PREFACE

The endless search for new materials resulted in the discovery of the exotic phenomenon called zero resistance state of matter—superconductivity. “Room temperature superconductivity” is the magic word supposed to revolutionise the modern world, ranging from micro-electronic circuitry to high speed computing, energy storage, magnetically levitated trains, superconducting devices like SQUIDS in the areas like magnetic resonance imaging (MRI) and spectroscopy and high speed computing switches.

The new wave of technological innovation started by K. Onnes, in pure metals, in the year of 1911, today crossed liquid Helium, liquid Nitrogen, barriers in the mixed oxide systems and moving towards solid carbon-dioxide or room temperature. The era of high temperature superconductivity started, when Bednorz and Muller obtained a transition temperature of 30 K in La-Ba-Cu-O system. Wu and his co-workers were the first to discover superconductivity with transition temperature greater than the liquid helium temperature in the mixed oxide system. Subsequently a series of Bismuth and Thallium compounds were discovered by Michel et al and Sheng and Hermann group respectively with progressively, high $T_c$ values as shown below.

1. $\text{La}_2x(\text{Ba},\text{Sr})_x\text{CuO}_4 \quad T_c = 30 \text{ K}$

2. $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \quad T_c = 90 \text{ K}$

3. $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta} \quad (n = 1, 2, \& 3) \quad T_c = 20 \text{ K}, 80 \text{ K}, \text{and 110 K}$

4. $\text{Tl}_m\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+\delta} \quad (m = 1, 2; \ n = 1-5) \quad T_c = 10 - 125 \text{ K}$
In the recent years \( \text{Ln}_{x}\text{CuO}_y \) based superconductors become popular after Tokura et al established electron doping in \( \text{Nd}_{x}\text{Ce}_y\text{CuO}_z \). This is the first copper oxide to exhibit in which current carriers are electrons. In all the copper oxide high \( T_c \) superconductors, like the Y-123, Bi and Tl systems, superconductivity is attributed to the presence of CuO planes which is responsible for the metallic as well as superconducting properties and the charge carriers reside in them.

Vibrational spectroscopy is a powerful tool for obtaining information about the lattice vibrations and electron-phonon interactions in these systems. More interesting are the questions of what all high \( T_c \) materials have in common in their phonon spectra and whether phonons are involved in the pairing mechanism for electrons. Analysis of both Raman and IR spectra are important in order to reach a better understanding of the results. Furthermore it is useful to consider the motions of the atoms in the different modes to better appreciate the phonon frequency and the relationship between the Raman and IR active modes.

Improvement in the material synthesis procedures, like reproducibility, single phase formation tempted us to prepare and characterize the Bi family of high temperature superconductors, through FTIR. Phonon properties of high temperature superconductors and related compounds are of importance in establishing whether or not the phonon mechanism is dominant in the superconducting behaviour of these compounds at a high \( T_c \) of about 90 K. Moreover, it seems that the electronic properties are very sensitive to small changes just near perfect stoichiometry. Single phase compounds are very difficult to
prepare due to the presence of impurity phases, and also the presence of stacking faults and intergrowths.

IR study reveals anomalies in frequency and line widths near zone centre optical phonons in the superconducting state constitute an important part of the study of bulk high $T_c$ superconductors. Depending upon the phonon energy relative to the superconducting energy gap, those IR active phonons which couple to the electronic states piled up near the band gap will broaden or sharpen and soft up or down in frequency as the sample changes from the normal to superconducting state. Therefore study of FTIR spectra are of paramount importance in understanding the mechanism governing the superconductivity in these materials.

This thesis is mainly devoted to the study of vibrational spectra of some well known copper oxide high $T_c$ superconductors which contain negatively charged two dimensional CuO$_2$ sheets. FTIR spectra of single phase stabilised compounds reveal the dependence of phononic structure and therefore the superconducting properties. Phonon characteristics of these Cu-O plane containing copper oxide is expected to throw some light on the pairing mechanism.

The contents of this thesis is sub-divided into four chapters. In chapter I, introduction to the basic physical properties are discussed in brief, giving importance to the spectroscopic investigation and recent advances in the field of Giant Magneto Resistance (GMR).
Chapter II deals with crystal chemistry of bismuth system which is highly complex due to the inherent problems such as the intergrowth of other phases, cationic vacancies or cationic disorder in the Bi site involving an interchange of the Ca and Sr sites and lattice mismatch. In addition the bismuth compound exhibits a structural modulation along the b-axis which is said to be incommensurate.

Even though exhaustive spectroscopic studies have been reported in the literature for bismuth family, single phase formation was not made authentic because of varying preparative conditions including stoichiometric composition and heating condition. Reproducibility is the vital point omitted by most of them. Care was taken to get single phase material by choosing proper stoichiometric composition to avoid lattice mismatch and incommensurability structure. Bismuth family of superconductors which includes 2201 phase, 2212 phase and 2223 phase were prepared choosing off- stoichiometry.

