
CHAPTER - IV

FURTHER STUDIES OF OXIDIC MATERIALS

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4.1 INTRODUCTION

With the publication of Bednorz and Muller's work,¹ a new feature of cuprate ceramic oxide materials was unearthed and most of the workers in allied areas of solid state physics, chemistry and material science entered into a new field of ceramic superconductors.

Onnes² liquefied helium in 1908 and in 1911 measured electrical resistivity of mercury in a capillary tube. It was found that at 4.1 K mercury become superconductor and in 1913 superconductivity of lead ($T_c=7.2$ K) was discovered. Even in earliest period of primitive experimentation it was realized that drastic lowering of resistance indicated the possibility of flow of enormous quantity of current through a thin conductor, enabling construction of mechanical (motor), power devices. It is obvious at this stage that the scientists dreamt of discovery of superconducting material (material with metal like properties) which would exhibit superconductivity at much higher temperature. Liquid helium being a scarce commodity difficult to get. It was obvious that temperatures attainable by other boiling liquids were considered as indices of achievement.

These temperatures being $H_2(l)$ 22.3 K, $Ne(l)$, 27.2 K, $N_2(l)$ 77.4 K, $O_2(l)$ 90.2 K and $H_2O(l)$ 373.16 K.

Further studies upto 1930 raised T_c upto 9.2 K with Nb. This is what could happen during the first 25 years and there was no way to get anything better with search of known metallic elements.

Conductor having T_c not higher than 27 K was considered to be reasonable relief since liquid neon would have taken the place of liquid helium. It took next 25 years. In 1954 an alloy Nb_3Sn with $T_c = 18.1$ K was discovered. Now the search continued in different alloys and a period of 25 years marked slow and marginal achievements by way of discovery of $Nb_3(Al_{0.75}Ge_{0.25})$ with $T_c \sim 20$ K, Nb_3Ga with $T_c \sim 20.3$ K in 1971 and Nb_3Ge with $T_c \sim 23.9$ K in 1973 were known.³ Although these achievements with respect to rise of T_c was small it gave a great technical relief that superconductivity can be basis of new technology with boiling liquid helium as the temperature at which devices may operate.

There is no doubt that the objective of superconductivity research should be to develop motive devices with electrical impulse. The more difficult problem which confronted the scientist were related to design of large and stable electro-magnets needed in experimentation in nuclear physics.

Once Tc near liquid nitrogen temperature was reality next target obviously would be to achieve Tc above 27.2 K so that boiling liquid neon can be used as a bath and still better if Tc crosses 77.4 K. When boiling liquid nitrogen can be used at this stage superconducting magnets of Nb alloy based winding became a commercial commodity on a production line of NMR instruments and larger magnets for some advanced laboratory experiments.

Next discovery came almost as surprise within next 13 years, which showed a small change of +6 K only, but from a totally different material ceramic oxide, lanthanum cuprate with Tc at 30 K.¹ We must go back to 1974 to trace origin of superconductivity in ceramics. $\text{Ba Pb}_{0.27} \text{Bi}_{0.25} \text{O}_3$ (Tc 13 K) was known in 1974.⁴ However, upto 1986 ceramic oxide remained nearly a laboratory curiosity because Nb_3Ge alloy with Tc 24 K was much ahead of many ceramic materials which were studied covering almost 200 research papers. The slowly trotting tortoise of oxide superconductors went ahead of alloy superconductors here with the publication of Bednorz and Mullers work on lanthanum cuprate $T_c \sim 30-40$ K in 1986. It is at this stage that neon superconductors as ternary and quaternary lanthanum cuprates were discovered. Importance of this work lies in not raising the Tc substantially but to indicate two important things firstly $T_c > 27$ K can be reality and secondly ceramic materials may prove to be interesting materials as much as the alloys.⁵ It was left

then to try to get new materials with higher and higher T_c initially with an object to push T_c above the temp. of boiling liquid nitrogen i.e. ~ 80 K and possibly ~ 230 K i.e. boiling liquid water. There is no harm in dreaming for still higher temperatures which prevent in many of the todays mechanical power devices. Wu et al. reported within months major break through by replacing lanthanum by yttrium to give a nitrogen superconductor $(Y_{0.6}Ba_{0.4})_2(CuO_{4-y})$ with T_c 93 K.⁶ In quick succession appear material with numerable new compositions resulting from using different stoichiometries and different cook book recipes which are now known to give different phases of molecular structure. In addition to this thallium and bismuth based materials have also become known.

