

## Raman Studies of $Hg_{1-x}Cu_xBa_2Ca_2Cu_3O_{8+\delta}$ Compounds

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### ABSTRACT

Solid state reaction method by two steps was used to synthesize  $Hg_{1-x}Cu_xBa_2Ca_2Cu_3O_{8+\delta}$  samples where  $x=0.1$  and  $0.5$ . Comparative Raman studies of Cu-doped  $Hg_{1-x}Cu_xBa_2Ca_2Cu_3O_{8+\delta}$  were presented in an attempt to clarify the phononic modifications induced by Cu substitution. A number of phonon peaks showed up in the spectra assigned to different phases, usually small amounts of starting material that did not react or secondary products were unintentionally grown. On other hand foreign phases have much larger Raman signals and showed up strongly in the spectra.

**Keywords:** Raman Scattering; Hg-1223 Compounds; Doping

### دراسات رامان لمركبات $Hg_{1-x}Cu_xBa_2Ca_2Cu_3O_{8+\delta}$

#### الخلاصة

استخدمت طريقة تفاعل الحالة الصلبة على خطوتين لتحضير نماذج  $Hg_{1-x}Cu_xBa_2Ca_2Cu_3O_{8+\delta}$  حيث كانت نسب التطعيم  $0.1$  و  $0.5$ . تمت المقارنة بين دراسات رامان لمركبات  $Hg_{1-x}Cu_xBa_2Ca_2Cu_3O_{8+\delta}$  كمحاولة لتوضيح التعديلات الفونونية المتسببة كنتيجة للتطعيم والتعويض بال Cu. اشيرت مجموعة القمم الفونونية في الطيف الى اطوار مختلفة عادة ما كميات صغيرة تعود الى المواد الاولية والتي لم تتفاعل او الى منتج ثانوي نما عند تحضير العينات. من جهة اخرى ظهرت اطوار غريبة بقوة في الطيف مع انماط رامان اكبر بكثير من غيرها.

### INTRODUCTION

Raman scattering in solids have been advanced to experiments on the absorption of solids in the advent of lasers and sensitive detectors. Small samples were nondestructively investigated at low temperatures, under electric or magnetic fields, as a function of excited energy, and under high pressure. Raman scattering is the inelastic scattering of electromagnetic radiation (photons) creating or annihilating an elementary excitation in the solids. The elementary excitations can, among others, be phonons, plasmons, excitons, or spin fluctuations. All these excitations have been observed and studied in high-Tc superconductors, which have contributed a lot to their understanding [1, 2].

The high superconducting (HTSC) transition temperatures ( $T_c$ ) were observed in the  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$  series, where  $n=1, 2, 3, \dots$ . Especially under high pressure, and have showed great interest in their structural and physical properties [ 3 and 4].

Unfortunately, there are still scientific and structural problems concerning the phase stability, especially the presence of carbon dioxide and humidity [5]

In the view of this, significant efforts have, recently, been made to improve the stability of the Hg bearing HTSC phases, particularly the Hg-1223 phase. 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.

It is known that the most effective way to improve the stability of the Hg-1223 phase is through suitable cationic substitution for Hg. Although the cationic substitution of Hg site lead to stability, it also affected the superconducting properties,  $T_c$  and the critical current ( $J_c$ ) [6-8].

The Knowledge of the strength electron-phonon coupling and its changes with doping is crucially important for this understanding. The phonon frequencies and the matrix elements of electron-phonon coupling are determined by the effect of the ion displacements on the electron band structure. Experimentally, phonons are seen directly in the inelastic (Raman) light scattering and infrared light absorption experiments [9].

Poulakis *et al.* [10] attempted by Raman investigation to clarify the structural and phononic modifications by Re-doped  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\square}$  with  $n=1, 3, 4, 5$ . A number of extra high-frequency phonon peaks showed up in the spectra of the Re-doped samples are attributed to the oxygen mode of strong bounds, moreover a narrow peak have been found, probably attributed to *c*-axis vibrations of Ba whose frequency shows a distinctive change with the number  $n$  of the  $\text{CuO}_2$  layers, providing an easy way to identify the various phases in the samples. Despite the experience accumulated by Raman studies on other compounds, but the case of the HTSC materials are much complicated, due to the difficulties in preparing pure enough compounds. However, the influence of the atomic substitution or doping is not yet fully understood in the cuprate superconductors, and this represents our active area of the current research.

