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Infrared spectra of bismuth family of superconductors $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n+y}$

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FTIR spectra of bismuth family of superconductors are studied. Polycrystalline samples of bismuth superconductors are prepared choosing an off-stoichiometric composition for phase stabilisation and reproducibility. Vibrational modes are strongly affected by the holes introduced into the CuO planes. Mid IR spectra of the Bismuth system was recorded using Bruker IFS 66v and the high frequency oxygen vibrations of the system is discussed based on the factor group analysis for both symmorphic and non-symmorphic space groups I4/mmm, F_{mmm} and A_{maa} of different structures based on the modulated superstructure.

1. Introduction

Study of phonon properties are very much important in understanding the crucial mechanism responsible for high temperature superconductivity. The Raman and IR spectroscopic techniques are highly accurate in providing information on (i) charge dynamics and phonon spectrum (ii) nature of phases present (iii) occurrence of structural changes and (iv) phonon softening-evidence of electron-phonon coupling etc. When compared with 123 system, bismuth family of superconductors has large potential in the area of application in the form of wires and tapes. The bismuth family of superconductors can hold very large current density upto an order of of 10^6 A/cm^2 making it feasible for technological revolution. This made the scientists to work on this system to open the new avenues.

Single phase formation of bismuth family of superconductors is very difficult to achieve, due to its incommensurate structural modulations and intergrowth of other related phases. Cationic vacancies/disorders are found to be responsible for this structural modulation. As the electronic properties are very sensitive to small changes, just near perfect stoichiometry, an attempt has been made here to prepare single phase of bismuth family of superconductors and their mid IR properties were studied, with reference to high frequency oxygen vibrations, based on normal mode analysis. As the high T_c superconductivity is induced by the excess holes in the oxygen sites of the CuO_2 planes (which in turn interact with the copper electrons) the study of vibrational modes of oxygen atoms are hence considered important in revealing the truth behind the mechanism responsible for superconductivity. Spectroscopic techniques are more sensitive than any other techniques such as XRD, resistivity and susceptibility, to the disorder in bismuth cuprates and give relevant information about the vibrational modes and the mechanism of high T_c superconductivity. FTIR is very much used in studying the physical properties of high T_c superconductors. For high T_c oxide superconductors, no matter which system (T1, Bi, Y-123 etc.) they belong to, the CuO planes play an essential role in their superconducting nature. Hence attention is focused on the phonon modes associated with Cu-O vibrations in the present work.

In general, the structure of the bismuth system is found to be complex. Common imperfection in the layered materials are stacking faults and intergrowth. Cationic vacancies, disorders like Bi vacancy and Bi cross over to Sr site are found to be responsible for incommensurate structural modulation. This in turn produces distortions in Bi-O, Sr-O and CuO_2 planes and due to this apparent disorder in the subcell the precise nature of Bismuth-oxygen bonding nature is not yet clear. The structure is described as a stacking of a basic $Bi_2Sr_2CuO_6$ unit with one or two $CaCuO_2$ layer inserted along the c-axis. The layer sequence is BiO-SrO-CuO_2-SrO-BiO, for $n = 1$, 2201 phase, BiO-SrO-CuO_2-Ca-CuO_2-SrO-BiO, for $n = 2$, 2212 phase and BiO-SrO-CuO_2-Ca-CuO_2-Ca-CuO_2-SrO-BiO, for $n = 3$, 2223 phase. Even though the average structure is taken as tetragonal [1] due to the change in oxygen position in the bismuth layers [2] two different non-symmorphic space groups F_{mmm} and A_{maa} were proposed by different authors [3, 4] for all the three phases. In bismuth system excess oxygen is placed as interstitial and cationic vacancies. Structural modulation in bismuth system is due to the addition of one in ten oxygen atoms in the Bi-O layers [5, 6]. The role of oxygen vibrations in the HTSC systems are clearly established beyond doubt. Hence the irreducible representation of all oxygen vibrations for all three phases for the three different structures are given in Table I.

