

**PHONON SPECTRA OF HIGH TEMPERATURE  
SUPERCONDUCTOR  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ :  
THEORY AND EXPERIMENT**

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**Abstract:** *Since the discovery of the high  $T_c$  superconductivity by Bednorz and Muller, several workers around the world have studied several systems to reach a really high  $T_c$  superconductor. As the strong electron-phonon coupling may be one of the possible origins of the high  $T_c$ , a knowledge about the phonon in these materials is essential. In order to investigate phonon spectra, Raman and infrared spectra of these systems have been studied. But there is a little information available in the literature for complete Raman and infrared absorption spectra. Infrared is of little use for characterization purposes but important for fundamental studies provided single crystals are used. Due to the nature of the superconductivity materials, it is not possible to obtain all the phonon frequencies experimentally through Raman and infrared spectra. Hence a theoretical evaluation of phonon frequencies of high temperature superconductors assumes importance. The Fourier transform Raman spectra of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  have also been recorded in the solid phase in the range of 700 to 100  $\text{cm}^{-1}$  using Bruker IFS 66V FTIR Spectrometer with FRA R06 Raman module for the experimental confirmation of the present assignment. Due to strong covalent bonding nature in high temperature superconductors, a normal coordinate analysis using Wilson's FG matrix is applied here to evaluate phonons frequencies of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ . The normal coordinate analysis of optically active lattice vibrations will be useful for the theoretical interpretation of vibrational spectrum at the center of Brillouin zone for  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  high  $T_c$  superconductor. Calculations of lattice dynamics is also performed using the modified three body force shell model (TSM). The present approach leads to a better understanding of phonons frequency of high  $T_c$  superconductor  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ . This calculation yields the zone center phonons modes and potential energy distribution helps to identify the pure and mixed frequencies. This gives further support in understanding the phonons spectra of the high temperature superconductors. Hence, the present approach is useful not only to obtain all the phonons frequencies of high temperature superconductor  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  reasonably but also to characterize it.*

**Keywords:** high temperature superconductors, Raman spectrum, phonons frequency, normal coordinate analysis, lattice dynamical calculations,  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$

## 1. INTRODUCTION

After the discovery of 30K Cu-O perovskites, solid state physicist and material scientists put an enormous effort to isolate the phases which are responsible for superconductivity as well as to search for new materials. This activity succeeded in the discovery of superconductivity in several compounds such as  $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_7$  (R = rare earths), Bi-Sr-Ca-Cu-O, Tl-Ba-Ca-Cu-O, Pb-Sr-(Ca, Ln)Cu-O, Hg-Ba-Ca-Cu-O systems and in non cuprates. In addition to the synthesis of new materials, a vast amount of investigations have also been carried out to understand the nature of superconductivity. One such investigation is to obtain the contribution of lattice interactions to the superconductivity. Raman and Infrared spectra give a few phonon frequencies at the centre of the Brillouin zone.

The assignments of spectral lines to lattice vibrations is an important step to understand their role in superconductivity. Raman and Infrared studies have contributed significantly for the interpretation of high  $T_c$  superconductor mechanism. In spite of several studies, the assignment of the vibrational normal modes remains controversial. The material characterization by Raman technique depends critically on the phonon assignments. Cardona and others [1–5] studied the Raman and Infrared spectra of the superconductivity cuprate perovskites and reported the origin of phonon softening and the systematic vibrations of phonon frequencies with ionic radius.

## 2. NORMAL COORDINATE ANALYSIS

A fairly good amount of literature is available on the vibrational spectra of high temperature superconductors. Yet, some specific features in the experimental vibrational spectra could not be assigned reliably to a definite type of vibration. Hence, a normal coordinate analysis (NCA) which is applicable to zero wave-vector normal-mode vibrations have been carried out for the high temperature superconductors and the assignment of specific modes are looked into for the clear understanding of the superconducting mechanism. This is not possible in lattice dynamical calculations. The normal coordinate analysis provides a more quantitative description of the vibrational modes. In this method, non central forces such as those involved in angle bending can be readily used. In this method the frequency of the normal vibration is determined by the kinetic and potential energies of the system. Wilson's FG matrix method [6] modified by Shimanouchi et al. [7] for solids is applied for the calculation of optically active vibrational frequencies. The kinetic energy is determined by the masses of the individual atoms and their geometrical arrangements in the molecule but the potential energy (PE) arises from interaction between the individual atoms described in terms of the force constants. Assuming reliable potential constants for various bonds, the vibrational frequencies have been evaluated. Fine tuning is