## EXPERIMENTAL DETAILS

Solid state reaction method by two steps was used to synthesize  $\text{Hg}_{1-x}\text{Cu}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  samples where  $x= 0.1$  and  $0.5$ . First of all the molar ratios of high purity powders of  $\text{CuO}$ ,  $\text{BaCO}_3$  and  $\text{CaCO}_3$  were adjusted, mixed and ground using an agate mortar. Then calcined at  $800^\circ\text{C}$  for 30hr, after regrinding and mixed the  $\text{BaCaCuO}$  precursor with powdered  $\text{Hg}_2\text{O}$ , pellets were pressed from the so obtained mixture. The sintered process for the pellets was performed by three steps.

In the first step the temperature of the furnace was raised to  $850^\circ\text{C}$  and held at this temperature for 50hr, then subsequently slow cooled to  $350^\circ\text{C}$ , the pellets annealed at this temperature for 3hr. In the second step, the pellets heated to  $850^\circ\text{C}$ , and annealed at this temperature for 20hr then cooled again to  $350^\circ\text{C}$ , held for 3hr, in the final third step the furnace was heated to  $850^\circ\text{C}$  and held for 130hr before cooling to room temperature. It should be mentioned that for every heating and cooling process the rate

was  $4^\circ\text{C} / \text{min}$ . All samples in the present investigations were subjected to gross structural characterization by X-ray diffraction (XRD), using Shimadzu unit- 2006, with  $\text{Cu-K}\alpha$  radiation. The lattice parameters have been estimated using  $\theta$ -values and  $hkl$  reflections of the observed X-ray diffraction pattern by a least square method and a computer program.

Iodometric titration was used to access the oxygen content in the samples.

The Raman spectra of the Hg-Cu samples were examined using a triple Raman spectrometer T64000 (Horiba-Jobin-Yvon) equipped with microscope and liquid nitrogen cooled detector. The excitation laser line was 488 nm of Ar<sup>+</sup> laser. For each composition there are three spectra assigned as HH, HV, and VV. H and V are two arbitrary orthogonal directions. HH and VV are spectra taken with parallel polarizations of incident and scattered light (along H or V direction, respectively). HV means that incident and scattered polarizations are less than  $90^\circ$ .

## RESULTS AND DISCUSSION

The XRD data collected from our various samples indicated that all samples are polycrystalline and correspond to tetragonal Hg-1223 phase with some impurity phases of vanishingly small concentrations. The representative XRD patterns are shown in Figure (1). It has been noticed from Table (1), that with the increasing of the Cu concentration  $x$ , the lattice parameter  $a$  increased while the parameter  $c$ , decreased, however, as whole the volume  $V$  increased.

In addition as shown in the Table (1) the oxygen content  $\delta$  increased with the increase of Cu substituted atoms which carried with them some oxygen into the structure [11].

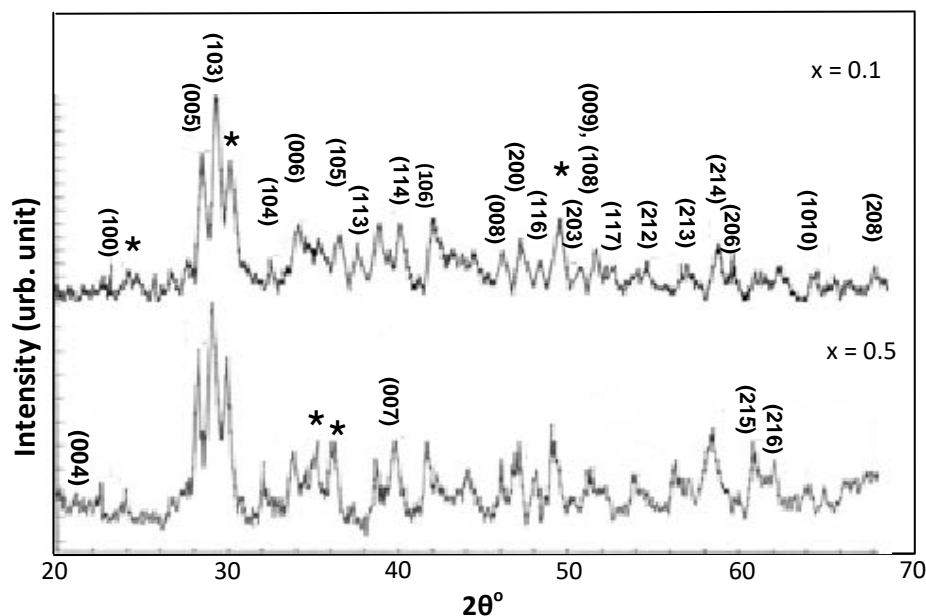


Figure (1) XRD pattern of Cu-doped  $\text{Hg}_{1-x}\text{Cu}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$   
With  $x$  concentration 0.1 and 0.5.