When today the history is being made the speed with which things happened gives a very strange mixture of conflicting data and it takes sometime to check all the reports to illuminate spurious, erroneous and wrong results and take out a few seeds of truth. However, some guiding principles have already been established and now a person taking up synthesis of new materials known certain few key points such as

- (1) Superconductivity sometimes is associated with a particular phase of a composition only.
- (2) The superconducting phases usually are confined to a particular crystallographic unit. Unless tetragonal

material is converted to orthorhombic Tc cannot be expected.

- (3) Due respect must be given to oxygen content of the sample, the procedure of synthesis can be monitored in such a way that the sample will drink or spit out oxygen to give a sample with exactly desired oxygen content. The location (occupation of points, lines or plans) and form (triplet singlet or peroxide).
- (4) The state in which copper occurs? The cuprates can be shown by method of valence accounting of both oxygen and copper to possess Cu^{I} , Cu^{II} or Cu^{III} . It is now known that it is a dangerous practice that the problem cannot be so easily tackled by a process of accounting.
- (5) Issue of non cuprate superconductors : Reports so far show that most of the ceramic materials are cuprate superconductors. Prof.C.N.R.Rao has very aptly described it as 'copper is born to conduct'.⁷ However, the issue is opened and there is no reason why non cuprate superconductors should not exist.
- (6) Are there non rare earth superconductors ? Now we know many of them.
- (7) Will there be a possible upsurge of organic superconductors? We know several organic metal systems but unfortunately Tc very low and with no indication of prospects. So far there is no indication organic super-

conductors joining in race with ceramic materials and any positive or negative remarks at the stage will be untimely.

(8) When we try to have a full view of the present state it appears that a nitrogen superconductors are constituting a useful, practical commodity. For sometime at least nitrogen superconductor technology can be a matter of concern of our civilization and the temper of science. But still not losing hopes for liquid water superconductors it appears that now are training for further break through. Nothing can be said about the material and the degree of achievement. It must be clearly understood that now is the time for preparing all possible compositions of the established system and to prepare materials by using various preparatory histories involving experimental techniques controlling grown size, purity and structure. In the present work 1,2,3 systems and their analogs were prepared by PFHS route and complex forming route. The raw oxides obtained by thermal decomposition of the precursor are used for further study as reported in the following few sections.

(9) Theory is the backbone of the experimental design and proof of result. Conversely experimental results either support, deport (validate or discard) or partly support the theory. Generally theory works as a

guiding star for further work but there are instances of theory keeping researchers on a wrong track.

Unique results many times shake the foundation of the theory. When the scientists reported high T_c for certain sample a theoretician was worried about his theory and questioned "Look your work stands against BCS theory". Quick came the reply from the experimentation, "I give importance to observed phenomenon. Your theory must follow my results. When observed high T_c is demonstrated and reproduced my purpose is served who cares for your theory.

However, it is true that he should have advised the theoretician to repair the existing theory or develop a new theory to explain new results!!

At a onset of any work many a times there is multitude of proposals. Soon most of the dust settles, and leads to the theory that explains the results and guides the further work.