done until the available observed frequency and the present evaluated frequency matches perfectly. Internal coordinates namely, bond lengths and bond angles are used in the kinetic and PE expressions. They have a clear physical meaning as these force constants are characteristics of bond stretching and angle deformation involved. The calculations are carried out using Simple General Valence Force Field (SGVFF) for the following reasons: (a) SGVFF has been shown to be very effective in normal coordinate analysis of superconductors, and (b) Valence force constants can be transferred between the related molecules. The normal coordinate calculations were performed by utilizing the program of Fuhrer et al. [8] with suitable modifications for computing the G and F matrices (G-MAT sets up the kinetic energy matrices G and FPERT evaluates the potential constants F and defines vibrational frequencies) and for adjusting a set of independent force constants [9–11].

Also, in NCA, Potential Energy Distribution (PED) indicates the contribution of an individual force constant to the vibrational energy of a normal mode for the clear understanding of the specific vibration of the species involved. The normal coordinate calculations were performed to support the assignment of the vibrational frequencies and to obtain PED for various modes. In the normal coordinate analysis, PED plays an important role for characterization of the relative contributions from each internal coordinate to the total PE associated with particular normal coordinate of the molecule. The contribution to the PE from the individual diagonal elements give rise to a conceptual link between the empirical analysis of vibrational spectra of complex molecules dealing with characteristic group frequencies and the theoretical approach from the computation of the normal modes. NCA gives complete assessment of all normal vibrational modes of the system. This technique is adopted here to study the phonon spectrum of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ .

### 3. LATTICE DYNAMICS

Phonons are useful in the study of the electron-phonon interaction in order to establish their role in the mechanism of superconductivity. Lattice dynamical calculations [12] for the high  $T_c$  superconductors have been performed for mainly two purposes. The first was to calculate the electron-phonon interaction and its influence on the increased transition temperature for high temperature superconductors. Secondly, a number of experiments on the phonon spectra needed a correct assignment on the phonon vibrational excitations. Apart from these studies of electron-phonon interaction, several authors have attempted to calculate the phonon frequencies [13–21] for a comparison with experimental results.

An attempt has been made in this paper to study phonon frequencies in  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  high temperature superconductor in the frame work of modified three body force shell model (TSM).

The calculations for high temperature superconductors are based on the use of long-range coulomb potentials, short-range repulsive Born-Mayer potentials and the ionic polarizabilities, in the frame work of the shell model. The pair potentials have been transferred from ion pairs in similar configuration in compounds for which phonon dispersion curves have been measured. With the shell model calculation, the equation of the motion for the core coordinates  $U$  and shell coordinate  $W$  are expressed by the following equations as [21]:

$$-M\omega^2 = (R + ZC'Z) U + (T + ZC'Z)W$$

$$O = (YC'Z + T) U + (YC'Y + S) W$$

The modified TSM gives the coulomb matrix  $C' = Z [ Z + 12f(a) ] C + V$  where  $V$  is the matrix corresponding to the terms containing the first derivative of the charge transfer function.  $M$ ,  $Z$  and  $Y$  are diagonal matrices representing the mass, ionic charge and the charge on the shell.  $R$ ,  $S$  and  $T$  are matrices specify short range core-core, shell-shell and core-shell interactions respectively and  $f(a)$  is related to overlap integrals of electron wave function.  $U$ ,  $W$  are displacements and  $C$  represents the coulomb terms.