**Table (1) Variation of lattice parameters, unit cell and oxygen Content for  $x=0.1$  and  $0.5$ .**

$x$	$a$ (Å)	$c$ (Å)	$V$ (Å) <sup>3</sup>	$Z$
0.1	3.840518	15.88519	234.2999	0.092
0.5	3.867768	15.84782	237.0775	0.605

Usually particular samples may consist of different phases, one may expect that tiny amounts of starting materials may not react or the reaction yields very small secondary products which were unintentionally grown. Foreign phases have much larger Raman signals and shows up strong phononic peaks in the spectra [1]. Such observations are further confirmed in the analysis of the patterns of these samples. The Raman spectra of the most important impurity phases for Cu concentration 0.1 and 0.5 doped Hg1223 are shown in Figure (2 and 3) respectively.

Figure (2) depicts spectra of  $\text{Hg}_{0.9}\text{Cu}_{0.1}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  sample. A group of high-frequency peaks out of which the ( $\sim 592\text{cm}^{-1}$ ), the phononic apical -O mode one in the  $c$ -direction dominates, the broadening phononic peak at  $\sim 240\text{cm}^{-1}$  corresponds to  $\text{HgCaO}_2$ . Moreover, due to the similarity to  $\text{HgO}$  mode  $332\text{cm}^{-1}$ , and consistent with a low-frequency shift the peak at  $350\text{cm}^{-1}$  assigned to  $\text{HgO}$ . Beside the mode at  $\sim 641\text{cm}^{-1}$  refers to either to  $\text{Hg1223}$  or to  $\text{HgBaO}_2$ .

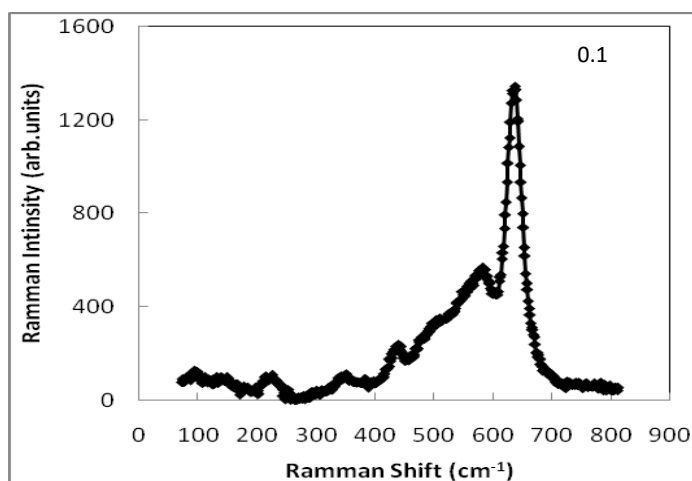
**Figure (2) Raman spectra for  $\text{Hg}_{0.9}\text{Cu}_{0.1}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  compound.**

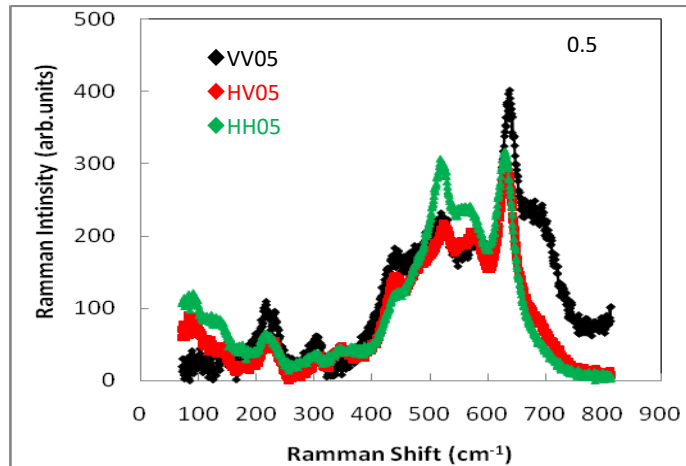
Figure (3) shows spectra of  $\text{Hg}_{0.5}\text{Cu}_{0.5}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  sample, one can discriminate new set of peaks appears, namely that at  $310\text{cm}^{-1}$  modes induced by substitution defects on Hg sites, since it is absent from the spectrum in Figure (2). On the other hand,  $\sim 536\text{cm}^{-1}$  mode correspond to  $\text{Hg-1201}$  due to the increasing partial substitution of Hg by Cu or the loss of Oxygen atoms in the  $\text{HgO}$  planes which

activates the in-phase mode. The origin of the  $\sim 670 \text{ cm}^{-1}$  shoulder is assigned to  $\text{HgCaO}_2$ . Moreover, the other point is that, Cu-induced a slightly broadening, shifting and increased the width up to a certain extent, the peak between  $570\text{-}590 \text{ cm}^{-1}$  mode (broad band), may be attributed to increasing the substituting of Hg by Cu attracts more oxygen which affect the intensity of the other modes and merge the modes of the apical -O, and  $570 \text{ cm}^{-1}$ . On the other hand it is more probably that  $570 \text{ cm}^{-1}$  mode is related to interstitial oxygen atoms, since our data showed considerable increase in  $\delta$ .

