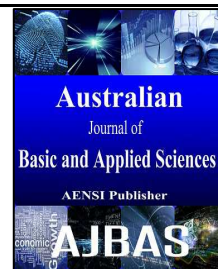




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Raman Study of $\text{Bi}_{2-x}\text{Cu}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ Compounds

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ABSTRACT

Samples of stoichiometric composition $\text{Bi}_{2-x}\text{Cu}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ with $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5 were prepared by a solid state reaction method. Comparative Raman studies of $\text{Bi}_{2-x}\text{Cu}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ were presented in an attempt to clarify the phononic modifications induced by Cu substitution. The results of Raman scattering measurements at room temperature show a number of phonon peaks revealed the presence of many phases, which is confirmed by X-ray diffraction. New phonon peak and broad band observed at 540 cm^{-1} mode which assigned for $\text{Bi}_{1.7}\text{Cu}_{0.3}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ and $\text{Bi}_{1.5}\text{Cu}_{0.5}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ respectively, could be to an intrinsic mode corresponds to Pb-O vibration mode. Furthermore, pronounced high-frequency mode found at 629 cm^{-1} is attributed to apical oxygen (i.e. Cu-O-Bi) vibration along the c axis in the Sr-O plane.

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INTRODUCTION

There are three superconducting phases in the Bi-Sr-Ca-Cu-O system which have an ideal structural formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$, with $n = 1, 2$ or 3 indicating the number of the CuO_2 planes. Bi2223 is well known as the compound that is difficult to synthesize in a single phase due to formation of intergrowth of the multiphase (Bilgili, O., 2008)

The formation and stability of the 2223 phase can be modified with many methods by the addition or substitution of elements of varying ionic radii and bonding characteristics. This variation is thought to be related to the density of charge carriers in the CuO planes. This variation is thought to be related to the density of charge carriers in the CuO planes. Weak coupling between BiO-BiO layers in the BSCCO system enables the substitution of the different oxides for Bi^{3+} site. Among these, addition or partial substitution of trivalent Bi with Pb has been found to be the most effective method (Sunshine, S.A., 1988; Takano, M., 1988).

Pb doping on Bi2223 has a bond-ordering effect and reduces sharply the structure modulation (Pham, V., 1993). Moreover it changes the holes concentration in CuO_2 planes, it also create an oxygen vacancies by being predominantly in a 2+ oxidation state (Karppinen, M., 2003; Paulose, P.L.,

1993). On other hand Pb atoms act as efficient nucleation and growth sites for the formation of the high- T_C phase and enhance the diffusion of the calcium and copper atoms (Williams, G.V.M., 2000).

The inspiration of the successful BCS theory in conventional superconductors, to reveal the mystery of high temperature superconductivity is ascribable to the studies of electron Cooper pairs. Geng and Feng showed that the density of Cooper pairs almost increases linearly with increasing doping concentration in the underdoped regime (Geng, Z.H., S.P. Feng, 2013).

One way to obtain how doping process affects the electronic structure would be to investigate the change optical-phonon spectrum with doping as well as there is experimental evidence for intrinsic inhomogeneous charge distribution in HTCS compounds.

Lattice vibrations in high- T_C cuprates attract attention as a factor which can influence both normal and superconducting states, as well as possible mediators of superconductivity. However, compared to normal metals, HTCS in their normal state, present many differences and different kinds of anomaly which render this normal state still a matter where of controversy.

Despite the experience accumulated by Raman studies on other compounds, but the case of the HTCS materials are much complicated, due to the

difficulties in preparing pure enough compounds. Moreover it has been known that the actual structure of Bi-based cuprates is only pseudo -orthorhombic due to stacking faults, extra-stoichiometric oxygen and incommensurate superstructure modulation along the b axis in BiO and SrO layers (Kovaleva, N.N., 2004).

These factors is adopted to make an assignment in the experimental phonon spectra, in which to distinguish the extra phonon mode due to the effects of superstructure incommensurate modulations and the presence of extra stoichiometric oxygen in the Bi-based compounds. Besides 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 to invest-igate the phonon modes and Raman scattering intensities as a function of doping in the normal state.