4.2 PRECURSOR TECHNIQUES

The preparatory methods can be broadly classified into two groups. (1) Direct synthesis by mixing oxides or similar solids. The mixing is done mechanically and the dry mixture is given appropriate heat treatments. Although CuO and $\text{Y}_2\text{O}_3/\text{La}_2\text{O}_3$ are easily available in any desired purity upto 99.99% the alkaline earth oxides are not stable and not available in standard purity. Alkaline earth oxides absorb

moisture and reversal by dehydration step is not possible $MO \cdot xH_2O$ is often indefinite composition with CO_2 from air and give carbonates. The formation of MO by thermal decomposition of M_2CO_3 is not a straightforward reaction because resulting MO may react with available oxygen to give MO_2 (peroxide). This reaction is more predominant in barium and somewhat less in strontium. Hence there is difficulty in getting stoichiometric amount of the constituents. Many authors have used CuO , ReO_3 , $BaCO_3$, $SrCO_3$, BaO_2 etc. The sintering of the mixture of the above components has been reported by several authors at $950^\circ C$ but there are reports of use of somewhat higher or lower temperature. The sintered mixture is then pelletized and further sintered over a period from 6 hours to 24 hours. The pellets are reground several times, reformed into pellets and sintering is repeated to give a multitude of resultant product and the black powder is likely to be leading to desired material. Any green or red material formed is likely to be different than what we want. The reaction of formation of cuprate is not similar to any simple chemical reaction and therefore a tricky process which needs certain experience and skill.

There are very few reports in which sufficiently high temperature leading to melting of the mixture has been reported.^{8,9} It appears that at higher temperature the cuprates are unstable and at lower temperature formation of cuprate is very slow. And therefore, optimum temperature

of 950°C is generally accepted. Chemical methods involve several variations. It has also been reported that barium cuprate and rare earth cuprate separately formed and $\text{BaCuO}_2/\text{Y}_2\text{CuO}_5$ are further heated strongly to give ceramics.¹⁰ The simplest one is the mixing of solid nitrate salts, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Y}(\text{NO}_3)_3 \cdot 7\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$ and after intimate mixing, the mixture is heated in a platinum crucible till all nitrates ultimately gave mixture of oxides. Apparently this is the simplest method but unfortunately copper nitrate and rare earth nitrates are extremely hygroscopic and deliquescent. In another method aqueous solutions of nitrate are prepared, their concentration determined accurately by standard chemical process and volumes of solutions corresponding to the desired metal content are mixed. The mixed solution is directly evaporated without sputtering and the resultant green solid is pulverized and heated strongly. It has been established that microcrystalline or very fine grained starting materials require less time of heating and therefore generally two techniques are used. In the first the aqueous nitrate mixture prepared¹¹ as described above is spray dried and scraped green dry powder used for further processing. Alternatively sole gel method is used. Aqueous mixture of nitrates is dispersed into another organic solvent in which solubility is very low and very fine grained powder is thrown out the residue is filtered out and further used. A large number of tech-

niques are available to the chemist in which several chemical reactions can be tried in which the desired goal is achieved. Metal complexes or coordination compounds are prepared by using suitable ligand and the complexes are mixed in definite proportion. A positive advantage in this case is that the complexes of all constituent metals can be prepared in desired purity and stability. The guiding principles in choosing the ligands are as follows :

- (1) The compound must be nonhygroscopic,
- (2) Its purity must be high.
- (3) No side reactions should be possible. The associated ligand must have a tendency to leave behind quantitatively the oxide residue. Oxalate, citrate and tartarate¹² are also used as ligands.

The stoichiometric mixture of nitrates in water can be treated with dilute ammonia to give green precipitate which is filtered and ignited but the hydroxide precipitates are gelatinous show adsorption and hence not convenient for handling.

Oxalates are the most preferred ligands for this purpose. The oxalates are easily filterable and therefore chemists prefer oxalates over gelatinous and slimy hydroxides.

Application of several ligands are reported in the present study acetylacetone has been used. In our laboratory

we have also studied salicylaldehyde,¹³ carboxylic acids¹⁴, oxines¹⁵ and similar ligands for this purpose.

There are reports in many other laboratories where several other metal complexes using ligands like EDTA¹⁶ have appeared.

