تأثير التطعيم بالثاليوم (Tl) في درجة الحرارة الحالية Tc وثوابت الشبيكة للمركب الفائق التوصيل Hg Ba2Ca2Cu3O8+ 8

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الخلاصة

في هذه الدراسة نبين تأثير استبدال الزئبق بالثاليوم (Tl) في طبقة Hg2-O في خصائص مركب الزئبق الفائق. حضرت العينات لهذا المركب على شكل طبقة سميكة متعددة التبليور باستخدام خطوطين بطريقة تفاعلات الحالة الصلبة. استعملت تقنية (4 point probe) لإيجاد درجة الحرارة الحالية Tc للمركبة. ووجدنا أن قيمة لـ Tc للمركبة فائق التوصيل Hg1-xTlxBa2Ca2Cu3O8+ x= 0.00, 0.05, 0.10, 0.15, 0.20, 0.25 (Tc(onset)=108, 102, 113, 118, 125 and 121K). أفادت هذه الدراسات أن ثبات Tc في المرتبة Tc(onset) ~ 136K و Tc(offset) = 125 K. جميع العينات حضرت تحت تأثير ضخ الأوكسجين الذي أدى إلى تحسين وزيادة الـ Tc. بنيت تحليلات الشاكلة السيني للمركبات ذو تركيب شباه معين قائم وأظهرت هذه التحليلات زيادة في قيمة التأثـب C مع تغير في الكثافة ونسب الاطوار للعينات المستعمل فيها الثاليوم مقارنة مع الخالية منه.
Influence of Simultaneous Doping of Tl on the Transition Temperature $T_c$ and the Lattice Parameters of HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ Superconductors

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Abstract

In the present study, we have reported investigations on the effect of simultaneous substitution of Tl at the Hg site in the oxygen deficient HgO$_\delta$ layer of Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ cuprate superconductor. Bulk polycrystalline samples were prepared by the two-step solid state reaction process. It was observed that the grown Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ corresponds to the 1223 phase. Electrical resistivity, using four probe technique, is used to find the transition temperature $T_c$. The highest $T_c$ (offset) were 108, 102, 113, 118, 125 and 121K for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ with x = 0.0, 0.05, 0.10, 0.15, 0.20 and 0.25 respectively. The optimum $T_c$ (offset) of $\sim$ 125 K and $T_c$ (onset) $\sim$ 136K was found for the composition Hg$_{0.80}$Tl$_{0.20}$Ba$_2$Ca$_2$Cu$_3$O$_{8.293}$. All the samples preparation with O$_2$ flow, we found that the O$_2$ flow in our samples produce high-Phase superconductors.

X-ray diffraction (XRD) analysis showed a pseudotetragonal structure with an increase of the c-axis lattice constant for the samples doped with Tl as compared with these have no Tl content. It was found that the change of the Tl concentrations of all our samples produces a change in the Mass density $\rho_m$, c/a and volume fraction $V_{ph(1223)}$.