The earlier investigators have assumed short range core-core, shell-shell and core-shell interactions equal. But our rigorous and detailed calculations on the matrices revealed differences in these interactions.  $R$  and  $C$  matrix elements have been worked out using the expression given by Kellerman [22]. The introduction of short range force constants  $A_1, A_{11}, B_1, B_{11}$  introduced from our work in a simple manner enables one to calculate  $T$  matrix elements. The constants connecting  $T$ ,  $R$  and  $S$  enabled us to calculate matrix elements. We have also kept the variation of  $T$ ,  $R$  and  $S$  to be identical with respect to symmetry directions. It is interesting to note that  $R$ ,  $S$  and  $T$  values show a difference from each other. With this modification, attempts have been made to evaluate phonon frequencies. This new approach with  $R \neq T \neq S$  is introduced for the first time and has been applied to alkaline earth oxide crystals and transition metal ions in our earlier work [23–26].

The short-range interactions between neighboring ions are represented by Born-Mayer potentials

$$V_{ij}(r) = a_{ij} \exp(-b_{ij} \cdot r)$$

where  $i, j$  label the ions and  $r$  is their distance. The parameters  $a_{ij}$  and  $b_{ij}$  are the pair potentials and the parameters  $Y_1$  determine the electronic polarizabilities.

It is encouraging to note that the evaluated phonon frequencies of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  agree quite well with Raman data, wherever they are available. Further, the evaluated phonon frequencies of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  from lattice dynamical calculation agree quite well with the phonon frequencies evaluated from normal coordinate analysis.

#### 4. Bi-2223 COMPOUND

Bismuth cuprate superconductors Bi-Sr-Ca-Cu-O system possess the different phases such as  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$  ( $n = 1, 2, 3$ ). The phases greater than  $n = 3$  cannot be prepared by solid state reaction. The molecular beam epitaxy-thin film techniques can only be applied for the preparation of higher phases. The phase  $n = 3$ , viz,  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  phase is extremely difficult to prepare as single phase compound. Raman and infrared studies help in probing the structure of the materials and contribute to the study of lattice vibrations. Such investigations can help to discriminate impurity phase from the superconducting phases. Bismuth-copper oxide superconductors have been studied by several investigators [27–31]. Raman spectra of ceramic BiSrCaCuO superconductors containing different phases other than 2122 have also been reported. Of these, Sapriel et al. [32] have reported the Raman spectra of BiSrCaCuO ceramic samples containing 15–20% of the 2223 phase. Cardona et al. [33] have investigated the Raman spectra of  $\text{Bi}_2(\text{Sr}_{1-x}\text{Ca}_x)_{n+2}\text{Cu}_{n+1}\text{O}_{(6+2n)+\delta}$  ( $n = 0, 1$ ) and have assigned some of the bands. As the spectral data for  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  is not available in the literature, it was decided to synthesize the compound and study the Raman spectrum.

#### 5. EXPERIMENTAL

The compound  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  has been prepared by the well known solid state reaction technique using high purity powders. A homogenous charge was first prepared by mixing appropriate amounts of  $\text{SrCO}_3$ ,  $\text{CaCO}_3$  and  $\text{CuO}$ . It was kept at  $940^\circ\text{C}$  in air for 16 hours and after which it was cooled, pulverized,

pelletized and heated till the reaction was complete and a good homogeneity is ensured. Appropriate amount of the matrix and  $\text{BiO}_3$  were mixed and pelletized and reacted at 1113 K for 4 minutes until the mass turned black. Then the samples were grinded and pelletized by applying a pressure. Finally the samples were sintered for 4 hours at 1098 K and they were furnace cooled to room temperature.

X-ray diffraction was performed using  $\text{CuK}_\alpha$  line on a Rigaku diffractometer and the X-ray pattern for  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  is shown in Figure 1. The XRD patterns of this compounds show a mixed phase namely 2212 (low  $T_c$ ) and 2223 (high  $T_c$ ) phases. Care has been taken to obtain the percentage of each phase of the ceramic sample to interpret the x-ray diffraction spectra accurately in the present work.

