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Synthesis and characterization of the Indium-doped Tl-1223 phase

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Superconductor of type $Tl_{1-x}In_xBa_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{9-\delta}$ for $x = 0$, 0.1, 0.2, 0.3 and 0.5 were synthesized using stoichiometric amount of $Ba_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{7+\delta}$ precursor, Tl_2O_3 and In_2O_3 in a tube furnace at 870°C. The samples were characterized using the x-ray powder diffraction and the scanning electron microscope (SEM) whereas the composition of these samples were determined by micro-probe analysis. The transition temperature T_c for as-synthesized (Tl, In)-1223 compound, determined from the electrical resistance measurements, varied from 122 K for $x = 0$ to 100 for $x = 0.6$ These results indicate that the addition of indium decrease the transition temperature of Tl-1223 phase. This is because the addition of indium changes the Tl-1223 phase to the over-doped region. The argon annealing for some of these samples were studied. The effect of external applied magnetic field on the stage of transition is reported. Our data show that the transition width is increased by the increasing of the external applied magnetic field. The samples are more affected by the magnetic field with increasing of indium content.

1. Introduction

The third member of the homologous series of $TlBa_2Ca_{n-1}Cu_nO_{2n+3+\delta}$ (Tl-1223) was reported to be a superconductor at a transition temperature of 118 K [1]. The Tl-1223 compound is known as a suitable material for practical applications because it has high T_c and J_c values [2]. The small spacing between the CuO_2 planes in Tl-1223 can avoid a large anisotropy in the superconducting properties.

The common structure of the high-temperature superconductors is divided in two structural units. The first unit is a superconducting CuO_2 layer and the second is consisted of a rock-salt (AO) planes. All superconducting materials have a similar CuO_2 layers but different rock-salt layers such as (BiO), (TlO) and (HgO) [3–5]. It is clear that most of the high-temperature superconductors materials have $6s^2\ 6p^n$ electronic configuration such as Tl, Bi, Pb and Hg. These metals play a role in enhancing the superconducting properties. This indicates that the unique overlap of metal 6s and oxygen 2p is crucial to the occurrence of the superconductivity.

The substitution of Hg into thallium sites in the Tl-1223 is studied by R. Awad *et al.* [6]. They found that a small addition of Hg enhances the transition temperature from 122 K to 131 K without oxygen annealing. Also the substitution of Pb, Bi into thallium sites in the Tl-1223 was reported [3, 4]. The difficulty to synthesize a single phase of Tl-cuprates is due to highly oxidized Cu-state higher than that in the case of Cu-oxide superconductors. Different groups reported the replacement of calcium with yttrium to stabilize the Tl-cuprate [7]. The substitution of trivalent yttrium ions for the divalent calcium ions, is probably reduced the Cu-valance to +2.

In this work, we study the substitution of indium into the thallium sites in the Tl-1223 type compound. The electronic configuration of In is $5s^2\ 5p^1$ and the ionic radius is nearly equal the ionic radius of thallium. This work presents a good comparison study between $6s^2\ 6p^n$ and $5s^2\ 5p^n$ substitution in (Tl-1223) system.

2. Experimental

Samples with nominal composition of $Tl_{1-x}In_xBa_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{9-\delta}$ ($x = 0$, 0.1, 0.2, 0.3 and 0.5) were synthesized by two steps of solid state reaction using stoichiometric amount of Tl_2O_3, In_2O_3 and $Ba_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{7-\delta}$. The precursor $Ba_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{7-\delta}$ was prepared by a solid state reaction as previous reported [8]. The stoichiometric amount of In_2O_3, Tl_2O_3 and $Ba_2(Ca_{0.9}Y_{0.1})_2\ Cu_3O_{7-\delta}$ were ground in a glove box under argon atmosphere, in order to prevent absorption of moisture and CO_2, using an agate mortar. The powder was pressed into disk that were wrapped in a silver foil to reduce the loss of thallium and indium that could eventually react with the quartz tube. Finally the sample was inserted into a tube furnace of length 30 cm and 3 cm diameter. The sample was heated to 870 °C at 400 °C/h, and held at this temperature for 2 h, and then cooled to room temperature by furnace cooling. The prepared samples were treated under organ atmosphere at 480°C for 6 h to investigation the annealing effect.

