Influences of the Cu Substitution at Hg Site in $Hg_{1-x}Cu_xBa_2Ca_2Cu_3O_{8+\delta}$ Superconductors

M. M. Abbas
Department of Physics, College of Science, University of Baghdad

Abstract:
The influences of the Cu substitution at Hg site in the HgO_δ layer, upon the microstructure, T_c and oxygen content of Hg-1223 have been investigated. High temperature superconductor with a nominal composition $Hg_{1-x}Cu_xBa_2Ca_2Cu_3O_{8+\delta}$ for Cu $(0 \le x \le 0.5)$ have been prepared by the two-steps solid state reaction method under optimum conditions. XRD showed a tetragonal structure with a high ratio of Hg-1223 superconductor phase. T_c enhancement has been determined with the Cu concentration was is found to be Tc = 153 K for x = 0.3, while the oxygen content observed variously with Cu concentration. $Hg_{1-x}Cu_xBa_2Ca_2Cu_3O_{8+\delta}$ structure, oxygen content and T_c behavior have been discussed.

تأثير التعويض بـ Cu عند مواقع Hg لـ $Hg_{1-x}Cu_xBa_2Ca_2Cu_3O_{8+\delta}$ فائق التوصيلية

منى موسى عباس
قسم الفيزياء / كلية العلوم /جامعة بغداد

الخلاصة:
درست تأثيرات التعويض بالنحاس عند مواقع الزئبق لطبقة HgO_δ على تركيب ودرجة الحرارة الحرجة T_c وكمية الأوكسجين للمركب Hg-1223. حضرت مركبات $Hg_{1-x}Cu_xBa_2Ca_2Cu_3O_{8+\delta}$ فائقة التوصيلية ذوات الحرارة العالية وللقيم $0 \le x \le 0.5$ بطريقة تفاعل الحالة الصلبة وبأمثل الظروف وعلى مرحلتين. بينت فحوصات حيود الأشعة السينية التركيب الرباعي للمركب مع نسبة عالية من طور Hg-1223 فائق التوصيلية. لوحظ تحسن درجة الحرارة مع نسب التعويض بالنحاس. أفضل T_c هي 153 كلفن عند x=0.3 بينما لوحظ تغير كمية الأوكسجين مع نسب التعويض. كما جرت مناقشة تركيب وكمية الأوكسجين و سلوك T_c لمركب $Hg_{1-x}Cu_xBa_2Ca_2Cu_3O_{8+\delta}$.

Introduction

Throughout history, the search for novel materials has been an important part of superconductivity research. Not only does the search provide us with a higher transition temperature T_c, it also broadens the material base with improved physical and engineering properties for scientific and technological endeavor.

Since the discovery of high T_c superconductors HTSC many efforts have been elevated to understand the sensitivity of T_c to the structural parameters. This knowledge can facilitate the determination of the mechanism beneath superconductivity and can provide a way to increase the T_c of these materials [1].

The first member $HgBa_2CuO_{4+\delta}$, of this $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ series, was invented in 1993 by Putilin *et al* [2] exhibiting superconductivity at 94K. Soon after, Schilling *et al* [3] observed superconductivity at 133.5K in the HgBaCaCuO system and reported the formation of Hg-1212 and Hg-1223 phases. The highest values of T_c's, which were determined as the onset temperature of Meissner signal, were 97K [4] , 127K [5], 135K [6], and 123K [7] for Hg-1201, Hg-1212, Hg-1223 and Hg-1234 phases, respectively.

To date, $HgBa_2Ca_{n-1}Cu_nO_y$ superconductors represent the most interesting series out of all known high temperature cuprates. Undoubtedly the primary reason for this is the high critical transition temperature exhibited by this series. The other reason for Hg based HTSC phases being interesting is the fact that the anisotropy of these HTSC phases is in between Y and Bi bearing cuprates and they are therefore, expected to show effective flux pinning and microstructure exhibiting good texturing of grains [8].

The superior superconducting properties of HBCCO, e.g. record high T_c, and J_c, suggest that the compound system and especially Hg-1223 should be an excellent candidate for applications.