TABLE I Oxygen vibrations of three structures of bismuth family of superconductors

System	Space group	Irreducible representation
2201	I4/mmm	$3A_{2u} + B_{2u} + 4E_u$
2201	F_{mmm}	$A_u + 3B_{1u} + 4B_{2u} + 4B_{3u}$
2201	A_{maa}	$3A_u + 4B_{1u} + 6B_{2u} + 5B_{3u}$
2212	I4/mmm	$3A_{2u} + B_{2u} + 4E_u$
2212	F_{mmm}	$A_u + 3B_{1u} + 4B_{2u} + 4B_{3u}$
2212	A_{maa}	$4A_u + 5B_{1u} + 8B_{2u} + 7B_{3u}$
2223	I4/mmm	$4A_{2u} + 2B_{2u} + 6E_u$
2223	F_{mmm}	$2A_u + 4B_{1u} + 6B_{2u} + 6B_{3u}$
2223	A_{maa}	$5A_u + 6B_{1u} + 10B_{2u} + 9B_{3u}$

2. Experimental

Infrared spectroscopic study of Bi family of superconductors are presented in this paper. As the structure of the bismuth family of superconductors are complex due to incommensurate structural modulation single phase formation and reproducibility is very difficult to achieve in this class of materials. An attempt is made here to prepare, phase stabilised, reproducible phases, for the spectroscopic investigation.

Bismuth family of superconductors are represented by the general formula $(A^{III}O)_2$ A^{II} $Ca_{n-1}Cu_nO_{n+2n+\delta}$ where A^{III} is Bi, A^{II} is Sr and n is the number of consecutive CuO_2 layers. EDX [7] measurements shows that Bi vacancies and Bi is also known to cross over and substitute at the Sr site as well. Hence a controlled Ca/Sr ratio controls incommensurate modulation to some extent. Moreover bismuth cuprates are greatly amenable to chemical substitution where by metallic and superconducting properties can be induced. Generally enhancement of T_c and consistency and reproducibility of single phase is also said to depend upon (i) starting composition/stoichiometry, (ii) dopants to stabilize the phase, (iii) different processing temperature, (iv) atmosphere and sintering periods and (v) changes in structure due to creation of cation vacancy and a change in bismuth valency and oxygen coordination.

Taking into consideration of above facts, 2201 phase was prepared by simultaneous substitution of bismuth by Pb and strontium by La. Following earlier work [8], 2201 phase is prepared using a composition of $Bi_{1.5}Pb_{0.5}Sr_{1.6}La_{0.4}CuO_{6+\delta}$ by solid state reaction. High purity Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO (All Cerac, USA, 99.9% purity) were taken in stoichiometric proportion, ground thoroughly and fired in air at 800 °C for 12 h and furnace cooled. The following schedule of heat treatments were further carried out with intermediate grinding: 820 °C for 12 h and 840 °C for 24 h. The final powder was grounded and pelletized. The pellets were sintered at 840 °C for 24 h in air and cooled to room temperature by furnace shut off. Subsequently sintering was repeated at a higher temperature 880 °C for 24 h.

Among all other phases, 2212 phase was widely studied due to its large T_c and its suitability to prepare wires and tapes. Ono [9] added excess bismuth to the off stoichiometry solid solution, which cross over and occupy either Sr or Ca plane to form a single phase. The controlled Sr/Ca ratio reduces the structural modulation due to excess/disordered occupation of oxygens atoms in the Bi plane. Following, Sumana prabhu *et al.* [10] an off-stoichiometric $Bi_{2.1}Sr_{1.93}$ $Ca_{0.97}Cu_2O_{8+\delta}$ quantities of Bi_2O_3,$SrCO_3$,$CaCO_3$, and CuO are ground well and calcined in air at 810 °C for 16 h. To increase the diffusion path length for homogeneous mixture at atomic level, heating and grinding was repeated at 840 °C for 6 h and 875 °C for 12 h and then pelletised. Pellets were sintered at 870 °C for 12 h and furnace cooled to room temperature. The T_c of the material was enhanced by introducing the pellets into a pre-heated furnace at 805 °C for 2 h and quenched in air.