Out of the three phases of the bismuth family of superconductors, 2212 phase is the most studied one due to its very large $T_c$ with single phase formation and its applicability for preparation in the form of wires and tapes to hold very large current density ($\approx 10^6$ Amp/cm$^2$). Also vibrational modes are strongly affected by the holes introduced into the CuO planes. In all the high temperature superconductors, the role of CuO$_2$ planes are considered very much important in controlling the charge carriers to make it semiconducting, or metallic or superconducting. Hence an attempt is made here to study the effect of substitution in the copper site by 3d transition metal nickel. The effect of $T_c$ suppression as a function of substituent concentration is presented. Even though a lot of literature is available on substitutional studies, care was not taken for reproducibility. Reproducible single phase nickel
doped 2212 phase Bi_{2-x}Sr_{1.89}Ca_{0.97}(Cu_{2-x}Ni_x)O_{8+x} was prepared for x=0.02,0.04,0.06,0.08 and 0.1 and electrical resistivity and AC susceptibility measurements were carried out to know the T_c suppression mechanism.

In principle the vibrational spectra contains information about all aspects of the molecular structure. This information can be evaluated comprehensively by calculation of phonon frequencies. For the first time the complete bismuth family of superconductors 2201, 2212 and 2223, IR reflectance spectra was recorded over a temperature range starting from 5 K to 300 K insteps of 50 K. Abnormal behaviour is commonly found not only in transport and magnetic properties of high T_c superconductors but also in the frequency and line width of phonons around the superconducting transitions.

The main idea of IR measurements is to look in for any phonon softening and any characteristic change in the phonon spectrum between 5 K, T_c and 300 K. In conventional superconductors the observation of substantial phonon softening - which is a shifting of the phonon modes towards lower energies as the system goes into superconducting state is taken as evidence of phonon involvement in the formation of superconductivity. In going from the insulator to the superconductor there is a general softening (decrease in energy) of the high energy phonon modes and a hardening (increase in energy) of low energy phonons modes. The hardening of the low energy spectra is in agreement with the stiffening of the transverse acoustic branches in the superconductor. Phonon shifts amounting to $\Delta\omega/\omega$, is commonly observed among the planar oxygen and apical oxygen along the C-axis, because only such phonons experimentally are found to have significant Raman/IR intensity.
For confirmation of our reflectivity results, transmission measurements were also carried out using Bruker IFS 66v at room temperature, which are found to agree very well with each other. Hermann et al. showed that the modulated superstructure arises because of additional oxygen atom inserted in the BiO layer. Hence the IR spectra shows dramatic change 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.

Chapter III deals with T'-structure materials, which evoked an interest since it break the common symmetry of all copper oxide superconductors. Considering the copper high $T_c$ superconductors, the empirical view has come to the following consensus on the requirement for high $T_c$ superconductivity. All high $T_c$ cuprates so far discovered have Cu-O layers with apical oxygen forming the two dimensional, arrays of Cu-O pyramids or octahedra. The charge carriers are holes doped into the parent compounds which are anti-ferromagnetic insulators as a consequence of strong correlation between Cu-3d electrons.

Contrast to these features, new superconducting cuprates $\text{La}_{2-x}(\text{Ce},\text{Th})_x\text{CuO}_4$ have been discovered very recently, which are composed of two dimensional sheet of Cu-O squares with no apical oxygen. In these new compounds, electrons were found to be the super-current carriers.

Moreover structurally similar compounds i.e., T-structure compounds exhibit isotope effect explaining the conventional electron phonon mechanism. Doping study of 214 compound is considered important since this is the only system in which electronic structure, lattice dynamics and isotope effect are intrinsically connected with superconductivity. Also
La$_2$CuO$_4$ was doped with alkaline earth impurity by Bednorz and Muller breakthrough was made in the history of superconductivity. The same parent compound for different rare earths (like Nd, Pr, Sm, Eu and Gd) other than La, when doped with tetravalent impurity Ce, Th lead to new electron superconductor establishing charge reservoir layers or block layers above and below the CuO$_2$ sheets, not only able to accept electrons but also can donate electrons. In T-structure (La$_{2-x}$Sr$_x$CuO$_4$) compounds copper is octahedral coordination whereas in T'-structure compounds (R$_{1.85}$(Ce, Th)$_{0.15}$CuO$_4$) it is in square planar coordination. These structural differences may be the origin in deciding the nature of the charge carriers in these systems.

Xue et al studied the effect of structural stability in terms of matching of R-O bond and Cu-O bond length which in turn change with ionic radii of the dopants in the 214 system. As the Cu-O bond is under compression, through proper doping/partial replacement of R$^{3+}$ by tetravalent Ce$^{4+}$/Th$^{4+}$ stable T'-structure could be produced for rare earths like Nd, Pr, Sm, Eu and Gd other than La$^{3+}$. But beyond Gd no stable T'-structure could be produced due to mismatching of R-O/Cu-O bond length.

