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تأثير التطعيم بالثاليوم (TI) في درجة الحرارة الحرجة T_c وثوابت الشبيكة للمركب (T_b الفائق التوصيل المركب Hg Ba₂Ca₂Cu₃O_{8+ δ}

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الخلاصة

في هذه الدراسة نبين تأثير استبدال الزئبق بالثاليوم (Tl) في طبقة Hg-O في خصائص مركب الزئبق الفائق التوصيل $Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+\delta}$. $Hg_{1-x}Ca_2Cu_3O_{8+\delta}$. $H_{1-x}Ca_2Cu_3O_{8+\delta}$. $H_{1-x}Ca_3Cu_3O_{8+\delta}$. $H_{1-x}C$

Influence of Simultaneous Doping of Tl on the Transition Temperature T_c and the Lattice Parameters of HgBa₂Ca₂Cu₃O_{8+δ} 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_{δ} layer of Hg_{1-x}Tl_xBa₂Ca₂Cu₃O_{8+ δ} 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_xBa₂Ca₂Cu₃O_{8+ δ} 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_xBa₂Ca₂Cu₃O_{8+ δ} with x = 0.0, 0.05, 0.10, 0.15, 0.20 and 0.25 respectively. The optimum T_{c(off)} of ~ 125 K and T_{c(onset)} ~ 136K was found for the composition Hg_{0.80}Tl_{0.20}Ba₂Ca₂Cu₃O_{8.293}. All the samples preparation with O₂ flow, we found that the O₂ 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 ρ_m , c/a and volume fraction $V_{Ph(1223)}$.

Introduction

The Hg-based high -Tc superconductor, HgBa₂Ca₂Cu₃O_{8+ δ} has attracted much attention due to the highest superconducting transition temperature $(T_c) \sim 135$ K 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 (~700-850 °C), formation of CaHgO₂ insulating phase at ~500 0 C and contamination from CO₂ and H₂O 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 states 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 TI 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 $Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+\delta}$ Superconductors. previously Tl as an individual was successfully employed for doping the Hg-1223. We have found that the maximum T_c (onset) of ~ 136 K which is the representative of undoped Hg-1223 is obtained for Hg_{0.80}Ti_{0.20}Ba₂Ca₂Cu₃O_{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 Koy ama 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 CuO₂ 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 Hg_{1-x}Tl_xBa₂Ca₂Cu₃O_{8+ δ} 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, , Tl₂O₃, BaCO₃, CaCO₃ 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 (BaCO₃, CaCO₃ 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 $^{\circ}$ C. The mixture was weighted (w₁) and put in alumina crucible. The mixture was put in tube furnace that has a programmable controller type [Eurptherm 818], for calcinations, which is the heat treatment to remove CO₂ gase from the mixture. For this process the powder was heated to temperature of 800 $^{\circ}$ C for 24 hours with a rate of 60 $^{\circ}$ 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 gase, 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 Ba₂Ca₂Cu₃O₇ precursor was mixed with HgO, Tl₂O₃ to obtain the nominal compositions Hg_{1-x}Tl_xBa₂Ca₂Cu₃O_{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/cm²). The pellets were presintered in air at (855-860) ⁰C for (24 h) with a rate of (60 ⁰C/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 ⁰C and annealed in oxygent 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 the 1223 phase of Hg-base and oroduces the pure 1223 phase more easily .Electrical transport}

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characterization by four- probe technique (Keithley resistivity setup) was used to measure the resistivity (ρ), 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 a bout ±0.1 nanovolt was used for voltage

measurements. The resistivity (ρ) could be found from the relation: $\rho = \frac{V}{I} \frac{\omega t}{L}$ Where : I is

the current passing through the sample, V is the voltage drop across the electrodes, ω 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 ω were made by using digital vernier. The exess of oxygen content (δ) 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 $Cu_{k\alpha}$ current (20 mA), voltage (40 KV) and λ =1.5405 A⁰. Phase transformation for many compositions was studied by using XRD to get the structure properties(13). The volume fraction of any phase (V_{phase}) in the

sample was determined by using the relation(14): $V_{\text{phase}} = \frac{\sum Ia}{\sum I1 + \sum I2 + \dots + \sum In} \times 100$

Where Ia is the XRD peak intensity of the phase which was determined, and $I_1, I_2, ..., I_n$ 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(15).

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)₂CuO₃, CaTlO₄ 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 T1=0.05.0.1, 0.15, 0.2 and 0.25, with the relative intensity of the same reflections of the sample with TI=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 Hpeaks is increased and Low-Tc is decreased by increasing Tl. The High-Tc phase reflections of the free sample (Tl=0) has a lower intensity than the samples whichhave Tl. 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(16), the parameters a, b, c, Mass density ρ_M and volume fraction (V_{phase}) shown in table(1).

Figures (2), (3) and(4) show an increase of the volume fraction (V_{phase}), c/a and decrease of ρ_M for Hg-doped samples for different compositions of Hg_{1-x}Tl_xBa₂Ca₂Cu₃O_{8+ δ} 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 A⁰)is longer than that of Hg⁺²(1.13 A⁰) 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-O₂ 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}Ti_xBa₂Ca₂Cu₃O_{8+ δ} 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 (ρ -T) behaviour of samples with various Tl concentrations are shown in figure(5).