Preparation of 2223 phase is very difficult to get a single phase. Generally dopants influence the crystal structure in many ways like phase stabilisation, increase in volume fraction and the ordering of Cu-O bonds along the *c*-axis etc. According to Dupouy *et al.* [11], as the amount of dopant increases, the impurity phases present in the system is also found to be increasing. From XPS studies, it was found that the divalent Pb was substituted for trivalent Bi in doped samples. Further Dupouy *et al.* [11] found that the displaced Bi^v ions would move into sites with higher coordinance state. These sites would be located between Bi-O and Cu-O planes and would compared to unfilled Sr sites.

Hence an off-stoichiometry proposed by Sasakura *et al.* [12] $Bi_{1.68}Pb_{0.32}Sr_{1.75}Ca_{1.75}Cu_{2.75}O_{10+\delta}$ is chosen with excess Pb, Ca and Cu, since excess Ca and Cu partially substitute for Sr and Bi. A solid solution of $Bi_{1.68}Pb_{0.32}Sr_{1.75}Ca_{1.75}Cu_{2.75}O_{10+\delta}$ was prepared by means of solid state reaction, doping approximately 20% Pb for phase stabilisation. Compared to other two phases, 2223 has to be annealed for a very long time. High purity oxides and carbonates were calcined in air at 795 °C for 24 h below the melting point of bismuth oxide. Sintering was carried out at 858 °C for 65 h. After grinding and pelletising, second sintering was carried out for 90 h at 858 °C.

All the ceramic bulk samples prepared by solid state reaction were characterised by XRD spectra (Fig. 1) using CuK_α radiation (Rich seifert, Germany). All the characteristic peaks corresponding to the respective phases were found to be present. Except 2223 all other phases are found to be single phasic and 2223 shows impurity phases due to 2212. This may be attributed to the unreacted $Ca_{2-x}Sr_xCuO_3$ [13].

IR spectra: Mid IR measurements were carried out on the polycrystalline samples. Sintered pellets were reground and mixed with KBr, then pressed in to pellets. Transmission mid IR was recorded for the samples using Bruker IFS 66v between 400 and 4000 cm^{-1}. The IR spectrum of pure KBr pellet of the same size was first recorded and then used to eliminate the background from the spectra of the mixed sample. The transmission minima which represents the absorption maxima, correspond to phonon frequencies, Burns *et al.* [14]. The recorded frequencies are tabulated in Table II and compared with the available literature [15–17].

3. Result and discussion

Orthorhombic lattice cell parameters of bismuth superconductors were refined using Autox programme [18]