FTIR spectroscopy is used to study the structural disorder induced due to doping of R$_2$CuO$_4$ (R=Nd, Pr, Sm, Eu and Gd) with tetravalent Ce$^{4+}$ and Th$^{4+}$ impurity. Weber indicated in La$_{2-x}$Sr$_x$CuO$_4$ system that the Cu-O plane atoms are the major contributors to the high energy vibration modes. From the factor group analysis of T and T'-structure it was found that the Cu-O plane atoms are do not participate in the Raman active vibrations. Hence it will be appropriate to study IR vibrations of these series in the high energy part of the spectrum to understand the role of oxygen in the mechanism responsible for superconductivity.
A series of Cerium doped and Thorium doped T'-structure compounds for R = Nd, Pr, Sm, Eu and Gd were prepared by high temperature solid state reaction technique. Recently developed Fourier Transform spectroscopy, has revolutionised the optical study of high temperature superconductors, in terms of resolution, absence of fluorescence effect, discrete sampling technique and signal to noise ratio. FTIR measurements were carried out for any characteristic change in the phononic spectrum due to structural disorder induced in the processing of doping. Even though Ce and Th, both are tetravalent, the effect of differences in the ionic radii is also studied.

This chapter deals with the phonon characteristics of these Cu-O Plane containing superconductors without CuO₆ or CuO₅ octahedra. This work is aimed at obtaining information on the mechanism of high T_c superconductivity from IR spectrum of these polycrystalline materials.

Chapter IV deals with the lattice dynamics of high temperature superconductors. Study of lattice dynamics started with the simple systems like ionic solids, with two number of atoms per unit cell. The first complete model to describe the lattice vibrations was proposed by E.W.Kellermann.

Three body force shell model (TSM) developed by Verma and Singh and Verma and Agarwal, which is a descendent of early work by Lundqvist, accounts for the short-range interaction between core-core, shell-shell and core-shell interactions represented by the matrices R, S and T respectively. Singh and Verma have assumed that these interaction matrices R, S and T are equal in order to restrict the disposable parameters. In the present
investigation, the interaction matrices were treated not equal to each other and the phonon dispersion relations are obtained based on that fact for simple systems like KCl and KF.

This modified three body force shell model is extended to high temperature superconductors, even though the number of atoms per unit cell is very large, based on the fact that interionic potentials for short range interactions can be transferred from one structure to the another in the similar environments. Systematic study of lattice dynamics of free carriers are important for understanding the physical nature of the high $T_c$ superconductors. Lattice dynamics provides information regarding microscopic description of the interactions of the lattice particles. For a quantitative estimation of the phonon contribution to high $T_c$, a detailed knowledge of the lattice vibrations is essential. This motivated the study of lattice dynamics and normal coordinate analysis of high $T_c$ superconductors.

Here the author present a vibrational analysis of high $T_c$ superconductors namely ErBa$_2$Cu$_2$O$_7$, NdBa$_2$Cu$_3$O$_7$ and Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ based on the modified three body force shell model. This study is supported by a group theoretical analysis at the zone centre and by lattice calculation. The lattice dynamical calculation provided not only the phonon frequency at $q=0$, but also the phonon dispersion curves in the three main symmetry directions $(q,0,0),(0,q,0)$ and $(q,q,0)$. The theoretical phonon frequency values obtained in this work comply with the available experimental values.
A part of the material presented in this thesis have been published/communicated for publication, in the form papers in various National/International journals as follows:


4. FTIR spectra of Bismuth family of superconductors Bi$_2$Sr$_2$Ca$_{1-n}$Cu$_n$O$_{2n+1+6}$, Presented in the MRSI conference, at I I T Madras,11-13 Feb 1998.

5. FTIR spectra of electron doped superconductors R$_{1.85}$Ce$_{0.15}$CuO$_4$ (R=Nd,Pr,Sm,Eu and Gd) Solid State Commun (communicated).

6. FTIR spectra of Thorium doped electron superconductors R$_{1.85}$Th$_{0.15}$CuO$_4$ (R=Nd,Pr,Sm,Eu and Gd), Physica Status Solidi (communicated).


8. FTIR spectra of Bismuth family of superconductors Bi$_2$Sr$_2$Ca$_{1-n}$Cu$_n$O$_{2n+1+6}$, J. Mater. Sci. (in correspondence)

9. Spectroscopic study of Thorium doped electron superconductors R$_{1.85}$Th$_{0.15}$CuO$_4$ (R=Nd,Pr,Sm,Eu and Gd), accepted for poster presentation in the XVIth International Conference on Raman Spectroscopy (ICORS) to be held at Cape Town, South Africa, on 6 - 11th September 1998.

10. Vibrational spectroscopic study of electron doped superconductors R$_{1.85}$Ce$_{0.15}$CuO$_4$
(R=Nd,Pr,Sm,Eu and Gd), accepted for poster presentation in the XVI\textsuperscript{th} International Conference on Raman Spectroscopy (ICORS) to be held at Cape Town, South Africa, on 6-11\textsuperscript{th} September 1998.

11. Lattice vibrations and Normal Coordinate Analysis of Nd\textsubscript{1.85}Ce\textsubscript{0.15}CuO\textsubscript{4}, accepted for poster presentation in the XVI\textsuperscript{th} International Conference on Raman Spectroscopy (ICORS) to be held at Cape Town, South Africa, on 6-11\textsuperscript{th} September 1998.