In this respect, as has been stated earlier the real advantage is expected provided, the chemical reaction brings the constituent together at atomic level rather than at particle level in mechanical mixing. It may be noted that a small grain of 0.01 mg CuO contains 8000000000000000 atoms of copper. An ideal situation will be preparation of binuclear complexes in which one copper and one barium atom will give rise to a binuclear complex molecule, M-M'L_x where M and M' are barium and copper and another binuclear complex in which M and M' are yttrium and copper respectively. Dissolution of these two complexes in a common solvent may give a desirable homogeneous composition. Three isomorphous complexes may be found out which will give triple salt like molecule $[Y_2L_3 \cdot 4BaL \cdot 6CuL]$. Next step will be to have a polynuclear isomorphous complex with a well characterizable single molecule of the formula $(M-M'_2 - M''_3 L_x)$ which will have a ligand framework holding one atom yttrium (M) two atoms barium (M') and three atoms of copper (M''). This ideal material on thermal decomposition may straight way give atom by atom proximity and would give 1,2,3 product in a more convenient manner, however, preparation of such a

complex is not an easy task. Extensive search for convenient ligand for binary ordinary systems indicated in the above discussion will have to be carried out.

Precipitation from homogeneous solution¹⁷ uses a chemical process in which the precipitating agent is generated in situ by kinetically governed chemical decomposition process. Decomposition of urea slowly liberates ammonia and it can give a better quality hydroxide precipitate. Diethyl oxalate on hydrolysis yields slowly oxalate ions giving fine grained oxalate precipitate by reaction with metal ion present in the solution and can be regarded as an improvement over a direct oxalate precipitation technique. In our study we have investigated the application of hydrolytic decomposition of diethyl oxalate to form 1,2,3 oxalate for further decomposition into oxide ceramics.

We have also proposed a new technique involving pyrofores. By the decomposition of citrates and tartarates pyrofores are observed. We are trying to develop pyrofore of 1,2,3 composition which ultimately will give decomposition product as mixture of oxides. However, we have observed that pyrofores of lead and bismuth are easy to prepare and hence we intend to take up the study in which lead and bismuth are constituents rather than YBa cuprates. The above discussion can be applied to other well proven compositions like lead-bismuth and thallium-bismuth based superconductors.

The analysis of the resultant material can be done by conventional chemical methods like EDTA titration, gravimetric determination of copper and rare earth. Atomic absorption or X-ray fluorescence can also be used.

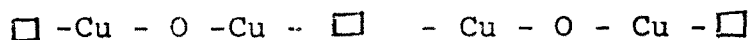
4.3 OXYGENATION, DEOXYGENATION REACTIONS

When ceramic materials are heated in presence of oxygen or dry air, there is addition of oxygen to the material and this has profound effects on structure and properties. The stoichiometric compositions of 1,2,3 compound assuming copper to the bivalent corresponds to the formula $M_1 M'_2 Cu_3 O_{6.5}$ (M is Y/La M'_2 is Ba_2/Sr_2 or Ba Sr). Depending on the preparatory method the addition of oxygen may correspond to one atom per mole of the substrate. There is a very large amount of conflicting reports regarding the chemical and physical behaviour of added oxygen. However, this conflict mainly arises because of the lack of information regarding this excess oxygen. The valence of copper can be I/II/III and if oxygen is straightway to be accounted in terms of valance of copper. The partial oxidation of Cu^{II} appears to be the simplest explanation but now it is known that Cu^{III} does not exist. Samples with oxygen less than 6.5 are also reported and it is generally thought that this may be due to partial reduction of Cu^{II} to Cu^I and thus the oxygen stoichiometry ranging from $M_1 M_2 Cu_3 O_6$ to $M_1 M_2 Cu_3 O_7$ with intermediate composition $M_1 M_2 Cu_3 O_{7-\delta}$ (i.e.

$M_1M_2Cu_3O_{6.5+\delta}$) are known and studied. The amount of oxygen depends on the temperature and the composition of the gas in which it is heated. It is well known that heating in air or oxygen at 560°C gives material which is superconducting. The oxygen content determines the crystal structure and the limiting values for conversion of tetragonal (nonsuperconducting) to orthorhombic (superconducting) are $\delta = 0.4$ ¹⁸