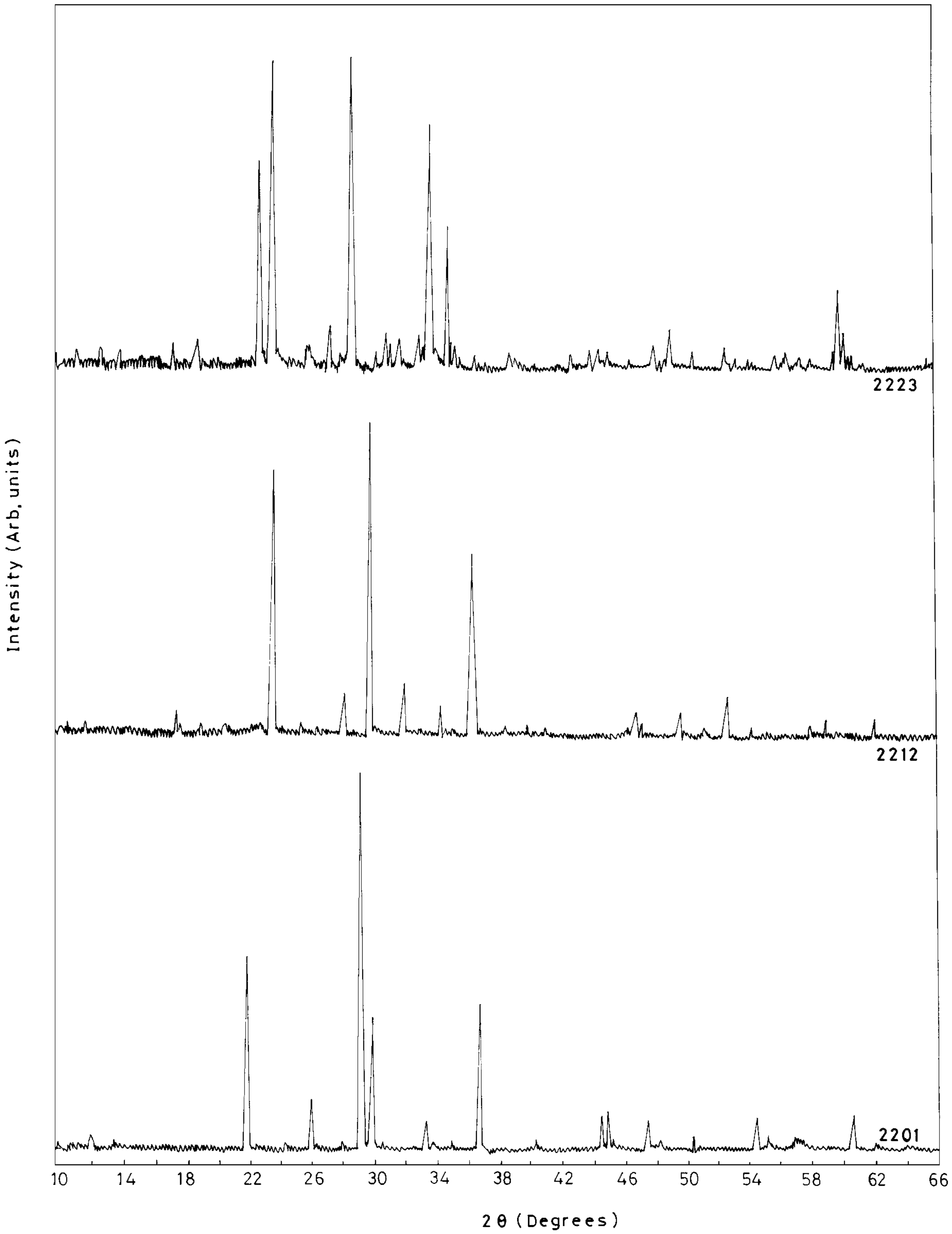

Figure 1 XRD pattren of bismuth family of superconductors: (a) 2201 phase (b) 2212 phase and (c) 2223 phase.

and they are presented in Table III. The values are in good agreement with the available literature. Resistivity of the bulk samples were measured using Vander Pauw's four probe method. Helium cooled closed cycle cryostat (Leybold, Germany) is used for resistivity measurements upto a temperature of 15 K, for 2212 and 2223 phases. Metallic behaviour and sharp transitions at 77 K for 2212 and 99 K for 2223 are observed. From the ρ-T plots given in Fig. 2, the room temperature resistivity was found to be 3.5 m Ωcm for 2212 and it is 2.68 m Ωcm for 2223 phase. AC susceptibility measurements (Sumitomo, Japan) were carried out for all the three phases of the bismuth family of superconductors and depicted in Fig. 3. Sharp transition observed for 2201 phase indicates the homogeneity of the sample whereas 2212 phase shows a broad transition at T_c.

IR spectra measurements reveal more information than the earlier works. Our spectra exhibit distinct structure which we attribute to the presence of single phase formation of the compounds. The characteristic change and the dependence of the phonon frequency on the number of CuO_2 layers are discussed from the point

TABLE II Mid IR phonon frequencies of bismuth family of superconductors

2201		2212		2223	
Present work	Reference [15]	Present Work	Reference [16]	Present work	Reference [17]
417	—	410	—	—	—
—	—	432	—	—	—
—	—	447	—	—	—
474	—	476	471	478	—
—	490	489	—	—	—
509	—	507	—	—	500
—	—	525	—	—	—
534	—	—	—	530	—
—	—	547	—	—	—
567	—	563	—	—	—
578	580	584	586	—	—
—	—	594	—	—	—
—	—	609	609	611	—
—	—	673	—	—	—

TABLE III Lattice parameters of orthorhombic phases of bismuth family of superconductors