In spite of these advantages their use is not yet as widespread as other HTSC materials. This is due to considerable difficulty experienced in the synthesis of Hg bearing HTSC phases including Hg-1223. The following problems make synthesis mercury cuprates a difficult task.

First notably, the high volatile nature of Hg and HgO oxides at relatively low temperatures of 360-500^oC, depending on the process technique [9]. So Hg-1223 is difficult to form and the compound is chemically unstable with a loss of Hg and the associated degradation at temperatures above 350^oC. Added to the difficulty is the fact that the Hg-released from the compounds attacks many metals, especially at high temperatures, and forms amalgams [10].

Besides the severe problem of reduction in Hg stoichiometry, the evolutions of this poisonous toxic mercury oxide vapor are dangerous for living being and creates environmental problem. Second, the formation of stoichiometric $Ba_2Ca_{n-1}Cu_nO_x$ precursor requires very high annealing temperatures of about 680-880^oC for longer times depending upon the process [11]. Further these precursors are very sensitive to air and humidity (12) 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 by two ways.

First, most of the researchers have adopted the two –step process as given below:

i) Precursor pellets/ films of $Ba_2Ca_{n-1}Cu_nO_x$ were synthesized by annealing at high temperature.
ii) Mercury was deposited or precursor was subjected in a controlled Hg atmosphere.

Other researchers mixed HgO with the BaCaCuO precursor palletized and then annealed at high temperature[8,12].

Second, Doping and ion-induced disorder have shown that a small change in physical structure can induce a dramatic change in the electronic structure in these materials[13].

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 i.e. greater than +2. A variety of cationic substitution such as Bi, Tl, Mo, Re, Sn, Pb etc have been attempted .Even though all of them lead to enhanced chemical stability, the influence of different cationic substitutions on the superconducting properties are different [8,13,14].

Although the cationic substitution of HgO_δ site leads to stabilization, it also affects the superconducting properties, T_c and J_c [8]. However, the influence of the atomic substitution or doping is not yet fully understood in the cuprate superconductors, and this represents an active area of current research.

Keeping the above said aspects in view, we have the exercise of stabilization will be only useful, if the superconducting properties remain as good as the unsubstantiated Hg-1223 or better than that.

Experimental details

Solid state reaction method by two steps was used to synthesize $Hg_{1-x}Cu_xBa_2Ca_2Cu_3O_{8+\delta}$ samples where x= 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5.

First of all the molar ratios of high purity powders of CuO, $BaCo_3$ and $CaCo_3$ were adjusted, mixed and grounded using an agate mortar. Then calcined at 800°C for 30hr. After successfully regrinding and mixed the BaCaCuO precursor with powdered Hg_2O ,pellets were pressed from the so obtained mixture under 7 ton/cm pressure for 2 mints .The sintered process for pellets done by two steps.

First step the temperature of the furnace was raised to 850°C hold at this temperature for 50 hr subsequent by slow cooling to 350°C the pellets annealed at this temperature for 3 hr. Second step, heated to 850°C annealed for 20 hr then cooled to 350°C held for 3hr.

Finally the third step the furnace was heated to 850°C and held for 130 hr before cooling to room temperature. The rate was 4°C/min for every heating and cooling process.

All samples in the present investigations were subjected to gross structural characterization by X-ray diffraction XRD, Cu K_α. The DC electrical resistance was measured with the four-probe technique [15]. Iodometric titration was used to access the oxygen content in the samples.

Results and discussion

The XRD data collected from various samples indicates that all samples are polycrystalline and correspond to Hg-1223 phase. Some impurity phases with vanish-ingly small concentrations. The representative XRD patterns are shown in Fig.(1) the lattice parameters have been estimated using θ-values and hkl reflections of the observed X-ray diffraction pattern by a least square method and a computer program.

Fig.(2) Expresses the unit cell volume (V) as a function of Cu concentration at room temperature for $Hg_{1-x}Cu_xBa_2Ca_2Cu_3O_{8+\delta}$.