Samples were characterized by x-ray diffraction. The x-ray diffraction scans (0.1°/sec) were done on a Philips

PW 1729 powder deffractometer using CuK_α radiation, $\lambda = 1.5418$ Å. The samples were examined in a Joel scanning electron microscope JSM-5300, operated at 15 kV, with resolution power of 4 nm. the real composition of the samples content were determined using an Oxford x-ray micro analysis system (25 kV).

The electrical resistance was measured by using a conventional four-probe technique in the temperature range from 30 K up to 227 K in a closed cryogenic system. The samples used for resistance measurements have a dimensions of about 1.4*0.3*0.3 cm^3 and the connection of copper leads with the sample was made using silver paint. The effect of applied magnetic field up to 4.9 kG on the transition stages were made using electromagnetic. The external magnetic field was applied perpendicular to the driving current.

3. Results and discussion

Fig. 1 shows X-ray diffraction (XRD) patterns for $Tl_{1-x}In_xBa_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{9-\delta}$ with $x = 0.2, 0.3$ and 0.5. Almost all diffraction peaks can be indexed by using a tetragonal lattice cell of (Tl,In)-1223 phase. The lattice parameters of all samples are nearly similar, where $a = 3.862 \pm 0.003$ Å and $c = 15.902 \pm 0.005$ Å. A few peaks from impurities are labeled by • $BaCuO_{2+\delta}$ and some of these peaks could not be known phases. Impurity peaks have much weaker intensities than those from the main phase. Thus, the volume fraction of impurities in the whole sample is expected to be very small.

Sample morphology as obtained through investigation of a fractured surface of reacted pellets ($Tl_{0.8}In_{0.2}Ba_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{9-\delta}$) is illustrated in Fig. 2. The sample consisted essentially of very small grown crystals with average dimension from 3 μm to 6 μm. Micro probe analysis of such crystal give the approximate ratios Tl : Ba : Ca : Y : Cu: = 7.46 : 3.41 : 28.63 : 2.19 : 19.48 : 38.83 close to stoichiometric starting composition.

Fig. 3 shows the variation of the normalized resistance $R(T)/R(227)$ with the temperature at driving current 10 mA for $Tl_{1-x}In_xBa_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{9-\delta}$ ($x = 0$, 0.1, 0.2, 0.3, 0.5). The transition temperature T_c, determined from electrical resistivty measurements, are 121.5, 100, 102, 107 and 100 K for $x = 0$, 0.1, 0.2, 0.3 and 0.5, respectively. It is clear that, the transition temperatures do not significantly vary by changing the ratio of In to Tl, but they are less than Tl-1223. This means that the addition of In ($4d^{10}5s^25p^1$) reduces the transition temperature, in contrary to the addition of [3], Bi [4] and Hg ($4f^{14}5d^{10}6s^26p^n$) [6] which increases the