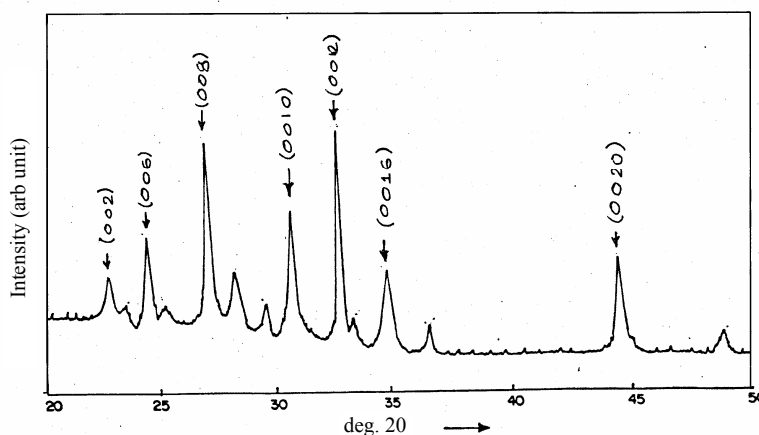


Figure 1: XRD Pattern of sample  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$

The resistivity of the sample was measured as a function of temperature using standard four probe technique. For the prepared  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  sample, the onset  $T_c$  is at 108 K and the resistivity drops to zero at 100 K.

The Fourier transform Raman spectrum was recorded in solid phase on Bruker IFS 66V FTIR spectrometer equipped with FRA 106 Raman module and Nd:YAG laser source operating at 10.6  $\mu\text{m}$  line with 200 mW power. The spectrum was recorded with a scanning speed of  $30 \text{ cm}^{-1} \text{ min}^{-1}$  with a spectral width of  $2.0 \text{ cm}^{-1}$ . The frequencies for all sharp bands were accurate to  $\pm 2 \text{ cm}^{-1}$ . The FT Raman spectrum of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  is shown in Figure 2.

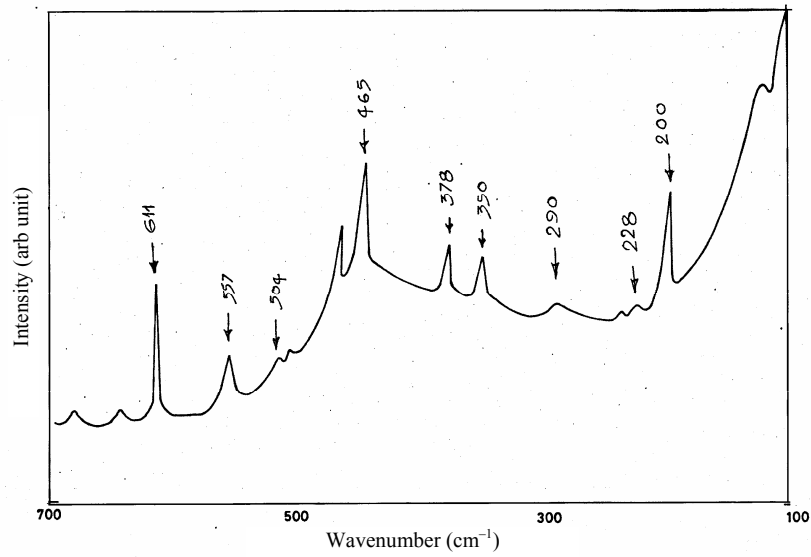


Figure 2: FT-Raman spectrum of Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub>

Apart from this experimental investigation, the phonon frequencies of Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> (2:2:2:3:10) have also been evaluated theoretically in the present work which agree well with the observed frequencies wherever such experimental data available.

Using group theory, the normal vibrational modes according to the irreducible representation of the point group for Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> (2:2:2:3:10) [grouped according to activity] are as follows:

$$\Gamma_{\text{Total}} = 7A_{1g}(\text{R}) + 1B_{1g}(\text{R}) + 8E_g(\text{R}) + 8A_{2u}(\text{IR}) + 2B_{2u}(\text{IR}) + 10E_u(\text{IR})$$

Here,  $\Gamma_{\text{Total}}$  refers to total number of vibrational frequencies and R and IR stands for Raman and infrared activity of the sample.