System	a (Å)	b (Å)	c (Å)	$T_{\mathrm{c,zero}}$ (K)	ac susceptibility $T_{\mathrm{c,onset}}$ (K)
2201	5.386	5.310	24.465	—	15
2212	5.132	5.123	29.175	77	84
2223	5.199	5.619	30.708	99	105

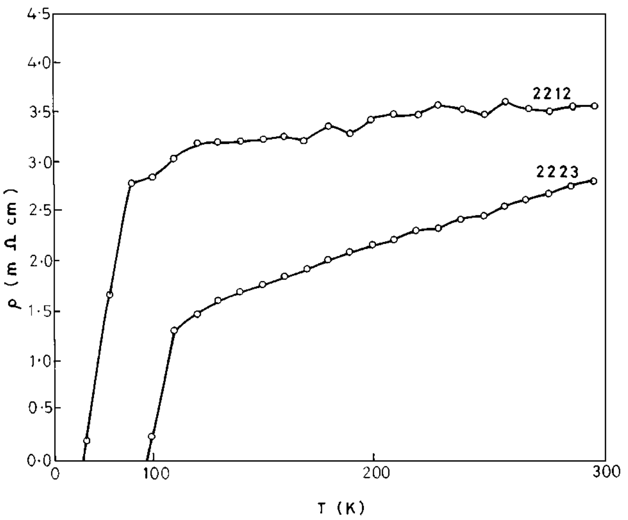

Figure 2 Resistivity plots for 2212 phase and 2223 phase.

of view of normal mode analysis. Clear-cut and unambiguous assignments are not possible in the case of IR spectra. However on the basis of some general points, the spectra is compared with the well known iso-structural systems like T1 system and Y-123 system. From the analysis of results of the three members $n = 1, 2, 3$ of bismuth family it is clear that there are characteristic phonon modes with frequencies that are not much different for the different compounds. The phonon frequencies at and around 470 cm^{-1} is found to be common in all the three phases and it is attributed to the similarity of the structure of the different phases.

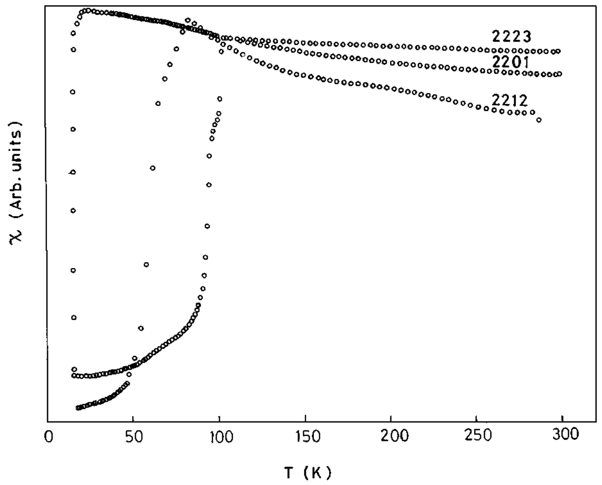

Figure 3 Susceptibility plots for (a) 2201 phase (b) 2212 phase and (c) 2223 phase.

