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Superconductivity studies on Tl–Th–Sr–Ca–Cu–O system

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Abstract. Superconductivity with a maximum $T_{c,zero}$ of 58 K for $x > 0.75$ has been observed in a nominal starting composition, $Th_xTl_2Sr_2Ca_2Cu_3O_y$. X-ray data show that the 1212 phase gets stabilized due to part substitution of Th at the Tl-site for $x \geq 0.25$; however, T_c is low for $x < 0.75$.

Keywords. Thallium; thorium; strontium; calcium; copper; oxides; superconductors.

1. Introduction

High T_c superconductivity in single and double layer thallium cuprates having the general formula $Tl_mBa_2Ca_{n-1}Cu_nO_{m+2(n+1)}$; $m = 1, 2$; $n = 1$–3 is now well known (Sheng *et al* 1988a, b; Parkin *et al* 1988a, b; Rao and Raveau 1989; Ramakrishnan and Rao 1989). The compound with $m = 2$ and $n = 3$ viz. $Tl_2Ba_2Ca_2Cu_3O_{10}$ (2223) possesses the highest known $T_{c,zero}$ of 125 K. These phases possess a layered structure with distorted rock salt-type layers of TlO and oxygen-deficient perovskite-type layers ($ACuO_{3-y}$) with A = (Ba, Ca). It is now well established that the Ca-site of the 1212 phase ($TlBa_2CaCu_2O_7$; $T_c = 80$ K) can be substituted either partly or fully by rare earths or Y to give isostructural phases (Manako *et al* 1988; Ganguli *et al* 1989; Rao *et al* 1989; Martin *et al* 1989). The fully substituted phases (e.g. $TlBa_2(Ln/Y)Cu_2O_7$) are not superconducting but semiconducting (Manako *et al* 1988; Ganguli *et al* 1989; Rao *et al* 1989; Martin *et al* 1989).

It is difficult to realize a 1212 phase in pure form in the Tl–Sr–Ca–Cu–O system. However it is possible to stabilize such a 1212 phase (with Sr) by partially substituting either (i) the Tl-site by Pb, Bi or Th (Subramanian *et al* 1989; Li and Greenblatt 1989; Thomas *et al* 1990a) or the Ca-site by Y or rare earth (Ganguli *et al* 1989; Rao *et al* 1989; Liang *et al* 1989; Sheng *et al* 1989; Thomas *et al* 1990a). Recently Rao *et al* (1989) have shown that the 1212 phase can also be stabilized without a calcium site occupancy, viz. phase of the type, $Tl_1Sr_{3-x}Ln_xCu_2O_y$. All the above phases are metallic and exhibit superconductivity. However, the $T_{c,zero}$ values do depend on the metal ion substituting at the Tl- or Ca-site (Ganguli *et al* 1989; Rao *et al* 1989; Subramanian *et al* 1989; Li and Greenblatt 1989; Liang *et al* 1989; Sheng *et al* 1989).

In our earlier studies (Thomas *et al* 1990a) we have shown that when Sm is substituted at the Ca-site in the Tl–Sr–Ca–Cu–O system a nominal composition of $x = 0.25$ is necessary and sufficient to stabilize the 1212 structure in a nominal composition $Sm_xTl_2Sr_2Ca_2Cu_3O_y$ and induce a $T_{c,zero}$ of 68 K. We thought it interesting to examine whether a similar behaviour would be exhibited by the nominal $Th_xTl_2Sr_2Ca_2Cu_3O_y$ system. The present studies show that indeed the 1212 superconducting phase gets stabilized with $T_{c,zero}$ of 58($\pm$ 1 K) for $x = 0.75$ and 1.00 but the $T_{c,zero}$ are lower for $x = 0.50$ and 0.25.

2. Experimental

Compounds with nominal composition of $Th_xTl_2Sr_2Ca_2Cu_3O_y$ ($x = 0{\cdot}0$ to $1{\cdot}0$) have been synthesized using a matrix method starting from high purity Tl_2O_3 (Cerac, UK; 99·9%), ThO_2 (Fluka, 99·9%), $SrCO_3$ (Cerac, 99.9%), $CaCO_3$ (BDH, 99%) and CuO (99·99%). Initially mixtures of $SrCO_3$, $CaCO_3$ and CuO were thoroughly mixed in the ratio 2:2:3 and heated at 950°C in air for 24 h with several intermittent grindings and heatings. The resulting multiphase mixture, $Sr_2Ca_2Cu_3O_y$ served as the master composition. Appropriate amounts of Tl_2O_3 and ThO_2 were then added to the master composition to give a nominal composition of $Th_xTl_2Sr_2Ca_2Cu_3O_y$, thoroughly ground and pelletized. The pellets were then introduced into a preheated furnace (900°C) in flowing oxygen gas and kept for 5 min. The pellets were then taken out of the hot zone and allowed to cool to room temperature by furnace shut-off in the flowing O_2-gas. The samples were characterized by X-ray powder diffraction (XRD, Philips PW 1140, Ni-filter). The theoretical d values and intensities were obtained using the LAZYPULVERIX programme (Siemens Computer, model 7580E). The lattice parameters were calculated from the high angle (hkl) reflections by the least squares (LSQ) method. Four-probe d.c. electrical resistivity was measured in the range 300–15 K on all the samples using a closed cycle He-refrigerator (CTI-Cryogenics, USA, model 21C) using ultrasonically-soldered In-metal contacts. AC magnetic susceptibility experiments were carried out down to 15 K using a closed cycle He-refrigerator (Sumitomo, Japan, model SCR 204 T).