It has been noticed from the table(1), the lattice parameters depend more dramatically on the Cu concentration. The lattice parameter (a) is found to vary unsystematically with increasing x. While it is systematically increasing for both lattice parameter (c) with increasing 0.3 < x< 0.5 and (V) for 0.4 < x < 0.5 The crystal structures are discussed with main attention focused on features such as [16,17]:

1- Concentration and location of oxygen atoms, static atomic displacement and cations ordered arrangement due to partial occupation of oxygen site in a Hg-layer.
2- The copper valance is remarkably enhanced with a partial formation of Cu+3 ions in the superconducting state, reflecting lattice instability around copper upon the superconducting transition.

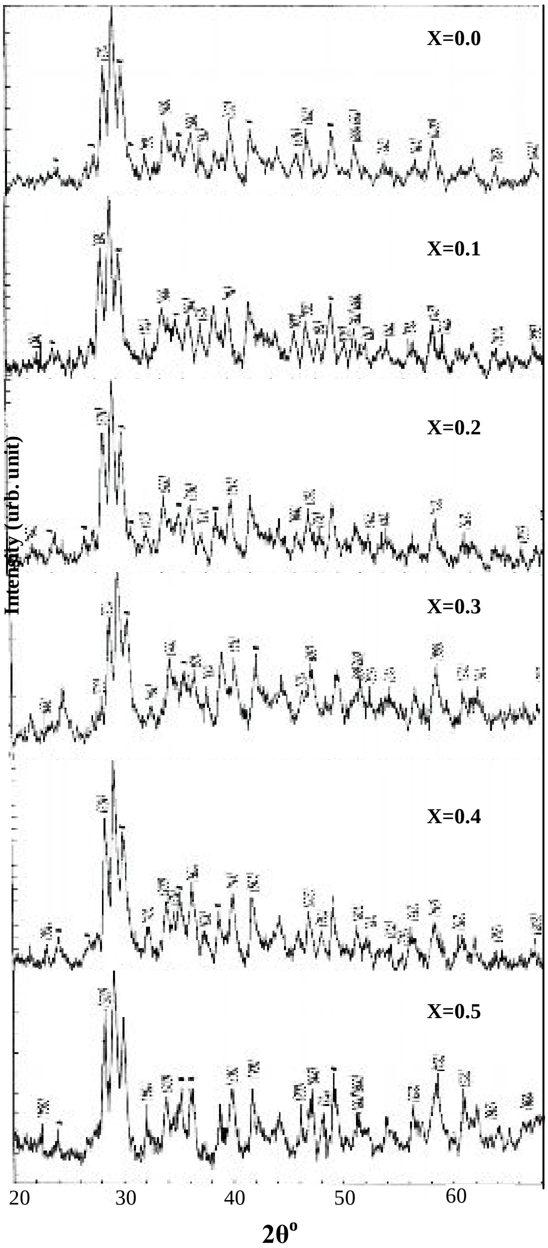

Fig. (1): XRD for $Hg_{1-x}Cu_xBa_2Ca_2Cu_3O_{8-\delta}$

Table (1): Values of T_c , lattice parameters, unit cell volume and oxygen content for different Cu concentration

x	T_c(K)	a (A)	c (A)	V $(A)^3$	δ
0.0	118	3.857465	15.83539	235.6312	0.209
0.1	123	3.840518	15.88519	234.2999	0.092
0.2	132	3.859612	15.74416	234.5345	0.036
0.3	153	3.841969	15.79734	233.1802	0.018
0.4	112	3.853276	15.82061	234.9002	0.099
0.5	118	3.867768	15.84782	237.0775	0.605

All samples reveals a superconductor behavior and T_c found to be (118, 123, 132, 153, 112 and 118) K for x= 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 respectively. A plot of the electrical resistivity vs. temperature behavior of samples with various Cu concentrations is shown in Fig. (3).

In general the increasing of Cu concentration increases T_c except for 0.4 T_c decreases.