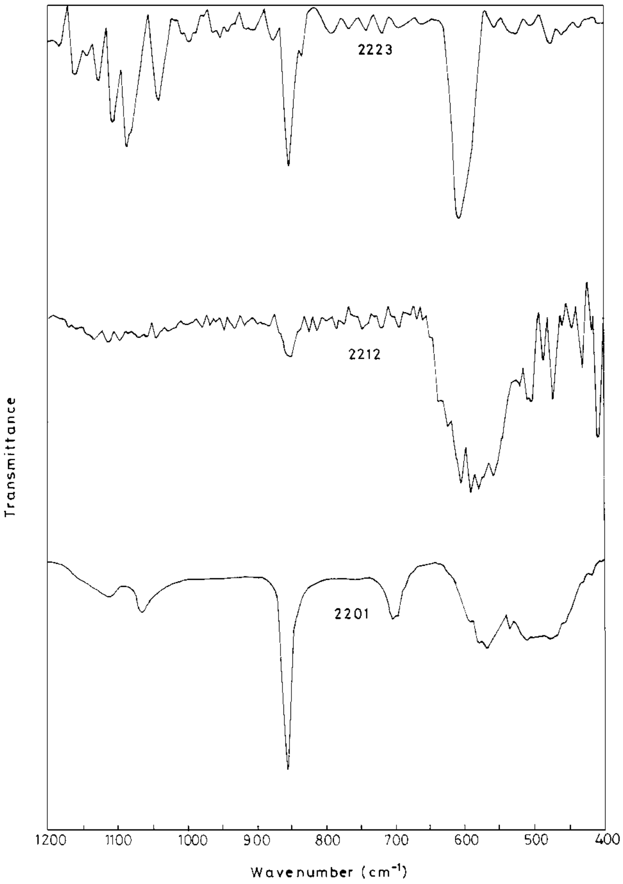

Figure 4 IR spectra of bismuth family of superconductors (a) 2201 phase (b) 2212 phase and (c) 2223 phase.

For the 2201 phase, eight theoretical IR modes are calculated from the factor group analysis. Out of the eight, all the B_{2u} modes involve only oxygen vibrations. In the observed spectra given in Fig. 4, there are seven prominent peaks occurring at 417, 474, 509, 534, 567 and 578 cm^{-1} omitting the higher frequencies. Independent assignment of the peaks are difficult even though the system is said to possess centre of inversion. IR frequencies in HTSC systems is used to analyse the Cu-O vibrations. Since the role of CuO_2 planes in superconductors can not be neglected. The peaks appearing close to 490–510 cm^{-1} are assigned to the out of phase vibrations of Cu-O. The highest value 578 cm^{-1} mode is assigned to z-direction stretching of CuO_6 octahedra. Of all these modes the one close to 490–510 cm^{-1}, having an absorbance 0.0177 is compared with the one reported by Popovic *et al.* [15] which is found to under go phonon softening at low temperature. This may be compared with T1-2201 system based on the LD calculations [19]. The highest peak at 578 cm^{-1} is attributed mainly to the vibrations of oxygen in the SrO plane against oxygen in the BiO plane.

For 2212 phase, out of the eight, five modes are due to oxygen related vibrations. Transmission minima (absorption maxima) occurs at 410, 432, 447, 476, 489, 507, 525, 547, 563, 584, 594, 609 and 673 cm^{-1} in the observed spectra. Unambiguous assignments are not possible due to mixing of modes or due to group vibrations. On comparing with the known similar structural compounds like Y-123 system and T1 counter part 2212 system assignments have been carried out. From the analysis of the spectra of the similar compounds, some general points can be made. The absorption peaks around 500 cm^{-1} and above correspond to Cu-O vibrations. Mainly high energy vibrations are due to oxygen bond stretching against copper atoms. In IR spectra of Y-123 system, there are mainly three high energy peaks due to Cu-O stretching involving two in-plane modes and one chain mode. The one occurring around 558 cm^{-1} is assigned to Cu(1)-O(4) stretching of the chain Cu(1)-O(4)-Cu(1)-O(4)-along the x-axis. In Y-123 system O(1) atoms along the z direction bridges Cu(1) and Cu(2) layers. In a similar way O(3) atoms of SrO layer bridges the BiO and copper layers in 2212 bismuth family. Moreover, the local structure of CuO_5 pyramids facing each other over Y atom is the same for bismuth and 123 system and the CuO chain structure in Y-123 is replaced by BiO, bi layer in the bismuth system. As the charge transfer of holes occurs between the adjacent layers, the high frequency vibrations of bridging oxygen is considered spectroscopically important in revealing the mechanism responsible for superconductivity.

The $n = 3$, 2223 phase has three CuO planes per unit cell and gives highest T_c among the three members. For all the three members of the family the absorption maxima is found to be varying with T_c. Compared to all the three members of the family, 2223 is said to have a very few absorption maxima namely at 478, 530 and 611 cm^{-1}. The dependence of phonon frequency on the number of CuO_2 layers is found to be increasing with the increase in the peak frequency. The phonon modes around 600 cm^{-1} is mainly attributed to the vibrations of the bridging oxygen ions against oxygen ions in the BiO layer.