The whole range of δ values from 0 to 1 have been studied. The earliest developed methodology for estimation of free oxygen was the Winkler's method which was formerly used for determination of dissolved oxygen in water. The material is added to oxygen free water in oxygen free atmosphere. Free oxygen is set free which oxidizes iodide to free iodine. This method is commonly used but is very crude and unreliable. More reliable results come from T.G.A. in hydrogen atmosphere. Free dissolved oxygen depletes in reaction with hydrogen and gives good results. The free oxygen is quantitatively expelled even by heating at high temperature. So T.G.A. profile and its high temperature tail also gives good results. Much of the confusion in these studies arises because of the nature of oxygen and debate still goes regarding whether part of the oxygen is peroxide oxygen or it is 100% triplet oxygen. In our laboratory we are trying to develop simple methodology for colorimetric estimation of free oxygen and trustworthy technique for decision regarding existence of peroxide oxygen.

The two types of oxygen ordering¹⁹ are possible. Interchain ordering of oxygen vacancies and interchain ordering of fully oxidized chains. At a composition $O_{6.5}$ interchain ordering within a b axis chain may be represented



This ordering would double the periodicity along the b axis and probably along the a axis as well as Cu(I) atoms would be uniformly oxidized to Cu(II) and have only three coplanar oxygens etc.

Oxygen desorption study was also carried out.²⁰ For $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta = 0.05, 0.5$) system, the highly sensitive mass-spectroscopic study does not show the presence of adsorbed oxygen containing impurities such as OH, H_2O , CO and O_3 but instead, the oxygen desorption is observed in two distinct steps below and above 470°C with activation energies 28 and 54 K cal/mole.

Oxygenation kinetics²¹ study was also reported. The materials with increasing yttrium concentration in $\text{Y}_{1-y}\text{La}_y\text{Ba}_2\text{Cu}_3\text{O}_x$ behave similarly to $\text{YBa}_2\text{Cu}_3\text{O}_x$ with increasing temperature. Both show an initial decrease in E_a and change to a parabolic rate law. The state O_4 which appears in both kinetics and superconductivity. The low E_a for $\text{YBa}_2\text{Cu}_{2.5}\text{Fe}_{0.5}\text{O}_x$ appears to be connected with a higher valency state

of iron compared to copper. This leads to a local enrichment with oxygen around the iron atom. This local cluster enhances the transport of oxygen.

4.4 OXIDATION STATES OF COPPER

There is no element other than copper which has attained importance in culture and civilization, craft and art, science and technology or agriculture and life. It was the most important native metal which was used in pre-historic time which marked the beginning of the new era i.e. copper age.

Copper was used for coins, ornaments, status, inscribed plates and decorative articles which preserved the history for the future studies, science, metallurgy and technology of alloys was mainly centered around copper. Recent studies have shown that the copper is an essential trace element in many biological processes. Copper was one of the elements which nature tried for oxygen carrier function in snail's blood through $\text{Cu}^{\text{I}} - \text{Cu}^{\text{II}}$ redox system. In the vertebrate blood although iron has replaced copper as an oxygen carrier, it is only to give a more important regulatory function to copper in oxygen carrying iron system. Since copper is the best electrical conductor, today's power transmission and electromotive devices mainly use copper wire although is next to silver in electrical conductivity. Its limitations obviously are due to its limited specific conductance which cannot eliminate the transmission losses.

A dream of the scientist and technologist will therefore be to discover material with almost zero specific resistivity. The work during the last eighty years centered around non-copper materials but a beginning of revolution in high temperature superconductivity has been marked with cuprates as nitrogen superconductors which today appear to be the most promising discovery that will take human civilization and technology to the 21st century. This happy involvement of copper from prehistoric time to the dawn of the future cannot be ignored.

Copper, the 9th element in the first transition series with $3d^9, 4s^2$ configuration has a peculiar behaviour where in its second oxidation state with $3d^9 4s^0$ configuration it exhibits the more common Cu^{II} chemistry with the loss of single electron $3d^{10}4s^0$ configuration is attained giving Cu^I chemistry. Still less common Cu^{III} chemistry is $3d^8 4s^0$ configuration. The redox chemistry both in solution and solid state has been extensively studied by physicist and chemists. It is obvious that while studying 1,2,3 compounds the conducting characters will be attributed to copper redox systems and attempts to define the composition in terms of Cu^I, Cu^{II}, Cu^{III} is but natural. Over almost three years of world wide research activity has only told us that we have started to know that we do not know anything much precisely about oxidation state of copper and proving something posi-

tive precisely is much more difficult than disproving the fallacy if any assumption in this regard.