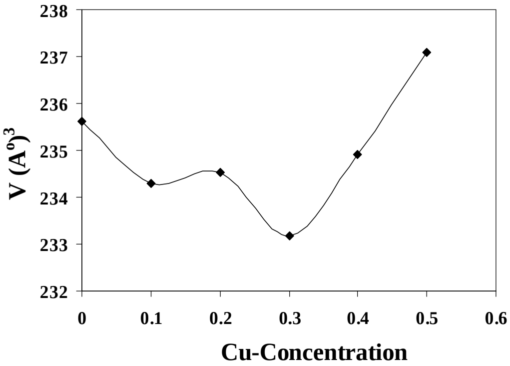

Fig.(2): Unit –cell volume V as a function of Cu-concentration for $Hg_{1-x}Cu_xBa_2Ca_2Cu_3O_{8+\delta}$.

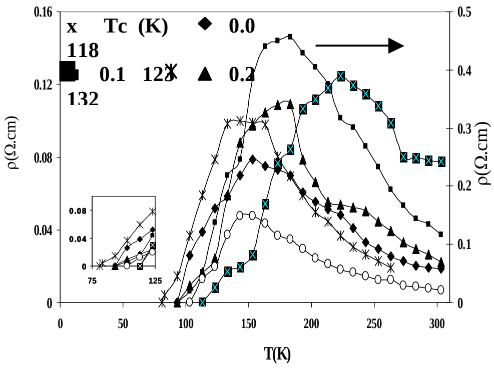

Fig (3): The electrical resistivity vs. temperature behavior of samples with various Cu concentrations

The oxygen content δ for all samples were calculated and listed in the table (1) it clearly, δ decreased with increasing x up to 0.3 after that δ increasing with increasing x.

Initially, as the hole carriers concentration decreases reducing δ [18] then increasing x would usually carry some oxygen into the structure i.e. δ increases [19].

The variation of T_c is associated with δ, this could be attributed to [10, 14, 18, 19, 20, 21, 22, 23]:

1- An interesting correlation between the occupation of the O(3) site which was randomly occupy by oxygen the centered O(3) in the Hg layer and the movement of the Ba ions towards the O(3) and a way from the Cu-O behavior. Planes. The Ba layer thus become s structurally disordered, and this disorder is found to closely mirror the T_c (δ) behavior.

2- Substitution Cu at the Hg into the Hg layer leading to a chemical pressure induced composition modulation in this plane since the pressure generally increases the hole concentration, thereby increasing doping.

3- The CuO chains contribute to the electrical conductivity if the oxygen content in the CuO chains is sufficient. Fig.(4) evident the relation of T_c and δ with x.

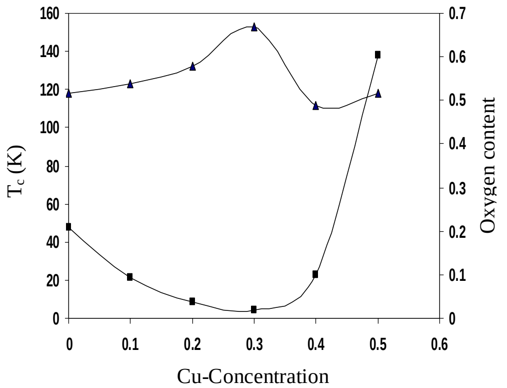

Fig. (4): The relation of T_c and δ with x

Conclusion

Cu doped Hg-based HTS have been prepared by solid state reaction. The structure was tetragonal with high ratio of Hg-1223 superconductor phase. The T_c of undoped 1223. was 118K.

In general, substitution Cu at Hg site in HgO_δ layer enhanced T_c. The high and low values of T_c 153K and 112K obtained for Cu concentration to be 0.3 and 0.4 Oxygen content δ have been found decreases with the increase of Cu concentration up to 0.3 after that additional substitution increased δ.

The results are related to the Cu-concentration since the substitution produced of local pressure, hole carrier concentration, variation electronic state and its distribution.