The values of critical transition temperature (T_c) for as grown HgBa₂Ca₂Cu₃O_{8.211}, Hg_{0.95}Ti_{0.05}Ba₂Ca₂Cu₃O_{8.221}, Hg_{0.9}Ti_{0.10}Ba₂Ca₂Cu₃O_{8.233}, Hg_{0.85}Ti_{0.15}Ba₂Ca₂Cu₃O_{8.26}, Hg_{0.8}Tl_{0.20}Ba₂Ca₂Cu₃O_{8.293} and Hg_{0.75}Ti_{0.25}Ba₂Ca₂Cu₃O_{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}Ba₂Ca₂Cu₃O_{8.293} would correspond to optimum level of hole doping.

Conclusions

We have investigated the effect of simultaneous substitution of Tl at the Hg site in the oxygen deficient HgO_{δ} layer of Hg_{1-x}Tl_xBa₂Ca₂Cu₃O_{8+ δ} 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}Ba₂Ca₂Cu₃O₈ where Tl =0.20.

References

- 1. Chmaissem, O.; Guptasarma, P.; Welp, U.; Hinks, D. G. and Jorgensen, J. D. (1997) Physica C 292 305
- 2. Schilling, A.; Cautoni, M.; Guo, J. D.; Ott, H. R. Ott, (1993) Nature 363, 56.
- 3. Richter, H.; Puica,I.; Lang,W.; Peruzzi,M.; Durrell,J. H.; Sturm,H.; Pedarnig,J. D. and B⁻auerle, D. (2006) J. Physics 43: 706–709
- 4. Meng, R. L.; Hickey, B. R.; Sun, Y. Y.; Cao, Y.; Kinalidis, C.; Meen, J. K.; Xue, Y. Y. and Chu, C. W. (1996) Physica C 260 1
- 5. Sastry, P. V. P. S. S.; Amm, K. M.; Knoll, D. C.; Peterson, S. C. and Schwartz, J.(1998a) Physica C 297- 223
- 6. Pandey, A. K.; Verma, G. D. and Srivastava, O. N. (1998) Physica C 306-3 47
- Balchev, N.; Allemeersch, F.; Van, Persyn F.; Schroeder, J.; Deltour, R. and Hoste, S. (1997) Supercond. Sci. Technol. 10 65
- 8. Sun, G. F.; Wong, K. W.; Xu ,B. R.; Xin, Y. and Lu, D. F. (1994) Phys. Letts A192-122
- Kirschner, I.; Laiho, R.; Lukács, P.; Bodi, A. C.; Lukács, M. D.; Lähderanta, E. and Zsolt, G.(1996) Z. Phys. B99- 501
- Fujii Hiroki; Kumakura Hiroaki and Togano, Kazumasa (1999) IEEE Trans. Appl. Supercond. <u>9</u>:1051
- Rajiv, G.; Singh, H. K.; Tiwari, R. S. and Srivastava, O. N. (2001) Bull. Mater. Sci., 24(5): October, 523–528
- 12. Xing,G.; Wang, M.; Fan ,X. and Tang,X. (1993) Appl. Phys. A56:99
- 13. Simon ,A.;Mukherjee ,P.S.; Sarma ,M.S. and Damodaram, A.D. (1994) J.Mater. Sci. <u>29:</u> 5059
- 14. Che, G.C.;Du Y.K.;Wu, F.;Yang, Y.; dong ,C. and Zhao, Z.X. , (1994). Solid state Commun., <u>89</u>(11) 903
- 15.Ferguson, I.F. and.Rogerson, A.H., (1984) Comput. Phys. Commun., 32:95

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16. Manivannan, V.; Gopalarishnan, J. and Rao, C.N.R.(1994)Journal of Sold state Chemistry <u>109</u>: 205-209

X	T _{c(OFF)} (K)	$T_{c(ON)}(K)$	δ(02)	$a(\mathbf{A}^0)$	$b(\mathbf{A}^0)$	$c(\mathbf{A}^0)$	c/a	$\rho_{\rm M} ({\rm g/cm^3})$	V _{Ph-1223}
0.00	108	123	0.211	3.8423	3.8422	15.75	4.099	5.5931	69.43
0.05	102	125	0.221	3.8429	3.8426	15.77	4.104	5.5846	71.11
0.10	113	128	0.233	3.8432	3.8435	15.77	4.103	5.5841	75.12
0.15	118	128	0.260	3.8434	3.8437	15.78	4.106	5.5787	76.80
0.20	125	136	0.293	3.8441	3.8438	15.80	4.110	5.5704	78.73
0.25	121	131	0.112	3.8382	3.8381	15.73	4.098	5.6122	63.53





Fig. (1) XRD Patterns for the sample $Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+\delta}$ for x=0.00, 0,05, 0.10, 0.15, 0.20 and 0.25



Fig.(2) volume fraction (V_{phase}) as function of deferent Tl for Hg₁₋ $_{x}Tl_{x}Ba_{2}Ca_{2}Cu_{3}O_{8+\delta}$



Fig. (3) C/a as function of Tl concentration for $Hg_{1-x}Tl_xBa_2Ca_2Cu_3O_{8+\delta}$



Fig. (4) Mass Density as function of Tl concentration for Hg_{1-x}Tl_xBa₂Ca₂Cu₃O_{8+ δ}



Fig. (5) Temperature dependence of resistivity for $Hg_{1-x}Tl_xBa_yCa_2Cu_3O_{8+\delta}$ at indicated values of (TI) at x =0.00, 0.05, 0.10, 0.15, 0.2 and 0.25