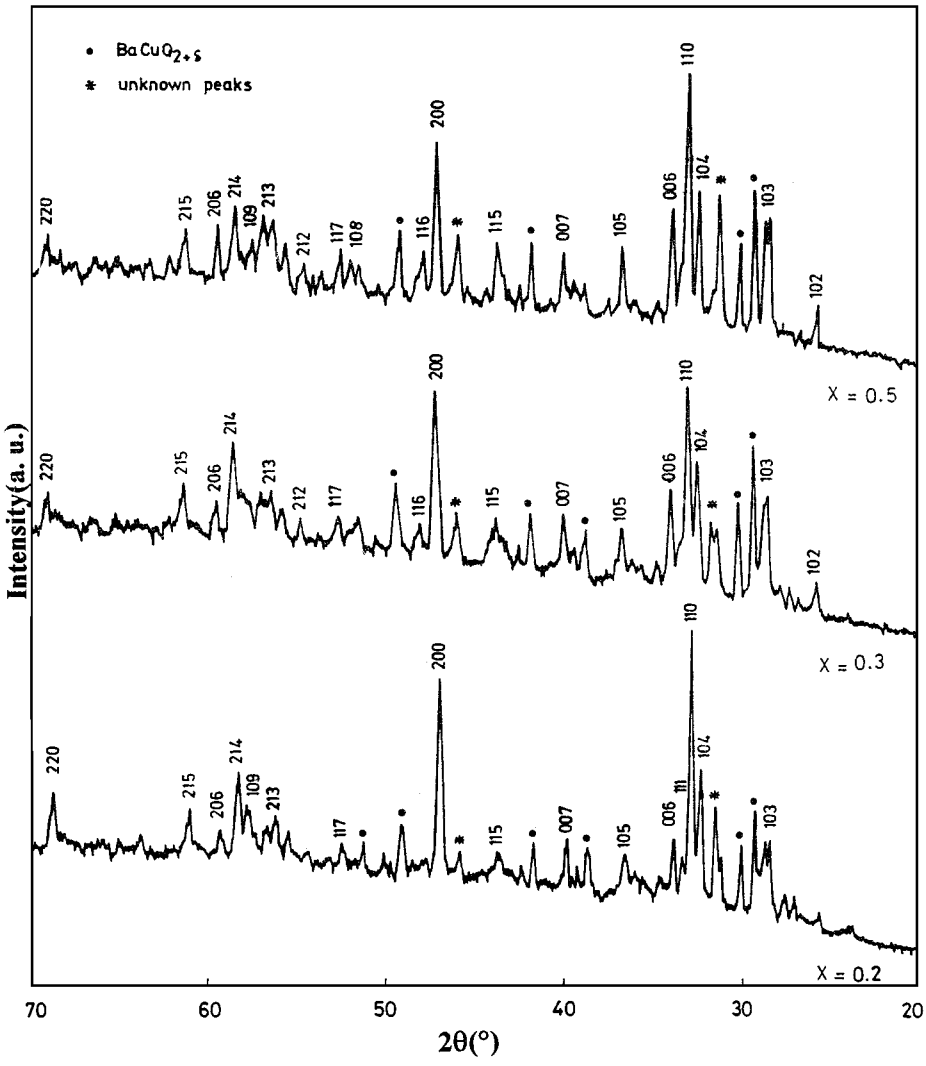

Figure 1 X-ray powder diffraction patterns for $Tl_{1-x}In_xBa_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{9-\delta}$ ($x = 0.2$, 0.3, 0.5).

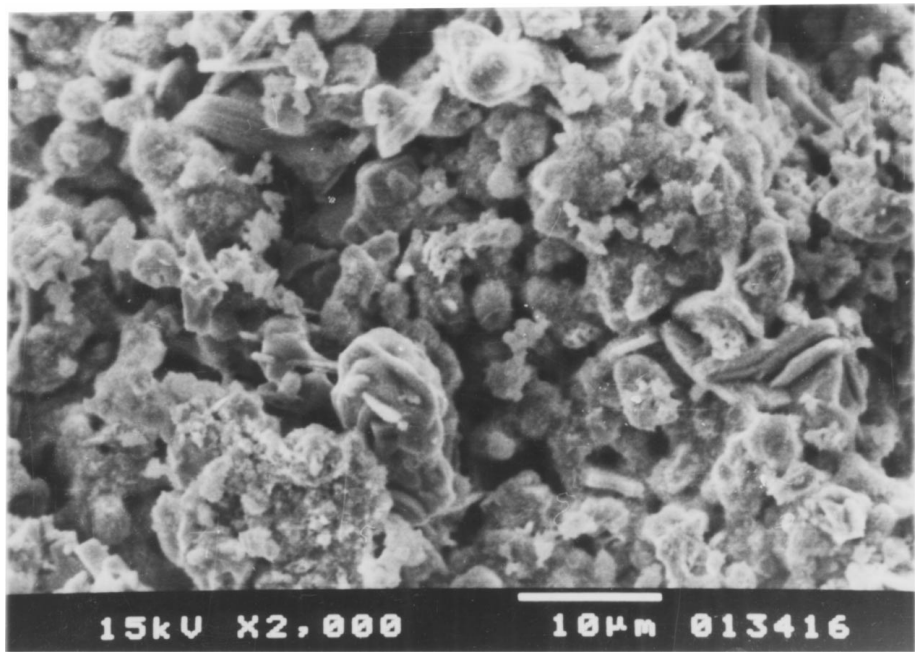

Figure 2 The typical morphology for $Tl_{0.8}In_{0.2}Ba_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{9-\delta}$.