I. *Experimental:*

The polycrystalline $\text{Bi}_{2-x}\text{Cu}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ samples with ($x=0.0-0.5$) were synthesized by the solid state reaction method. First of all the molar ratios of high purity powders of Bi_2O_3 , Pb_3O_4 , $\text{Sr}(\text{NO}_3)_2$, CaCO_3 and CuO were taken accurately. Then the powders were well mixed using agate mortar. A sufficient quantity of 2-propane was used to homogenize the mixture. The mixture was ground to a fine powder and then calcined in air at 800°C for (20-24) hrs with repeated intermediate re-grinding. The powder pressed into disc-shaped pellets with 13mm in diameter and (25-28) mm thickness using a manually hydraulic press type (Specac) under different pressures around 0.5 GPA. After that pellets sintered at 860°C for 140 hrs then air cooling to room temperature.

All samples in the present investigations were subjected to gross structural characterization by X-ray diffraction (XRD), using Shimadzu unit- 2006, with $\text{Cu-}\alpha$ radiation. The lattice parameters have been estimated using θ -values and hkl reflections of the observed X-ray diffraction pattern based on Cohen's least square method.

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

The Raman spectra of the Bi-Cu samples were examined using a triple Raman spectrometer T64000 (Horiba-Jobin-Yvon) equipped with a microscope and a liquid nitrogen cooled detector. The excitation laser line was 488 nm of Ar^+ 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° .

RESULTS AND DISCUSSION

The XRD patterns of the $\text{Bi}_{2-x}\text{Cu}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ samples indicated that all samples are polycrystalline and correspond to orthorhombic structure as shown in Figure 1. Most of them exhibited two main phases, i.e., high- T_C phase (2223) and low- T_C phase (2212). The indices of the patterns are similar to refs. (Primo, V., 1992).

Some intensity of the high- T_C (2223) phase reflections is higher than those of the low- T_C phase. This case appears more clearly with increasing Cu content and it indicates the increasing of the crystalline arrangement degree.

The lattice constants a,b,c, unit cell V and c/a were calculated from the XRD analysis as shown in Table (1). This Table indicates that c/a increases with the increasing of the Cu concentration. This behavior may be explained by the differences in the ionic radii for both of Cu, Pb and Bi.

Moreover, as shown in the Table (1) excess oxygen δ decreased in general, although not systematic. The addition of oxygen perhaps led to increase in the mean valence of copper ion, thus increasing of the substitution will increase the amount of Cu^{+3} with respect to other valences, (Cu^{+2} and Cu^{+1}). Holes are present on oxygen rather than on copper as it pronounced (Kim, S.H., 1994) this could be attributed to the presence of excess oxygen atoms in the CuO_2 layers so those atoms will create more holes in the perovskite layers (Khaled, J., 1997).

Figure 2 shows the image of the polished surface of three samples (0.0, 0.3 and 0.4) as seen under microscope with x100 magnification. The viewing area is approximately ($0.08 \times 0.08 \text{ mm}^2$). As shown, there are dark and bright spots. The spectra obtained from the dark areas correspond to Bi-based HTCs, but there are at least two other phases, which constitute a significant part of the total volume. The brighter areas corresponds to one of these phases, which could be impurity Pb-rich phase.

Figure 3 illustrated the Raman mapping for small area in combined with Raman scattering for sample $x=0.4$. The areas giving different types of spectra are imaged with different colours. There is an excellent agreement between the visuals, Raman image and the three main phases which are clearly distinguished. Such observations are further confirmed in the analysis of the X-ray pattern of this sample.