As discussed earlier, a normal coordinate analysis of the zero wave vector vibrations is attempted to (2:2:2:3:10) bismuth cuprate high temperature superconductor. The bond distances and force constants employed in the present investigation (transferred from allied molecules) are given in Table 1 for the above compound [21,23–26]. The evaluated phonon frequencies using normal coordinate analysis is given in Table 2 for (2:2:2:3:10) superconductors.

Table 1: Bond distances and force constants for  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ 

	Bond type	Distance (Å)	Initial value- Potentials constants*
$f_a$	Ca-O(1)	2.371	1.29
$f_b$	Ca-Sr	3.004	0.16
$f_c$	Ca-Cu	3.179	0.48
$f_d$	Sr(1)-O(1)	2.484	0.17
$f_e$	Sr(1)-O(3)	2.868	0.49
$f_g$	Sr(1)-Cu(2)	3.000	5.32
$f_h$	Sr(2)-O(1)	2.484	1.11
$f_k$	Sr(2)-O(3)	2.868	1.77
$f_l$	Sr(2)-Cu(1)	3.000	0.50
$f_m$	Bi(1)-O(3)	2.115	2.33
$f_n$	Bi(1)-O(2)	2.695	1.78
$f_p$	Bi(1)-O(1)	3.127	0.48
$f_u$	Bi(2)-O(3)	2.115	2.11
$f_v$	Bi(2)-O(2)	2.695	0.99
$F_\alpha$	Bi(2)-O(1)	3.127	1.21
$F_\beta$	O(1)-O(2)	3.465	0.40
$F_\gamma$	O(2)-O(3)	3.426	1.27
$f_r$	Cu-O(1)	1.932	1.41
$f_s$	Cu-O(2)	2.610	1.40
$f_t$	Cu-O(3)	2.411	1.38
$f_w$	O(1)-O(3)	3.410	1.87

Note: \* in units of  $10^2 \text{ Nm}^{-1}$  (stretching) and  $10^{-18} \text{ Nm rad}^{-2}$  (bending)

Table 2: Calculated phonon frequencies of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ 

Symmetry species	Frequency ( $\text{cm}^{-1}$ ) using normal coordinate analysis
$A_{1g}(\text{R})$	112 (122)
	144
	196 (200)
	236 (228)
	448 (445)
	498 (504)
	564 (557)
$B_{1g}(\text{R})$	400 (378)
	102
$E_g(\text{R})$	119
	228 (239)
	280 (290)
	328 (350)
	456 (465)
	522 / 518
	610 (611)

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Table 2–(continued)

Symmetry species	Frequency (cm <sup>-1</sup> ) using normal coordinate analysis
A <sub>2u</sub> (IR)	101
	186
	241
	281
	329
	458
	486
	570
	631
B <sub>2u</sub> (IR)	416
	260
	381
E <sub>u</sub> (IR)	88
	142
	240
	292
	338
	392
	424
	496
	559
631	

Notes: Values in parentheses are experimental values  
 \* present work

The study of the lattice dynamical calculations of the high temperature superconductors is of importance, not only for the observed physical characterization of these compounds but also for an assessment of the role played by the phonons in the superconducting phenomenon. The modified TSM was also employed in the present work to evaluate phonon frequencies of (2:2:2:3:10) bismuth cuprate high temperature superconductor. The same methodology described elsewhere [10,21] is adopted for this compound. The model parameters determined using the TSM for Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> are given in Table 3. The phonon frequency evaluated for these compounds using the modified TSM are given in Table 4. A complete phonon frequency obtained through normal coordinate analysis and lattice dynamical calculations, observed frequencies and PE distributions are given in Table 5 for (2:2:2:3:10) bismuth cuprate compound.