Low dimensionality and mixed valence state of copper are two important factors for the existence of superconductivity. The number of ultraviolet photon spectroscopic and X-ray photon spectroscopic studies have been carried out²² with the specific objective of determining the presence of copper valence states in the superconducting oxides. Many of them report the presence of Copper(II) and possibly copper(I) state but none reported the presence of Cu(III) ions in these oxides. The speculative reporting on the basis of oxygen contents or arguments in favour of disproportionation ($2\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}} + \text{Cu}^{\text{III}}$) are now mostly withdrawn.

The Cu (2p) spectrum shows the presence of a well screened d^{10} state (CuII) at 933 eV along with a poorly screened d^9 state (Cu^{2+}) at 942 eV. There is no proof for Cu^{3+} in the Cu(2p) or Auger spectra. Oyangi et al²³ from the X-ray absorption study reported that the spectra show the copper ions in d^{10} states as the predominant ones. At the same time, Strobel et al.²² show that there was matching between the thermodynamics of copper(I) and copper(II) in ternary and quaternary oxides with that of the binary oxides.

Results contrary to the above are reported by various investigators. The various investigators assumed that a

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fraction of copper ions in these superconducting phases are in copper(III) state and its superconducting property depends upon the small concentration of copper (III) ions. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-x}$ ²³ shows the presence of mixed valence state of copper(II) - Cu(III) and this mixed valence state is necessary for the presence of metallic and nonmetallic behaviour. $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, $\text{La}_4\text{BaCu}_5\text{O}_{12+\delta}$ ²⁴ or $\text{La}_{8-x}\text{Sr}_x\text{Cu}_8\text{O}_{20-\varepsilon}$ ²⁵ show the metallic behaviour. Mixed valence state of copper allows the delocalisation of holes over the "copper oxygen framework".

The tervalent state of copper is difficult to stabilize at normal pressure. The only known oxide was $\text{LaCu}^{\text{III}}\text{O}_3$ which was synthesized under high pressure (65 K bars). In order to favour the partial oxidation of Cu(II) into Cu(III) under normal oxygen pressure the insertion of basic ion such as an alkaline earth is necessary. The preparation of La_2CuO_4 at normal oxygen pressure does not allow the mixed valence state of copper to be reached, but the crystal contain Schottky defects on all their sites according to the formulation $\text{La}_{2-\varepsilon}\text{Cu}^{\text{II}}_{1-\varepsilon}\text{O}_{4+4\varepsilon}$. The application of high oxygen pressure allows the anionic vacancies to be filled in mixed valence oxide $\text{La}_{2-2\varepsilon}\text{Cu}^{\text{II}}\text{Cu}^{\text{III}}_{1-\varepsilon}\text{O}_4$.^{26,27} It is necessary to use an excess of copper oxide for the synthesis of La_2CuO_4 at normal oxygen pressure.

The $\text{YBa}_2\text{Cu}_3\text{O}_7$ confirms the presence of mixed valence of copper in superconducting properties of those oxide. The molar ratio of Cu^{III} to Cu^{II} is 0.5. But in case of the $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ This molar ratio value is very less. Several authors show that T_c decreases as $\text{Cu}(\text{III})$ content decreases. $\text{YBa}_2\text{Cu}_3^{\text{II}}\text{O}_{6.5}$ would only contain $\text{Cu}(\text{II})$ from the charge balance and should not be a superconductor. Consequently whenever δ is different from 0 to 1, 0 may observe the disproportionation of $\text{Cu}(\text{II})$ in $\text{Cu}(\text{III})$ and $\text{Cu}(\text{I})$ leading to $\text{Cu}(\text{II})$ - $\text{Cu}(\text{III})$ superconducting region and $\text{Cu}(\text{II})$ - $\text{Cu}(\text{I})$ as insulating domains coexisting in the same crystal. Contrary to $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ the La_2CuO_4 type oxides will not have this disproportionation. The observations of noticeable amounts of $\text{Cu}(\text{I})$ was in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by X-ray absorption spectroscopy²⁸ whereas no $\text{Cu}(\text{I})$ was detected by Bianconi et al.²⁹ in La_2CuO_4 type oxides.