Introduction

The Hg-based high-$T_c$ superconductor, HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ has attracted much attention due to the highest superconducting transition temperature ($T_c$) $\sim$135K at ambient conditions (1,2) and modest flux pinning strength (3), particularly at temperature above 77K. However, the synthesis of these materials at ambient pressure is challenging due to high vapour pressure of Hg at synthesis temperature ($\sim$700-850°C), formation of CaHgO$_2$ insulating phase at $\sim$500°C and contamination from CO$_2$ and H$_2$O present in the atmosphere (4). In addition to these, the as synthesized phases are oxygen deficient leading to under doped materials. Due to these, the as synthesized Hg-12(n-1)n phases are not so stable as the other HTSC phases of cuprate oxide family. Many attempts to overcome these problems were made, but they have only limited success (5-7). The considerable difficulty experienced in the synthesis of Hg bearing HTSC phases including Hg-1223 because of their extreme sensitivity towards contamination from humidity and carbon dioxide. The Hg-1223 samples are known to degrade rapidly after synthesis. In view of this, significant efforts have recently been made to improve the stability of the Hg bearing HTSC phases, particularly the Hg-1223 phase. It is now known that the most effective way to improve the stability of the Hg-1223 phase is through suitable cationic substitution for Hg. Typically suited cations are those having oxidation state higher than that of Hg$^{+2}$ greater than +2. They bring in more oxygen in the oxygen deficient HgO$_\delta$ layer leading to phase stability. The higher oxidation state cations also lead to hole optimization in the hole deficient as grown Hg-1223 phase, thus producing optimum critical transition temperature ($T_c$). A variety of cationic substitutions such as, Tl$^{+3}$, Sn$^{+4}$, Bi$^{+3}$, Pb, Mo, Re, etc were attempted(8). Even though, all of them lead to an enhanced chemical stability, the
influence of different cationic substitutions on the superconducting properties are different. As for example, whereas Tl substitution was found to optimize easily hole concentration and hence $T_c(9)$. It may be pointed out that the specific substituted cationic characteristics taken into account generally concerns the oxidation number. However, the influence of another important dopant cationic parameter i.e. the cationic size, has not been studied in detail. The dopant cation size is likely to influence some important characteristics. The $T_c$ will depend on the size of the dopant ions, since mismatch of dopant ions sizes with native Hg ions will produce local pressure. Also band overlap will change on substitution of cation of different sizes and this may also lead to change in $T_c$. The other characteristics which will be influenced by the cationic size will be the degree of stability and microstructure through the strain they produce in the HgO layer. Keeping the above said aspects in view, we have doped Hg-1223 with Tl taken in varying concentrations stability of Hg-1223 phase. We have investigated the $\text{Hg}_{1-x}\text{Tl}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ Superconductors. previously Tl as an individual was successfully employed for doping the Hg-1223. We have found that the maximum $T_c$(onset) of $\sim 136$ K which is the representative of undoped Hg-1223 is obtained for $\text{Hg}_{2/80}\text{Tl}_{0.2}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.293}$. Using flow rate of oxygen higher than 0.25 L/min would produce deformed samples. The deformation of the samples with oxygen flow is also noted by Koyama et al(10) as well, the oxygen stoichiometric Hg-based superconductors with $\delta=0$ are unstable(11) but the structure can be stabilized by the insertion of extra oxygen, which will create more holes in the CuO$_2$ layers. The increasing of the holes concentrations in the high-$T_c$ phase will lead to the improvement of the $T_c$(off) and $T_c$(onset)(12).

**Experimental**

The synthesis of $\text{Hg}_{1-x}\text{Tl}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ HTSC phases $(x=0.00, 0.05, 0.10, 0.15, 0.2$ and $0.25)$ samples were prepared by solid state reaction, using appropriate weights of pure powders materials HgO, Tl$_2$O$_3$, BaCO$_3$, CaCO$_3$ and CuO, and in proportion to their molecular weights. The weight of each reactant was measured by using a sensitive balance type [Mettler H35 AR]. The synthesis of the samples was carried out by two step precursor method. In the first step, the powders (BaCO$_3$, CaCO$_3$ and CuO) were mixed together by using agate mortar; a sufficient quantity of 2-propane was to homogenization the mixture and to form slurry during the process of grinding for about (40-60) minute. The mixture was dried in an oven at 150 °C. The mixture was weighted $(w_1)$ and put in alumina crucible. The mixture was put in tube furnace that has a programmable controller type [Eurpherm 818], for calcinations, which is the heat treatment to remove CO$_2$ gas from the mixture. For this process the powder was heated to temperature of 800 °C for 24 hours with a rate of 60 °C /h, then cooled to room temperature by the same rate of heating. The weight of mixture after calcinations was measured $(w_2)$, the colour of it was black. If the difference in the sample weight before and after the calcinations process $(w_2-w_1)$ is less than the theoretical value of gas, then the step above should be repeated again, and the calcined powder was reground again, for two or three times to remove the whole gases from the mixture.