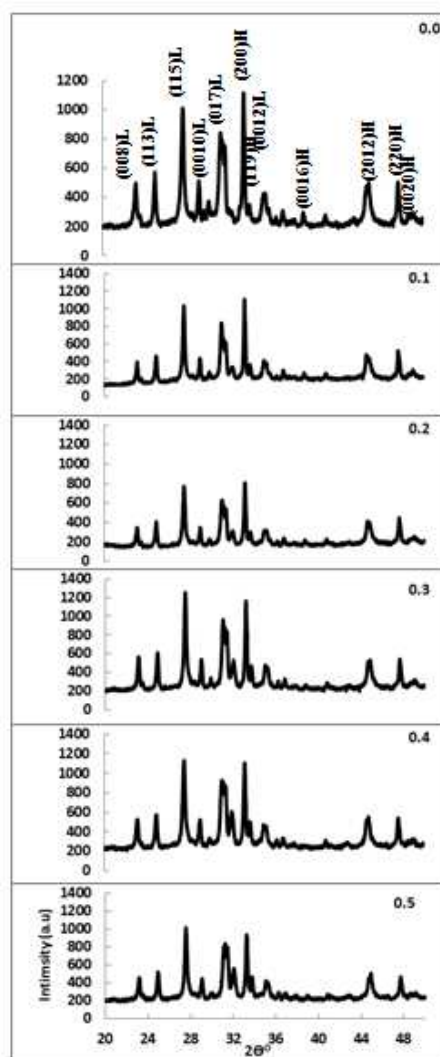


Fig. 1: XRD Patterns for the samples $\text{Bi}_{2-x}\text{Cu}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ for $x=0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5 .

Table 1: Values of $a, b, c, V, c/a$ and oxygen content for different composition of $\text{Bi}_{2-x}\text{Cu}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$.

x	a (Å)	b (Å)	c (Å)	V(Å) ³	□
0.0	5.433089	5.390899	37.44233	1096.65717	-0.4861
0.1	5.473081	5.385728	37.69735	1111.1869	-0.5724
0.2	5.476838	5.379963	37.7678	1112.83524	-0.1543
0.3	5.476861	5.368564	37.74897	1109.92839	-0.2445
0.4	5.473932	5.382677	37.74053	1112.00237	-0.4721
0.5	5.468495	5.375503	37.76442	1110.11954	-0.4182

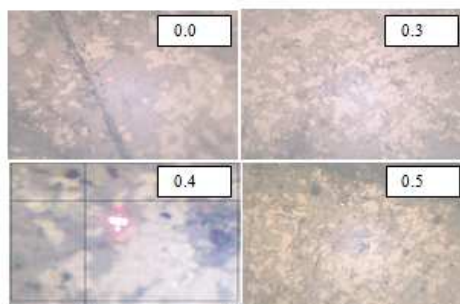


Fig. 2: The image of the polished surface of three samples (0.0, 0.3 and 0.4) as seen under microscope with x100 magnification.

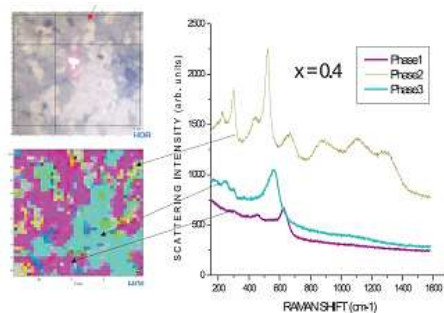


Fig. 3: The Raman mapping for small area in combined with Raman scattering for sample $x=0.4$.

Figure 4 depicts Raman spectra of $\text{Bi}_{2-x}\text{Cu}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ compounds. The assignments of phonon peaks are made by comparison with other Bi2212 and Bi2223 high-TC superconductors since it is evident that the electronic Raman scattering look rather similar for both.

One can discriminate set of peaks appear, namely that at 90 and 116 cm^{-1} . These superlattice modes are clearly seen at room temperature, the origin of 90 cm^{-1} mode is related to motion of Bi atoms, which is strongly mixed with out-of-phase motion of Sr, Cu1 and Ca, with a small oxygen contribution from different planes. While the 116 cm^{-1} corresponds to Bi2212 is tentatively attributed to the motion of the Cu1 against Sr, with a small contribution from Ca ions.

On the other hand, slightly broadening phononic peak (broad band) observed around 325 cm^{-1} which belongs to Bi2212 disappeared with substitution due to the formation and stability of the 2223 phase modified. The results above adopted in accordance with reported works [4, 9, 16, 17 and 18].