One of the features chemist would like to investigate in cuprate superconductor will be to resolve the average valance of copper into either involvement of $\text{Cu}^{\text{I}} \rightarrow \text{Cu}^{\text{II}}$, $\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{III}}$. Single electron redox process or copper disproportionating into $\text{Cu}^{\text{I}} - \text{Cu}^{\text{III}}$ system. The experimental techniques like energy band spectroscopy, ligand field calculations, X-ray absorption spectroscopy and X-ray photoelectron spectroscopy are being used for ascertaining the role and identity of the oxidation state of copper. In our

laboratory we have started study of applications of EXAFS. These studies do not constitute the part of this thesis.

4.5 SYNTHESIS OF CERAMIC MATERIALS FROM OXALATE AND ACETYLACETONATE PRECURSOR

Mixed oxalates having desired compositions were prepared by taking mixed solution of nitrates of the constituent metals which were treated with diethyl oxalate to give precipitates of the ternary and quaternary oxalates.

By using a mixture of constituent metal nitrates ternary and quaternary acetylacetonate complexes were also prepared.

The complexes of both the above types were then incinerated in silica crucibles by slow heating upto 600°C . The temperature was maintained at 600°C for three hours. The crucibles were then taken out of the furnace and cooled. The resultant flubby drosses were ground carefully and converted into pellets by applying 7 tons pressure. The pellets were about 1 mm thick and 10 mm in diameter. These were sintered in a platinum crucible at 960°C for 6 hours. The annealed pellets were reground, pressed into pellets and again sintered. In some cases the powder as well as pellets showed green colour. With repeated heating a few samples showed improvement. Finally the pellets were ground very finely and 1 mm thick pellets were prepared. These

were heated to 960°C for 4 hours and cooled in the furnace by keeping the cooling rate 100°C per hour. The pellets were charged in zirconia boats and were transferred to an oxygenation furnace maintained at 560°C . Oxygen gas was passed through a decarbonizing tower containing flakes of NaOH followed by dehydrating Dreschel bottle containing conc. H_2SO_4 as a dehydrant. Oxygenation was carried out for six hours and the furnace was allowed to slowly cool down when oxygen was still flowing. The cooling rate was maintained at 50°C per hour. The pellets were then removed from the furnace and kept in wads of cotton properly protected in capped vials. Analysis of the resultant product, the chemical composition of nonoxygenated and oxygenated sintered ceramics was carried out for Y, La, Ba, Sr and Cu content by using methods reported earlier. As noted earlier desired excess of Ba and Sr based on analytical results of single complexes was added so as to maintain the final composition - $(\text{Y} + \text{La})_1 (\text{Ba} + \text{Sr})_2 \text{Cu}_3\text{O}_{6.5}$. The δ oxygen was estimated by two techniques. In the first method samples were weighed before and after oxygenation and from the gain in weight δ values were calculated. In the second method about 25 mg of the oxygenated product was heated in thermobalance in nitrogen atmosphere to 800°C and from the weight loss the δ values were computed. There was good agreement between δ values calculated by weight gain and weight loss methods. Many workers have reported the iodometric method of determination of oxygen, but iodometric

Table 4.1 Chemical Composition of samples prepared by using oxalate route.