Table 3: Shell parameters of the model for  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$   $a, b$  are Born-Mayer constants;  $Z, Y, K$ : ionic charge, shell charge and on-site core-shell force constant of the ion,  $v_a$  is the volume of the unit cell

Interaction	$a_{ij}(eV)$	$b_{ij}(A^{-1})$
Bi-O	3010	3.00
Sr-O	3020	2.90
Ca-O	2513	3.06
Cu-O	1259	3.50
O-O	1000	3.00

Ion	$Z( e )$	$Y( e )$	$K(e^2/V_a)$
Bi	2.60	2.42	1127
Sr	2.35	2.32	212
Ca	2.00	-2.50	1387
Cu	2.00	3.22	1281
O <sup>a</sup>	-1.99	-2.70	323
O <sup>b</sup>	-1.99	-2.70	2146
O <sup>c</sup>	-1.99	-2.70	323 ( $k_{  }$ ) 2146 ( $k_{\perp}$ )

Notes: <sup>a</sup> For O in the Cu-O planes

<sup>b</sup> For O in the Bi-O planes

<sup>c</sup> For O in the Sr-O planes

Table 4: Calculated phonon frequencies of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$

Symmetry species	Frequency ( $\text{cm}^{-1}$ ) using lattice dynamics
$A_{1g}(\text{R})$	112
	141
	191
	230
	440
	494
	569
$B_{1g}(\text{R})$	401
$E_g(\text{R})$	98
	117
	222

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Table 4–(continued)

Symmetry species	Frequency (cm <sup>-1</sup> ) using lattice dynamics
	281
	320
	445
	518
	617
A <sub>2u</sub> (IR)	96 / 111
TO/LO	180 / 192
	231 / 262
	284 / 302
	325 / 312
	451 / 468
	475 / 486
	572 / 599
B <sub>2u</sub> (IR)	264
	396
E <sub>u</sub> (IR)	83 / 96
TO/LO	139 / 145
	242 / 268
	295 / 321
	330 / 366
	386 / 404
	414 / 434
	485 / 502
	555 / 568
	620 / 646

Note: TO/LO corresponds to the frequencies of the transverse optical and longitudinal optical modes

Table 5: Phonon frequencies of Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub>

Symmetry species	Frequency (cm <sup>-1</sup> )			PED (%) <sup>*</sup>
	Using lattice dynamics	Using normal coordinate analysis	Observed	
A <sub>1g</sub> (R)	112	112	122	f <sub>d</sub> (42)f <sub>n</sub> (28)f <sub>m</sub> (14)
	141	144		f <sub>h</sub> (50)f <sub>k</sub> (41)
	191	196	200	f <sub>g</sub> (51)f <sub>v</sub> (25)
	230	236	228	f <sub>β</sub> (49)f <sub>α</sub> (21)
	440	448	445	f <sub>t</sub> (51)f <sub>w</sub> (21)f <sub>β</sub> (18)
	494	498	505	f <sub>n</sub> (59)f <sub>r</sub> (30)f <sub>c</sub> (10)

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Table 5--(continued)

