K, but zero resistance is not achieved.

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