In the second step, the $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_7$ precursor was mixed with HgO, Tl$_2$O$_3$ to obtain the nominal compositions $\text{Hg}_{1-x}\text{Tl}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ where $x=0.00, 0.05, 0.10, 0.15, 0.2$ and 0.25. The powder was pressed into disc-shaped pellets (1.3 cm) in diameter and (0.2-0.3) cm thick, using hydraulic press type (Specac) under a pressure of (7 ton/cm$^2$). The pellets were presintered in air at (855-860) °C for (24 h) with a rate of (60 °C/h) and then cooled to room temperature by the same rate of heating. The presintered pellets were reground, repressed and resintered in the oxygen (oxygen rate 0.3 L/min) at the same range of temperature for further (200 h) and then cooled to 500 °C and annealed in oxygen for (10 h) and then cooled to room temperature by same rate of heating. By regrinding and resintering 1212 phase can be exposed and directly take part in the reaction which can accelerate the formation rate of the1223 phase of Hg-base and produces the pure 1223 phase more easily. Electrical transport
characterization by four-probe technique (Keithley resistivity setup) was used to measure the resistivity ($\rho$), at temperature range (77-300K), and to determine the critical temperature ($T_c$). The sample was fixed in the cryostat instrument which was joined to a rotary pump to get a pressure of $10^{-2}$ mbar inside the cryostat, and also joined to a sensor of digital thermometer (type Pt 100 resistance to temperature detection RTD) near the sample position. Find copper wires attached to the sample by furnace-dried silver paste served as the current and voltage leads. A 10 mA current was supplied to the sample by a current source D.C power supply type (Electronica- Veneta DV 30/V3); the voltage drop was measured by a Keithley model 180 nanovoltmeter with sensitivity of about $\pm 0.1$ nanovolt was used for voltage measurements. The resistivity ($\rho$) could be found from the relation: $\rho = \frac{I \omega t}{L}$ Where: $I$ is the current passing through the sample, $V$ is the voltage drop across the electrodes, $\omega$ is the width of the sample, $L$ is the effective length between the electrodes, $t$ is the thickness of the sample. All of the measurement of $L$, $t$ and $\omega$ were made by using digital vernier. The excess of oxygen content ($\delta$) could be determined by using a chemical method called Iodometric titration.

The structure of the prepared sample was obtained by using X-ray diffractometer (XRD) type (Philips) which has the following features, the source Cu$_{\text{K\alpha}}$ current (20 mA), voltage (40 KV) and $\lambda=1.5405$ A. Phase transformation for many compositions was studied by using XRD to get the structure properties. The volume fraction of any phase ($V_{\text{phase}}$) in the sample was determined by using the relation:

$$V_{\text{phase}} = \frac{\sum I_a}{\sum I_1 + \sum I_2 + \ldots + \sum I_n} \times 100$$

Where $I_a$ is the XRD peak intensity of the phase which was determined, and $I_1, I_2, \ldots, I_n$ are the peaks intensity of all XRD. A computer program was established to calculate the lattice parameters $a, b, c$ this program is based on Cohen's least square method.

**Results and Discussion**

All the samples in the present investigation were subjected to gross structural characterization by X-ray diffraction. The XRD data collected from various samples (samples having various Hg, Ca, Ba,Cu and Tl concentration) were all polycrystalline and correspond to Hg(Tl)-1223 phases. The XRD also shows some impurity phases with vanishingly small concentrations. The representative XRD patterns are shown in figures(1). It could be seen from the spectra that there were two main phases in all samples of the Hg-base systems, high-$T_c$ phase (1223), low-$T_c$ phase(1212) and a small amount of impurity phases of (Ca, Ba)$_2$CuO$_3$, CaTiO$_4$ and CuO. The appearance of more than two phases could be related to the stacking faults along the c-axis. The comparison between the relative intensities of XRD patterns for the samples with $T_l=0.05, 0.1, 0.15, 0.2$ and 0.25, with the relative intensity of the same reflections of the sample with $T_l=0.0$ shows that all the samples have reflection intensity of the High-$T_c$ phase reflections (peaks H), and Low –$T_c$ phase reflections (peaks L) the $H$-peaks is increased and Low-$T_c$ is decreased by increasing $T_l$. The High-$T_c$ phase reflections of the free sample ($T_l= 0$) has a lower intensity than the samples which have $T_l$. The lattice parameters were estimated by using d-values and (hkl) reflections of the observed x-ray diffraction pattern through the software program based on Cohen's least square method, the parameters $a, b, c$, Mass density $\rho_M$ and volume fraction ($V_{\text{phase}}$) shown in table(1).