3. Results and discussion

The phases were black in colour and stable under normal atmospheric conditions. The XRD patterns of all the compositions (except when $x = 0{\cdot}0$, viz. $Tl_2Sr_2Ca_2Cu_3O_y$) indicated the formation of 1212 as the major phase with other impurity phases (figure 1). The LSQ-fitted tetragonal lattice parameters are given in table 1. We notice a decrease in the c lattice parameter with increasing x whereas a lattice parameter remains almost the same in the range $0{\cdot}25 \leqslant x \leqslant 0{\cdot}75$. The phases with $x \geqslant 0{\cdot}50$ showed fewer impurity lines compared to that with $x \leqslant 0{\cdot}25$. The theoretically calculated and observed intensities of the (hkl) lines agree only when we assume fractional occupancy of the Th at the Tl-site.

All the phases presently studied are metallic and exhibit superconductivity. The resistivity vs temperature plots are shown in figure 2 and the T_c data are summarized in table 1. $T_{c,\mathrm{zero}}$ values of 58 K and 57 K were noticed when $x = 1{\cdot}00$ and $0{\cdot}75$ respectively. The $T_{c,\mathrm{zero}}$ are lower (< 50 K) when $x = 0{\cdot}25$ and $0{\cdot}50$. The parent compound, viz. $Tl_2Sr_2Ca_2Cu_3O_y$ (nominal composition) showed a $T_{c,\mathrm{zero}}$ of 22 K with a step (50% drop in resistivity) around 80 K (not shown in figure 2). For the same phase superconductivity with a $T_{c,\mathrm{zero}}$ ranging from 20–80 K, depending on the details of the preparative conditions, has been reported in the literature (Sheng *et al* 1988a; Hayri and Greenblatt 1988).

Magnetic susceptibility vs temperature plots for the system $Th_xTl_2Sr_2Ca_2Cu_3O_y$ ($x = 0{\cdot}25, 0{\cdot}50, 0{\cdot}75$) are shown in figure 3. All the samples showed transition to diamagnetic state indicating that the superconducting properties of these phases are bulk in nature. For $x = 0{\cdot}25$ and $0{\cdot}50$, the T_c (onset of diamagnetism) measured from χ-T

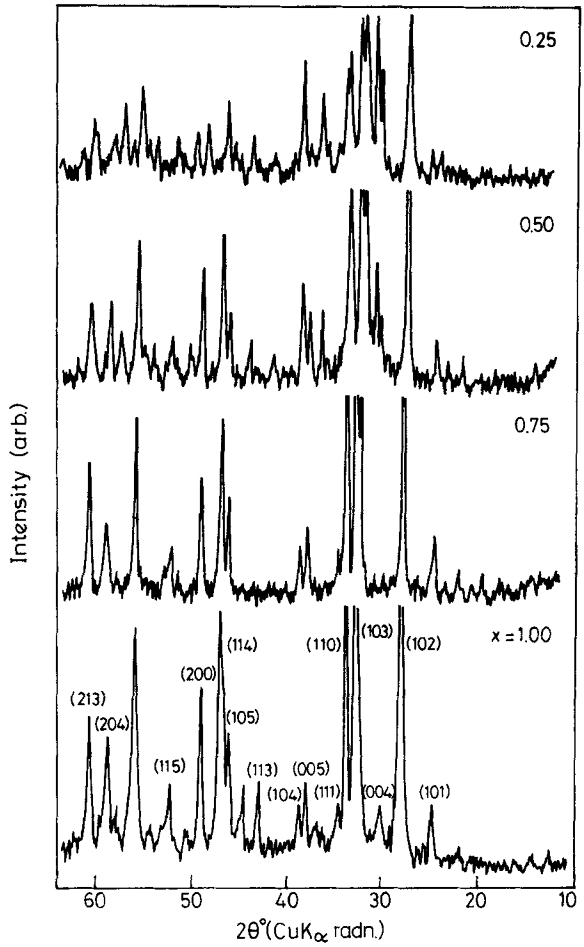

Figure 1. XRD patterns of the phases with the nominal composition, $Th_xTl_2Sr_2Ca_2Cu_3O_y$. x values are indicated. The phases can be indexed as the tetragonal 1212 structure with Th partly occupying the Tl-site.

Table 1. Structure and T_c data on $Th_xTl_2Sr_2Ca_2Cu_3O_y$.