Symmetry species	Frequency (cm <sup>-1</sup> )			PED (%) <sup>*</sup>
	Using lattice dynamics	Using normal coordinate analysis	Observed	
B <sub>1g</sub> (R) E <sub>g</sub> (R)	569	564	557	f <sub>n</sub> (66)f <sub>β</sub> (15)f <sub>n</sub> (10)
	401	400	378	f <sub>s</sub> (42)f <sub>m</sub> (24)f <sub>α</sub> (24)
	98	102		f <sub>k</sub> (61)f <sub>h</sub> (14)
	117	115		f <sub>w</sub> (48)f <sub>β</sub> (18)f <sub>c</sub> (16)
	222	228	239	f <sub>β</sub> (51)f <sub>v</sub> (30)f <sub>α</sub> (16)
	281	280	290	f <sub>v</sub> (56)f <sub>β</sub> (18)f <sub>m</sub> (15)
	320	328	350	f <sub>t</sub> (55)f <sub>β</sub> (28)f <sub>g</sub> (15)
	445	456	465	f <sub>s</sub> (62)f <sub>β</sub> (15)f <sub>w</sub> (11)
	518	522	518	f <sub>r</sub> (70)f <sub>β</sub> (20)
	617	610	611	f <sub>β</sub> (47)f <sub>α</sub> (27)f <sub>v</sub> (16)
A <sub>2u</sub> (IR) TO/LO	96 / 111	101		f <sub>a</sub> (36)f <sub>c</sub> (25)f <sub>b</sub> (27)
	180 / 192	186		f <sub>β</sub> (54)f <sub>a</sub> (21)f <sub>s</sub> (11)
	231 / 262	241		f <sub>β</sub> (59)f <sub>r</sub> (32)f <sub>c</sub> (13)
	284 / 302	281		f <sub>v</sub> (30)f <sub>u</sub> (21)f <sub>n</sub> (28)
	325 / 312	329		f <sub>v</sub> (56)f <sub>m</sub> (24)f <sub>β</sub> (12)
	451 / 468	458		f <sub>t</sub> (54)f <sub>β</sub> (21)f <sub>g</sub> (14)
	475 / 486	486		f <sub>n</sub> (67)f <sub>β</sub> (22)f <sub>h</sub> (10)
	572 / 599	570		f <sub>s</sub> (71)f <sub>β</sub> (26)
B <sub>2u</sub> (IR)	264	260		f <sub>r</sub> (41)f <sub>w</sub> (28)
	396	381		f <sub>a</sub> (47)f <sub>β</sub> (33)
E <sub>u</sub> (IR)	83 / 96	88		f <sub>t</sub> (41)f <sub>h</sub> (21)f <sub>r</sub> (14)
	139 / 145	142		f <sub>c</sub> (46)f <sub>b</sub> (22)f <sub>a</sub> (11)
	242 / 268	240		f <sub>β</sub> (55)f <sub>k</sub> (22)
	295 / 321	292		f <sub>r</sub> (48)f <sub>w</sub> (31)
	330 / 366	338		f <sub>a</sub> (52)f <sub>β</sub> (30)
	386 / 404	392		f <sub>v</sub> (48)f <sub>m</sub> (21)f <sub>w</sub> (15)
	414 / 434	424		f <sub>n</sub> (41)f <sub>v</sub> (28)f <sub>c</sub> (22)
	485 / 502	496		f <sub>r</sub> (72)f <sub>u</sub> (14)
	555 / 568	559		f <sub>t</sub> (70)f <sub>w</sub> (19)
	620 / 646	631		f <sub>t</sub> (44)f <sub>α</sub> (21)f <sub>β</sub> (20)

Note: <sup>\*</sup> only contributions greater than 10% are included

## 6. RESULTS AND DISCUSSION

Group theoretical considerations indicate that Cu-O(1)-Cu in-plane bending and Cu-O(1) stretching vibrations of Cu<sub>2</sub>O layers mix with each other giving two Davydov ( $E_u$ ,  $E_g$ ) pairs. The lower frequency in this pair involves Cu-O(1) stretching. Using these considerations as guidelines, the evaluated phonon frequencies as well as observed spectra are interpreted in this work.

The band observed in FTR spectra at  $465\text{ cm}^{-1}$  is assigned to the oxygen atom that bridges the BiO and  $\text{CuO}_2$  planes. Boekholt et al. [34,35] have assigned this mode to the in-phase out-of-plane vibrations of the same oxygen atoms relative to the Cu atoms. Raman spectrum recorded in the present work for  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  gives peaks at 122, 200, 228, 239, 290, 350, 378, 430, 445, 465, 505, 518, 557, 611, 640 (weak) and  $680\text{ cm}^{-1}$  (weak band).

The  $465$  and  $630\text{ cm}^{-1}$  lines are the most prominent lines in the Raman spectra of the BSCCO system [36]. The  $465\text{ cm}^{-1}$  band is assigned to a collective motion parallel to the  $c$ -axis of oxygen atoms surrounding bismuth atoms. It has  $A_{1g}$  symmetry and it shows a softening of the phonon frequency with the onset just below  $T_c$ . This band is also considered as the vibrations of the oxygen atom that bridge the BiO and  $\text{CuO}_2$  planes [33,37].