In addition, Figure (3) shows peak at  $440 \text{ cm}^{-1}$  which doesn't appear in other members of Hg-family and splitting of the mode at  $240 \text{ cm}^{-1}$ . The origin of the additional modes and of the splitting is still controversial.

Upon Cu substitution, a clear redistribution of Raman spectra is observed due to an excess of the oxygen content. Another result could be noticed near  $100 \text{ cm}^{-1}$ , tentatively attributed to c-axis vibrations of Ba.

The results above in accordance with previously reported works [4, 10 and 12].



**Figure (3) Raman spectra for  $\text{Hg}_{0.5}\text{Cu}_{0.5}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  Compound.**

## CONCLUSIONS

It has been demonstrated that Raman studies of Cu-doped  $\text{Hg}_{1-x}\text{Cu}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  compounds a number of phonons peaks show up in the spectra assigned to different phases, usually small amounts of starting material that did not react or secondary products which were unintentionally grown. Foreign phases have much larger Raman signals and showed up strongly in the spectra. In addition, upon Cu substitution, a clear redistribution of Raman spectra is observed due to an excess of the oxygen content.

## REFERENCES

- [1]. Thomsen and G. Kaczmarczyk, C. Vibrational Raman spectroscopy of high – temperature superconductors, John Wiley and Sons Ltd, Chichester, (2002).
- [2]. GENG and S. FENG, Z. Modern Physics Letters B Vol. 27, No. 9 (2013) 1330006, pp1-19. World Scientific Publishing Company DOI: 10.1142/S0217984913300068.
- [3]. Y-Y. Xie ), J. Z. Wu , A. A. Gapud , Y. Yu , Y. Xin, Synthesis of Hg-1223 superconductors using a cation-exchange process, Physica C 322 ,(1999), pp. 19–24.
- [4]. Krantz, M.C. C. Thomsen, Hj. Mattausch, and M. Cardona, Raman –active phonons and mode softening in superconducting  $\text{HgBa}_2\text{CuO}_{4+\delta}$  Phys. Rev. 50, (1994), pp.1165-1170.
- [5]. Babych, O. Ya. Boyko, I. Gabriel, R. Luticiv, M. Matviyiv and M. Vasyuk, Preparation and properties of doped Hg-based superconducting copper oxides. Proceedings of the International Workshop “Oxide Materials for Electronic Engineering” (OMEE-2009), Lviv 2009 ACTA Physica Polonica A, V.117, No.1 (2010).
- [6]. Schuller, I.K. A. Bansil, D. Basov, 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. van Harlingen, D. Welch, A Snapshot View of High Temperature Superconductivity (2002).
- [7]. Giri, R. H. K. Singh, R. S. Tiwari and O. N. S. rivastava, Effect of cationic size in  $\text{Hg}(\text{Tl}/\text{Bi})\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  on superconducting and microstructural characteristics Mater. Sci., V. 24, No. 5, (2001), pp. 523–528.
- [8]. Jover, D.T. R.J. Wijngaarden, H. Wilhelm, and R. Griessen, Pressure dependence of the superconducting critical temperature of  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+y}$  and  $\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+y}$  up to 30 GPa Phys. Rev. B V.54, No.6, (1996), pp.4265-4274.
- [9]. Ambrosch-Draxl and E Ya Sherman, C. The puzzling Hg family revisited: a comprehensive study based on density functional theory. Iranian Journal of Physics Research, V. 6, No. 3 (2006), pp.103-116.
- [10]. Poulakis, N. D. Lampakis, and E. Liarokapis Akira Yoshikawa, Jun-ich Shimoyama and Kohji Kishio, G. B. Peacock, J. P. Hodges, I. Gameson, and P. P. Edwards and C. Panagopoulos, Re-induced Raman active modes in  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$  compounds, Phys. Rev. B V. 60, No.5 (1999), pp.3244-3251.
- [11]. Chmasisssem and Z. Z. Sheng, O. A new (Hg, V)-based 1212-type cuprate  $(\text{Hg}, \text{V})\text{Sr}_2(\text{Y}, \text{Ca})\text{Cu}_2\text{O}_z$  with  $T_{c(\text{onset})}$  up to 110 K, Z. phys. B99 (1996), pp.179-184.
- [12]. Liarokapis, E. Raman studies of local structure, superstructure and phases in high temperature superconductors, Physica C 341 (2000), pp. 2185-2188.