Composition x	Tetragonal lattice param, Å a	c	T_c (onset) K	T_c (zero) K	$\rho_{300\,K}$ mΩcm	$(1/\rho_{300K})(\partial\rho/\partial T) \times 10^{-3}$ (100–300 K)
0·0	—	—	40	22	1·8	2·4
0·25	3·81	12·08	70	46	7·0	1·4
0·50	3·80	12·07	70	52	8·8	1·8
0·75	3·81	12·03	80	57	9·1	2·0
1·00	3·77	11·94	85	58	10·6	2·0

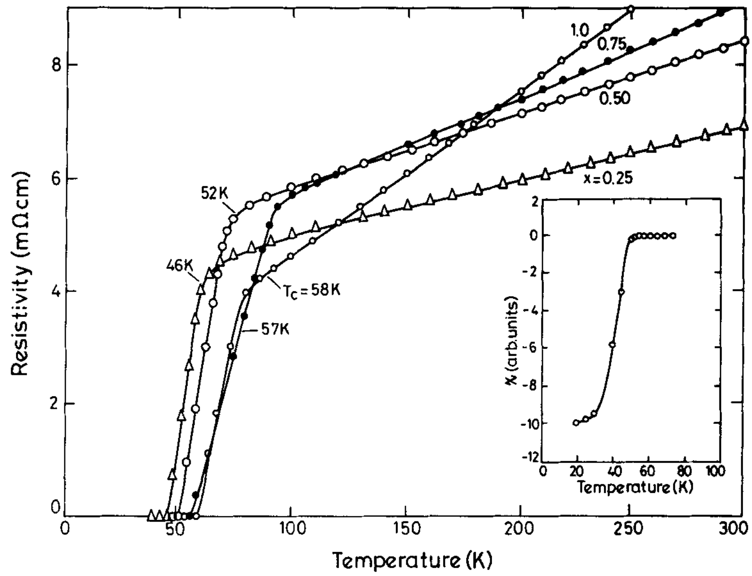

Figure 2. ρ-T plots for $Th_xTl_2Sr_2Ca_2Cu_3O_y$ showing superconducting transitions. The x values are indicated. Inset shows χ-T plot for $x = 1{\cdot}0$.

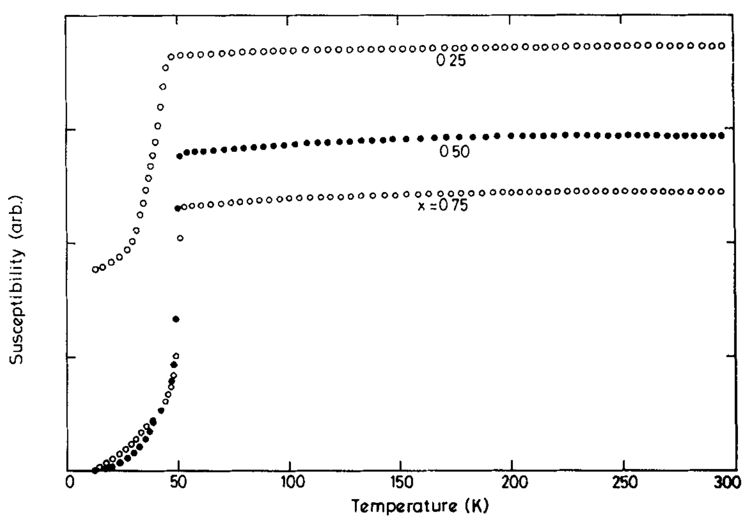

Figure 3. χ-T plots for the nominal $Th_xTl_2Sr_2Ca_2Cu_3O_y$ compositions showing onset of diamagnetism (superconductivity). The x values are indicated.

measurements (48 K and 50 K respectively) is only slightly different from the $T_{c,\text{zero}}$ encountered in ρ-T measurements (table 1, figure 2). For $x = 0{\cdot}75$ and $1{\cdot}0$, the $T_{c,\text{zero}}$ of 57 K and 58 K respectively are larger than the T_c obtained from χ-T measurements (50 K).

We notice a larger room temperature resistivity ($\rho_{300\,K}$) for the Th-containing phases compared to that for the nominal $Tl_2Sr_2Ca_2Cu_3O_y$ phase (table 1 and figure 2). This suggests that addition of Th, which will partly substitute the Tl-site, stabilizes a

1212 phase and drives the parent phase towards the metal-semiconductor phase boundary and induce superconductivity around 50 K. Similar behaviour was observed in the $Ln_xTl_2Sr_2Ca_2Cu_3O_y$ (Thomas *et al* 1990a) and $M_xTl_2Ba_2Cu_3O_y$ (Thomas *et al* 1990b) systems.

4. Conclusions

The present study indicates that addition of Th stabilizes the 1212 structure in the Tl–Sr–Ca–Cu–O system and induces superconductivity with a $T_{c,\text{zero}}$ of 58 K. It appears that the added Th occupies the Tl-site and not the Ca-site in the 1212 lattice as it occurs in the Ln–Tl–Sr–Ca–Cu–O system. While a nominal composition of $x = 0{\cdot}25$ in $Th_xTl_2Sr_2Ca_2Cu_3O_y$ is sufficient to stabilize the 1212 phase, a $T_{c,\text{zero}}$ of 57 K is induced only for $0{\cdot}75 \leqslant x \leqslant 1{\cdot}0$.

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