The number of  $\text{CuO}_2$  layers is more in the 2223 phase than in the 2212 phase. Sapriel et al. [32,38] have proposed that additional copper-oxygen layers may give rise to Raman inactive lines. But more copper-oxygen layers offer long range forces leading to the broadening of the spectral line. The weak Raman lines at  $640$  and  $680\text{ cm}^{-1}$  are due to oxygen related vibrations in BiO plane. The intensity of the lines is very much less than that observed by Sapriel et al. [38] in ceramic samples. Cardona et al. [33] have also noted the same feature in the phonon spectra.

The intense mode in the  $\text{BiSrCaCuO}$  system is at  $122\text{ cm}^{-1}$ . This mode arises from the vibrations of the Cu atoms normal to the Cu-O plane. According to Sapriel et al. [32,38], the  $122\text{ cm}^{-1}$  mode is due to collective motion of copper and strontium atoms. Boekholt et al. [39] assigned the mode to the vibrations of strontium atoms. This assignment is well supported by PED which indicates it as a mixed mode. The line at  $290\text{ cm}^{-1}$  corresponds to the bond bending vibrations of the  $\text{O}_4$  and  $\text{O}_5$  atoms in the BiO layer. This is due to the incomplete occupation of the  $\text{O}_5$  sites in 2212 plane [40] and PED calculations lend support to this conclusion. The band at  $200\text{ cm}^{-1}$  is assigned to  $A_g$  mode. This is associated with Sr or Cu atoms vibrating along Y. Cardona et al. [33] observation support this assignment. The present PED calculations agree with the present assignment. According to Popovic [41], the modes at  $390$ ,  $500$  and  $580\text{ cm}^{-1}$  originate from the CuO and BiO vibrations. In the present Raman spectra, the bands at  $378$  and  $505\text{ cm}^{-1}$  are assigned to these vibrations. All the observed Raman frequencies agree very well with the evaluated frequencies in the  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_7\text{O}_{10}$  superconductors. Several salient features of phonon frequencies of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_7\text{O}_{10}$  agree very well with the other bismuth compounds available in the literature. However, a brief discussion on the evaluated phonon frequencies are given below.

The phonon frequencies evaluated around  $400\text{ cm}^{-1}$  includes infrared active phonons involving metal ion vibrations and  $\text{CuO}_2$  and Bi-O-Cu bending modes. Similarly phonon frequency around  $600\text{ cm}^{-1}$  correspond to in plane Cu-O(1) stretching modes of  $\text{CuO}_2$  layers and to Bi-O(2)-Cu stretching modes of the bridging O(2) oxygen. The evaluated frequencies around  $350\text{ cm}^{-1}$  is assigned to Bi-O(2)-Cu bending which agrees with the experimental values [41]. Finally, the oxygen Bi-O(2)-Cu stretching mode in the infrared is assigned to around  $500\text{ cm}^{-1}$ . This conclusion agrees quite well with other bismuth compounds as well as the conclusions arrived by Piro et al. [42].

Recently, Kovaleva et al. [43] reported c-axis lattice dynamics study in  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$  ( $n = 1, 2, 3$ ) cuprate superconductors based on spectral ellipsometry studies on single crystals and theoretical calculations. The c-axis IR phonon spectra reported by them agree quite well with the phonons spectra evaluated for  $n = 3$ ,  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  by two different methods in the present work.

Summarizing, the prepared  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  superconductor has been utilized to study the Raman spectrum, hitherto not available in the literature to the author's knowledge. The spectrum was interpreted to assign the frequencies reasonably with PED. The evaluated phonon frequencies using normal coordinate analysis and lattice dynamical calculations agree very well with the observed experimental frequencies. The PED associated with the normal coordinate analysis is also considered in proposing the assignments. It is concluded that the normal coordinate analysis and lattice dynamical calculations of the optically active lattice vibrations are useful for the theoretical interpretation of Raman and infrared spectra at the center of Brillouin zone in high temperature superconductors.

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