However, oscillator strength of the modes between 300-350 cm^{-1} correlates with partial substitution of Bi by Cu and with the amount of extra oxygen. It is likely related to the effects of O3 and O1 vibrations against Sr and Ca atoms. Since the resonance effect is the evidence that the electronic state in the inner CuO2-planes is different from that of the outer CuO2-planes, the results in this range ascribed could be to in-phase and out phase vibrations of the Ca atoms with oxygen in the outer CuO2 planes.

For Bismuth cuprates, the Raman anisotropy is well observed with the bands around 630 and 460 cm^{-1} . The peak at 458 cm^{-1} assigned to Bi2212 in the Raman spectrum. It can be seen that the intensity of the peak decreases with increasing doping. However, this decrease in intensity may not be only to disorder-induced scattering effect, it may be to vibrations of apical oxygen atoms in the BiO planes. Where, increasing substituting attracts more oxygen atoms in the BiO layers, since our data showed considerable increase in.

In addition, one can discriminate new strong phonon peak and broad band named at 540 cm^{-1} for

$\text{Bi}_{1.7}\text{Cu}_{0.3}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ and $\text{Bi}_{1.5}\text{Cu}_{0.5}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ respectively. This mode could be assigned to be an intrinsic mode corresponds to Pb-O vibration mode, induced by Pb-rich impurity phase rather than a Cu-O-Pb mode. The effect of Pb on the position of the Cu-O-Bi Raman mode cannot yet be conclusively explained. We speculate that the appearance of this mode is only for $x=0.3$ and 0.5 and its disappearance in the other samples could be due to the change in the relative distribution of the sites occupied by Pb. Although it is generally assumed to primarily substitute as Pb^{2+} on the Bi^{3+} site, resulting in an increase in the hole concentration it could conceivably substitute onto the Sr, or Ca sites.

At higher frequency side, a pronounced mode observed at 629 cm^{-1} corresponding to both Bi2223 and Bi2212 phases. Feature is in fact the most commonly observed one arise from apical oxygen (i.e., Cu-O-Bi) vibration along the c axis in the Sr-O plane. Most authors have assigned the doublet mode at 650-625 cm^{-1} in undoped Bi-based compounds disappears and is reduced to a single band around 630 cm^{-1} with doping. Thus, the absence of doublet mode in our Raman spectrum suggests that a spectral and microstructure changes are mostly induced by an additional bond-ordering occurs and the bond distribution becomes more homogeneous i.e., a structure modulation decreases due to Cu doping or it might be Pb^{+4} preferentially substitutes for Bi^{+5} in the BiO layers (Pham, V., 1993; Kovaleva, N.N., 2004; Huong, P.V. and S.A. Ndiaye, 2004; Kakihana, M., 1996; Mej1-a-Garci, C., 2004).

III-Conclusion:

It has been demonstrated that Raman studies of Cu-doped $\text{Bi}_{2-x}\text{Cu}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ compounds a number of phonons peaks show up in the spectra assigned to different phases such observations are further confirmed by the microscope image, Raman mapping and XRD.

Decreasing the intensity and broadening of the low phase peaks with increasing the substitution indicate promote the high phase. In addition, pronounced single band high-frequency mode observed at 629 cm^{-1} infers that an additional bond-

ordering occurs and the bond distribution becomes more homogeneous.

Upon Cu and Pb doping, a clear redistribution of Raman spectra is observed due to an excess of the oxygen content moreover, are infer that an additional

bond-ordering observed a consequence of a sharp reduction of the structural modulation which initially occurring in Bi223.

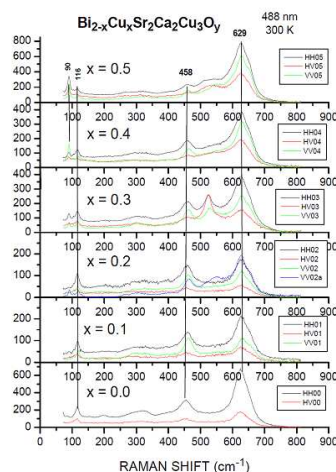


Fig. 4: Depicts Raman spectra of $\text{Bi}_{2-x}\text{Cu}_x\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ compounds.

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