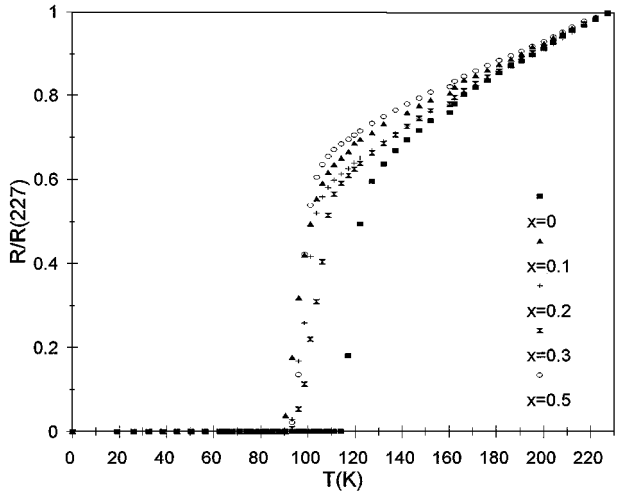

Figure 3 The normalized resistance for $Tl_{1-x}In_xBa_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{9-\delta}$ ($x = 0$, 0.1, 0.2, 0.3, 0.5).

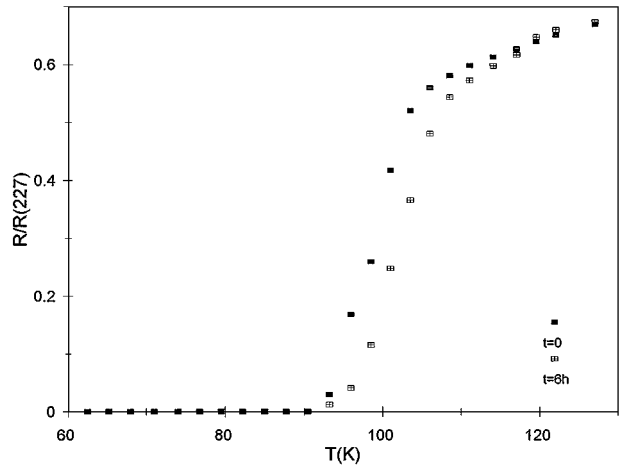

Figure 4 The normalized resistance for $Tl_{0.8}In_{0.2}Ba_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{9-\delta}$ as prepared and after argon annealing.

transition temperature. This can be accounted for the electronic configuration of metal cations. It is known that the 6s orbital of a metal and 2p orbital of oxygen are well hybridized and this leads to the enhancement of the superconductivity. This result suggests that the change from 6s to 5s metal state affects the energy level balance of the metal and oxygen, which could result in the depression of superconductivity.

Fig. 4 shows the relation between normalized resistance and temperature for $Tl_{0.8}In_{0.2}Ba_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{9-\delta}$ under argon annealing and as prepared sample. We notice that the transition temperature in (Tl, In)-1223 phase is strongly dependent on the argon annealing. The argon-annealed sample shows significant increase of T_c up to 108 K, indicating that the as prepared sample is in an overdoped state. An explanation of this annealing effect on (Tl, In)-1223 is that the oxygen in the rock-salt [(Tl, In)O] plane is loosely bound to the metal cation, this is also observed in the Hg-based superconductor [9], which makes the intercalation of the oxygen easier.