Hewat *et al.* [5] showed that the modulated superstructure arises because of additional oxygen ion inserted in the BiO layer. IR spectra reveals dramatic changes in the intensity as a consequence of increasing carrier concentration for some of the modes due to the additional oxygen atoms, which are at an IR active lattice. For the mode occuring around 400 cm^{-1} the reduction of the absorption intensity occurs as we go from higher phase to the lower phase. It is noted that the peaks occuring at and around 580–600 cm^{-1} are hardly affected in all the three phases. Of all peaks the absorption peak occuring at around 475 cm^{-1} is a common peak for all the phases.

4. Comparison with impurity phases

In almost all the bismuth family of superconductors, $Ca_{2-x}Sr_xCuO_3$ is found as impurity. We have compared our IR transmission spectra with the spectra of $Ca_{2-x}Sr_xCuO_3$ [13]. In $Ca_{2-x}Sr_xCuO_3$, copper ions are coordinated with four coplanar oxygen ions forming infinite Cu-O chains as found in the 123 system. Hence the study of vibrations of Cu-O chains in $Ca_{2-x}Sr_xCuO_3$ is compared with that of the bismuth system. In Table IV, the IR transmission peaks of $Ca_{2-x}Sr_xCuO_3$ are compared with the rest of the bismuth family. The intensities of the peaks at 534 cm^{-1} in 2201 (97%, absorbance 0.0132) and 530 cm^{-1} in 2223 (99%, absorbance 0.00436) are to be taken in to account for comparison with the peak at 530 cm^{-1} in $Ca_{2-x}Sr_xCuO_3$ which appears as a broad shoulder in the transmission spectra reported by Zlateva *et al.* [13]. This broad shoulder shows dramatic change in the intensity when the doping level is increased. When $x = 0.4$ the peak completely disappears.

The common building blocks (Cu-O layer) found in all the superconductors are vital important in deciding the nature of superconductivity. Even though the structural transitions are not related to superconductivity except for 123-system, their contribution to the normal mode analysis provides an insight for the spectroscopic understanding of these superconductors.

IR frequencies of the bismuth system is compared with the other simple Cu-O plane containing systems like CuO [20], $CaCuO_2$ [21] and Nd_2CuO_4 [22]. In CuO, copper and oxygen atoms form a simple planar coordination. The strong bonds are observed between 400 and 600 cm^{-1}. Out of these 483 cm^{-1} mode is found to be strong compared to the rest.

TABLE IV Comparison of phonon frequencies of impurity phases of $Ca_{2-x}Sr_xCuO_3$ with the bismuth family of superconductors

Bismuth system			$Ca_{2-x}Sr_xCuO_3$		
2201	2212	2223	Frequency	Mode	Assignment
417	410	—	412	B_{1u}	O(1)
—	432	—	—	—	—
—	447	—	457	B_{3u}	O(2)
474	476	478	—	—	—
—	489	—	—	—	—
509	507	—	—	—	—
—	525	—	—	—	—
534	—	530	530	B_{1u}	O(2)
—	547	—	—	—	—
567	563	—	—	—	—
578	584	—	—	—	—
—	594	—	—	—	—
—	609	611	—	—	—
—	673	—	682	B_{2u}	O(2)

In $Ca_{2-x}Sr_xCuO_3$, copper ions are coordinated with four coplanar oxygens along the *b*-axis forming infinite Cu-O chains. Mainly the vibrations around 300–525 cm^{-1} are attributed to motions involving copper (D_{2h} symmetry) and oxygen O_2 (D_{2h} site symmetry) atoms.

Burns *et al.* [21] have reported five IR modes ($2A_{2u} + 3E_u$) in their reflectance spectrum for $CaCuO_2$ which is said to have infinite number of Cu-O planes having Ca atoms in between them. This structure is closely related to ABO_3-perovskite structure if an additional oxygen atom is included. At room temperature the TO (the peaks in the reflectance are associated with absorption by TO phonons at $q = 0$, and the position of these peaks are in reasonable agreement) modes at 183, 231, 320, 424, and 598 cm^{-1} are found in the reflection spectra. The vibration due to A_{2u} modes are observed along the *c*-axis and the degenerate E_u modes are observed in the ab-plane.