Figures (2), (3) and(4) show an increase of the volume fraction ($V_{\text{phase}}$), $c/a$ and decrease of $\rho_M$ for Hg-doped samples for different compositions of $\text{Hg}_{1-x} \text{Tl}_x \text{Ba}_2 \text{Ca}_2 \text{Cu}_3 \text{O}_{8+\delta}$ as comparable with the free sample. The reason is due to the substitution of Tl for Hg where the ionic radii of Tl$^{3+}$ (2.08 A) is longer than that of Hg$^{2+}$ (1.13 A) which render c-parameter to
be longer or get deformed. From the above discussion, we propose that the conduction path in Hg-base are holes in the Cu-O\(_2\) layers which are enhanced by the Hg-O layer. The deformation in the c-axis adjusts the amount of charge transfer from Hg layer to Cu layer of Hg-1223. This will force the generation of hole pairing in the Cu(3d)-O(2p) band. The variation of resistance with the temperature of the as synthesized Hg\(_{1-x}\)Tl\(_x\)Ba\(_2\)Ca\(_2\)Cu\(_3\)O\(_{8+\delta}\) HTSC samples were measured by the standard four-probe technique. The normal state resistance of all the samples shows metal like behaviour with respect to temperature. A plot of the normalized resistivity vs temperature (\(\rho–T\)) behaviour of samples with various Tl concentrations are shown in figure(5).

The values of critical transition temperature \(T_c\) for as grown HgBa\(_2\)Ca\(_2\)Cu\(_3\)O\(_{8.211}\), Hg\(_{0.95}\)Tl\(_{0.05}\)Ba\(_2\)Ca\(_2\)Cu\(_3\)O\(_{8.221}\), Hg\(_{0.90}\)Tl\(_{0.10}\)Ba\(_2\)Ca\(_2\)Cu\(_3\)O\(_{8.233}\), Hg\(_{0.85}\)Tl\(_{0.15}\)Ba\(_2\)Ca\(_2\)Cu\(_3\)O\(_{8.26}\), Hg\(_{0.8}\)Tl\(_{0.20}\)Ba\(_2\)Ca\(_2\)Cu\(_3\)O\(_{8.293}\) and Hg\(_{0.75}\)Tl\(_{0.25}\)Ba\(_2\)Ca\(_2\)Cu\(_3\)O\(_{8.212}\) phases are 108, 102, 113, 118, 125 and 121 K, respectively. In view of the quality characterization provided by Kirschner et al (1996), it can be categorically stated that our samples are of ‘good quality’. Since the maximum value of \(T_c\) is expected to be for optimum hole doping, the concentration Hg\(_{0.8}\)Tl\(_{0.20}\)Ba\(_2\)Ca\(_2\)Cu\(_3\)O\(_{8}\) where Tl =0.20.

### Conclusions

We have investigated the effect of simultaneous substitution of Tl at the Hg site in the oxygen deficient HgO\(_\delta\) layer of Hg\(_{1-x}\)Tl\(_x\)Ba\(_2\)Ca\(_2\)Cu\(_3\)O\(_{8+\delta}\) cuprate superconducto have been prepared under optimum conditions. X-ray diffraction analysis showed a pseudotetragonal structure with an increase of the c-axis lattice constant for the samples doped with Tl as compared with these have no Tl content. The transition temperature of as grown samples is found to be sensitive to the Tl concentrations. It has been observed that maximum \(T_c = 125\) (K) is achieved for Hg\(_{0.8}\)Tl\(_{0.20}\)Ba\(_2\)Ca\(_2\)Cu\(_3\)O\(_{8}\) where Tl =0.20.

### References


Table (1) Values a, b, c, c/a, δ and ρM for the samples for different composition of Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$

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<th>T$_{c\text{ON}}$(K)</th>
<th>δ(°2)</th>
<th>a(A$^3$)</th>
<th>b(A$^3$)</th>
<th>c(A$^3$)</th>
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Fig. (1) XRD Patterns for the sample Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$ for x=0.00, 0.05, 0.10, 0.15, 0.20 and 0.25

Fig. (2) volume fraction (V$_{\text{phase}}$) as function of deferent Tl for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+δ}$
Fig. (3) C/a as function of Tl concentration for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$

Fig. (4) Mass Density as function of Tl concentration for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$

Fig. (5) Temperature dependence of resistivity for Hg$_{1-x}$Tl$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ at indicated values of (Tl) at $x=0.00$, 0.05, 0.10, 0.15, 0.2 and 0.25