The normalized resistance-temperature dependence for $Tl_{0.5}In_{0.5}Ba_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{9-\delta}$ at different external magnetic field is shown in Fig. 5. According to these data the transition to the superconducting state could be divided into two stages. The first stage (high temperature region) starts at T_c (onset transition temperature) and consist of a rapid decrease in resistance about an order of magnitude of few Kelvin. In the second stage of transition (low temperature region) the resistance observed to be smoothly decrease to zero as the temperature approaches T_0 (zero resistance temperature). This behavior can be explain according to the granular structure of high temperature superconductors [10]. In the first stage of transition the grains become superconduting forming "grain-boundary-grain" Josephson junctions. In the second stage of transition, the junctions phase lock in a random succession and, consecountly, the superconducting region extends its area reaching the

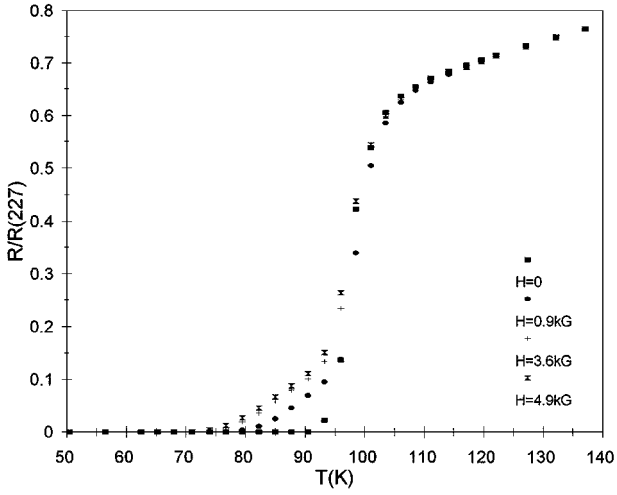

Figure 5 The temperature dependence of normalized resistance for $Tl_{0.5}In_{0.5}Ba_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{9-\delta}$ at different applied magnetic fields.

TABLE I The variation of temperature width ΔT at different applied magnetic fields vs. the In- content

	ΔT (K)			
In-Content	$H = 0$ k.G	$H = 0.9$ k.G	$H = 3.6$ k.G	$H = 4.9$ k.G
0	8	23.5	28.75	31.5
0.1	12.25	23.25	32	34.75
0.2	11.5	17	22.5	28
0.3	16.5	22	27.5	30.25
0.5	9.5	26	32	37

size of the sample at T_0. Also we notice that the magnetic field has no effect in the first stage of the transition, the curves obtained at different applied magnetic field overlap in the high-temperature region. In the second stage we observe, for the higher value of the magnetic field, the transition temperature is enlarged. This data could contain some information concerning the spatial distribution of the "strong" superconducting grains and "weak" superconducting boundaries.

Table I shows the variation of temperature width ΔT at different applied magnetic fields with the In-content for $Tl_{1-x}In_xBa_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{9-\delta}$ ($x = 0$, 0.1, 0.2, 0.3, 0.5). It is clear that the temperature width is enlarged by increasing of the applied magnetic field. This enlargement in the temperature width Could be explained as the sample cooled in a magnetic field, applied perpendicular to the driving current direction, a number of randomly oriented grains will freeze and cluster in random position. Such situation leads to a more defected specimen, consequently, an amount of flux is trapped. As a result, the length of the vortex pinning is weakened and the specimen is in a more resistive state by the loss of complete superconducting current path.

4. Conclusion

We have successfully synthesized a new indium-doped Tl-cuprates $Tl_{1-x}In_xBa_2(Ca_{0.9}Y_{0.1})_2Cu_3O_{9-\delta}$ ($x = 0$, 0.1, 0.2, 0.3, 0.5). The x-ray diffraction patterns indicate that the lattice parameter of all samples are nearly similar, where $a \cong 3.862$ Å and $c \cong 15.902$ Å. The electrical resistance results show that the addition of indium depressed the transition temperature in contrary to the addition of Hg, Pb and Bi which are increases the transition temperature. This is due to the difference in the electronic configuration of In ($4d^{10}5s^25p^1$) compared to other 6s metal cations ($4f^{14}5d^{10}6s^26p^n$). The transition temperature in (Tl, In)-1223 phase is strongly dependent on the argon annealing. The transition width is increased by increasing the external magnetic fields and these fields do not affect the first stage of transition.

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