References

[1] M. Monteverde, M. Nunez-Regueiro, C. Acha, D. A. Pavlov, K. A. Lokshin, S. N. Putilin, E. V. Antipov, Physica C: Superconductivity, 408-410 (2004) 23-24.

[2] N.Putilin, E. V. Antipov, O. Chmaissem and M. Marezio, Nature, 362 pp.226, 1993.

[3] Schilling, M. Cantoni, J. D. Gao and H. R. Ott, Nature, 363 (1993) 56.

[4] Fukuoka, A. Tokiwa - Yamamoto *et. al.*, Physics C, 265 (1996) 13.

[5] Tokiwa - Yamamoto, S. Adachi, K. Isawa *et.al.*, Advances in Superconductivity, VI /Proc.ISS' 93 (Oct 26 - 29, 1993 Hiroshima, Japan) eds. T. Fujita, Y. Shiohara (Springer - VerlagTokyo 1994) P 247.

[6] K. Isawa, A. Tokiwa - Yamamoto, M. Itoh et. al. Physica C, 222 (1994) 33.

[7] R. Usami, S. Adachi, M. Itoh, et. al. Physica C, 262 (1996) 21.

[8] R. Giri, H. K. Singh, R. S.Tiwari and O. N. S.rivastava Mater. Sci., Vol. 24, No. 5, pp. 523–528, 2001.

[9] D. D. Shivagan, P. M. Shirage, L. A. Ekal and S. H. Pawar Physica C, V.398, Issue 1-2, pp. 53-72, 2003.

[10] C. W. Chu Chinese Journal of Physics V. 34, NO. 2-11, pp.166-183, 1996.

[11] A. Schilling, O. Jeandupeux, J. D. Gao, and H. R. Ott, Physica C 216 (1993) 6.

[12] R. L. Meng, L. Beauvais, X. N. Zhang *et. al.*, Physica C, 216 (1993) 21.

[13] I. K. Schuller, A. Bansil, D.Basov1, M. R. Beasley, J. C. Campuzano, J. P. Carbotte, R. J. Cava, G. Crabtree, R. C. Dynes, D. Finnemore, T. H. Geballe,

K.Gray, L. H. Greene, B. N. Harmon, D. C. Larbalestier, D. Liebenberg, M. B.Maple, W. T. Oosterhuis, D. J. Scalapino, S. K. Sinha, Z. Shen, J. L. Smith, J. Smith, Tranquada, D. J. vanHarlingen, D. Welch, A. Snapshot View of High Temperature Superconductivity 2002.

[14] D.T.Jover, R.J.Wijngaarden, H. Wilhelm, and R.Griessen,. Phys. Rev. B V.54, No.6, pp.465-4274, 1996.

[15] M. M. Abbas "Effect of the Electron Beam and Laser Radiation on T_C of $Y_{1-x}(Gd, Pr)_xBa_{2-Y}Sr_YCu_3O_{7-\delta}$ compounds". Ph.D. Thesis, Baghdad University College of Science, 2003.

[16] E.V.Antipov, A. M. Abakumov and S. N. Putilin, Sup.Sci.Tech.15 R31-R49, 2002.

[17] S. Hwang, J. Choy and N. H. Hur, Phys. Rev. B 57, 1259–1265, 1998.

[18] C. J. Liu C. Q. Jin, T and H. yamauchir, Phy. Revi B V. 53. No.9, pp.5170-5173, 1996.

[19] O. Chmasissem and Z. Z. Sheng, Z. phys. B99, pp.179-184, 1996.

[20] Z. Iqbal, T. Datta, D. Kirven, and A. Lungu, J. C. Barry, F. J. Owens A. G. Rinzler, D. Yang and F. Reidinger, Phys. Rev. B 49, 12322–12325, 1994.

[21] O. Osawa, physica C V.281, No. 2&3, pp.37-243, 1997.

[22] J. L. Wagner, B. A. Hunter D. G. Hinks and J. D. Jorgensen, Phys. Rev. B 51, 15407– 15414,1995.

[23] C. C. Lam, L. J. Shen and H. M. Shao, J. Supe.V.15, No.3, pp.225-229, 2002.