The T′ structure compound Nd_2CuO_4 is also said to possess CuO planar structure like CuO and $CaCuO_2$. It possess tetragonal structure, having a simple CuO plane without apical oxygen. Crawford *et al.* [22] reported seven IR phonons ($3A_{2u} + 4B_u$) occurring at 129, 134, 269, 300, 350, 505 and 509 cm^{-1} in their reflection spectra. The copper oxygen symmetry in these different compounds and their contribution to the normal modes are listed in the Table V.

The phonon frequencies measured experimentally for bismuth system in our work is compared with the values reported by other authors even though the second neighbours are different. Presence or absence of apical oxygen atoms in these compounds makes the difference in the observed spectra. Except for CuO, all the compounds possess D_{4h} as factor group, whereas CuO transforms as C_{2h}. The infinite CuO chain compound $Ca_{2-x}Sr_xCuO_3$ possess D_{2h} symmetry. As the total number of atoms in the unit cell are different also the second neighbour environment is different and hence the total number of vibrational frequencies are different for the different systems. High frequency vibrations in these compounds could not be assigned unambiguously like the vibrations of cationic masses. Even though all these compounds possess common CuO plane the unit cell structure leads to different IR phonons.

5. Conclusion

FTIR spectra of bismuth family of superconductors are analysed based on the oxygen related vibrations of Cu-O planes in the high frequency region. The similarity of the structure of the system is exhibited by the commonly found peak occurring at 470 cm^{-1} which is attributed to the bridging oxygen vibration common for all the three phases. The weak structures present in the spectra may be due to phonon modes associated with local distortion of the Cu-O bond. IR spectra shows dramatic changes in intensity as a consequence of the increasing carrier concentration for some of the modes due to the additional oxygen atoms which are at an IR active lattice. For the mode occurring around 400 cm^{-1} the reduction of the absorption intensity occurs as we go from higher phase to the lower phase. The peaks occurring at and around 580–600 cm^{-1} are hardly affected in all the three phases.

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TABLE V Copper-Oxygen symmetry in bismuth, $Ca_{2-x}Sr_xCuO_3$, CuO, $CaCuO_2$ and Nd_2CuO_4 compounds

2201-Tetragonal D_{4h}	2212-Tetragonal D_{4h}	2223-Tetragonal D_{4h}	CuO-Monoclinic C_{2h}	$Ca_{2-x}Sr_xCuO_3$ Orthorhombic D_{2h}	$CaCuO_2$ D_{4h}	Nd_2CuO_4 Tetragonal D_{4h}
Cu-C_{4v} O-C_{4v}	Cu-C_{4v} O-C_{4v}	Cu-C_{4v} O-C_{4v}	Cu-C_i O-C_2	Cu-D_{2h} O_1-C_{2v} O_2-D_{2h}	Cu-D_{4h} O-D_{2h}	Cu-C_{4v} O-D_{2h}
A_{2u}, E_u	A_{2u}, B_{2u}, E_u	A_{2u}, B_{2u}, E_u	A_u, B_u	B_{1u}, B_{2u}, B_{3u}	A_{2u}, E_u, B_{2u}	A_{2u}, E_u, B_{2u}
Transmission spectra	Transmission spectra	Transmission spectra	Transmission spectra	Transmission spectra	Reflection spectra (TO)	Reflection spectra (TO)
417	410	—	—	412	—	—
—	432	—	—	—	424	—
—	447	—	452	457	—	—
474	476	478	—	—	—	—
—	489	—	483	—	—	505
509	507	—	—	—	—	509
—	525	—	—	—	—	—
534	—	530	—	530	—	—
—	547	—	542	—	—	—
567	563	—	—	—	—	—
578	584	—	583	—	—	—
—	594	—	—	—	598	—
—	609	611	—	—	—	—
—	673	—	—	682	—	—

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