Temp. - 650°C Time - 6 hours Cooling rate - 50°C/hour

Obs. No.	Formula of the complex before oxygenation	Formula of the complex after oxygenation	δ value
1.	$Y_1Ba_1Sr_1Cu_3O_{6.5}$	$Y_1Ba_1Sr_1Cu_3O_{6.7}$	0.2
2.	$Y_1Ba_2Cu_3O_{6.5}$	$Y_1Ba_2Cu_3O_{6.8}$	0.3
3.	$La_1Ba_1Sr_1Cu_3O_{6.5}$	$La_1Ba_2Cu_3O_{6.9}$	0.4
4.	$La_1Ba_2Cu_3O_{6.5}$	$La_1Ba_2Cu_3O_{6.9}$	0.4

Table 4.2 Chemical composition of samples prepared by using acetylacetonate route.

Temp. - 650°C Time - 6 hours Cooling rate - 50°C/hour

Obs. No.	Formula of the complex before oxygenation	Formula of the complex after oxygenation	δ value
1	$Y_{1.0}Ba_2Cu_3O_{6.5}$	$Y_{1.0}Ba_2Cu_3O_{6.9}$	0.4
2	$Y_{0.9}La_{0.1}BaSrCu_3O_{6.5}$	$Y_{0.9}La_{0.1}BaSrCu_3O_{6.78}$	0.28
3	$Y_{0.8}La_{0.2}BaSrCu_3O_{6.5}$	$Y_{0.8}La_{0.02}BaSrCu_3O_{6.78}$	0.28
4	$Y_{0.7}La_{0.3}BaSrCu_3O_{6.5}$	$Y_{0.7}La_{0.3}BaSrCu_3O_{6.85}$	0.35
5	$Y_{0.6}La_{0.4}Ba_2Cu_3O_{6.5}$	$Y_{0.6}La_{0.4}Ba_2Cu_3O_{6.9}$	0.40
6	$Y_{0.5}La_{0.5}BaSrCu_3O_{6.5}$	$Y_{0.5}La_{0.5}BaSrCu_3O_{6.939}$	0.439
7	$Y_{0.4}La_{0.6}Ba_2Cu_3O_{6.5}$	$Y_{0.4}La_{0.6}Ba_2Cu_3O_{6.86}$	0.36
8	$Y_{0.3}La_{0.7}BaSrCu_3O_{6.5}$	$Y_{0.3}La_{0.7}BaSrCu_3O_{6.73}$	0.23
9	$Y_{0.2}La_{0.8}Ba_2Cu_3O_{6.5}$	$Y_{0.1}La_{0.9}Ba_2Cu_3O_{6.81}$	0.31
10	$Y_{0.1}La_{0.9}BaSrCu_3O_{6.5}$	$Y_{0.1}La_{0.9}BaSrCu_3O_{6.89}$	0.39
11.	$Y_{0.0}La_1Ba_2Cu_3O_{6.5}$	$Y_{0.0}La_1Ba_2Cu_3O_{6.9}$	0.40
12	$Y_{0.0}La_1BaSrCu_3O_{6.5}$	$Y_{0.0}La_1BaSrCu_3O_{6.89}$	0.39

method is not sufficiently sensitive to discriminate to ± 0.01 level. The various compositions prepared are reported in tables 4.1 and 4.2. Our work on photometric study of δ -oxygen will appear elsewhere.

4.6 PHASE STUDIES OF MULTICOMPONENT SYSTEM

Single component or two component systems can be studied very easily but the study of three component systems although difficult is necessary for better understanding of possible variable molecular compositions representing separate phases. Ceramic materials like clays and refractories with $(\text{MgO})_n (\text{AlO}_{1.5})_m (\text{SiO}_2)_p$ with Mg, Al, Si as the three components or alloys like stainless steel with iron, nickel and chromium are two of the many such examples. Newly added $(\text{YO}_{1.5}), (\text{BaO}), (\text{CuO})$ that is YBaCu ceramic superconductor is the most important amongst them. Since YBaCu system is thermodynamically unstable - it is possible that at some chosen temperature a multitude of compositions may exist and a very careful preparatory technique will be necessary to get a single phase 1,2,3 ceramic. This three component system will speak about concentration of three variables Y, Ba, Cu or the different crystal habits, as shown in the three Gibbs triangles. Fig. 4.1. It must also be noted that this three component diagram will be a frozen diagram at any one chosen temperature. Alternatively another diagram may be drawn in which contours of materials with variable

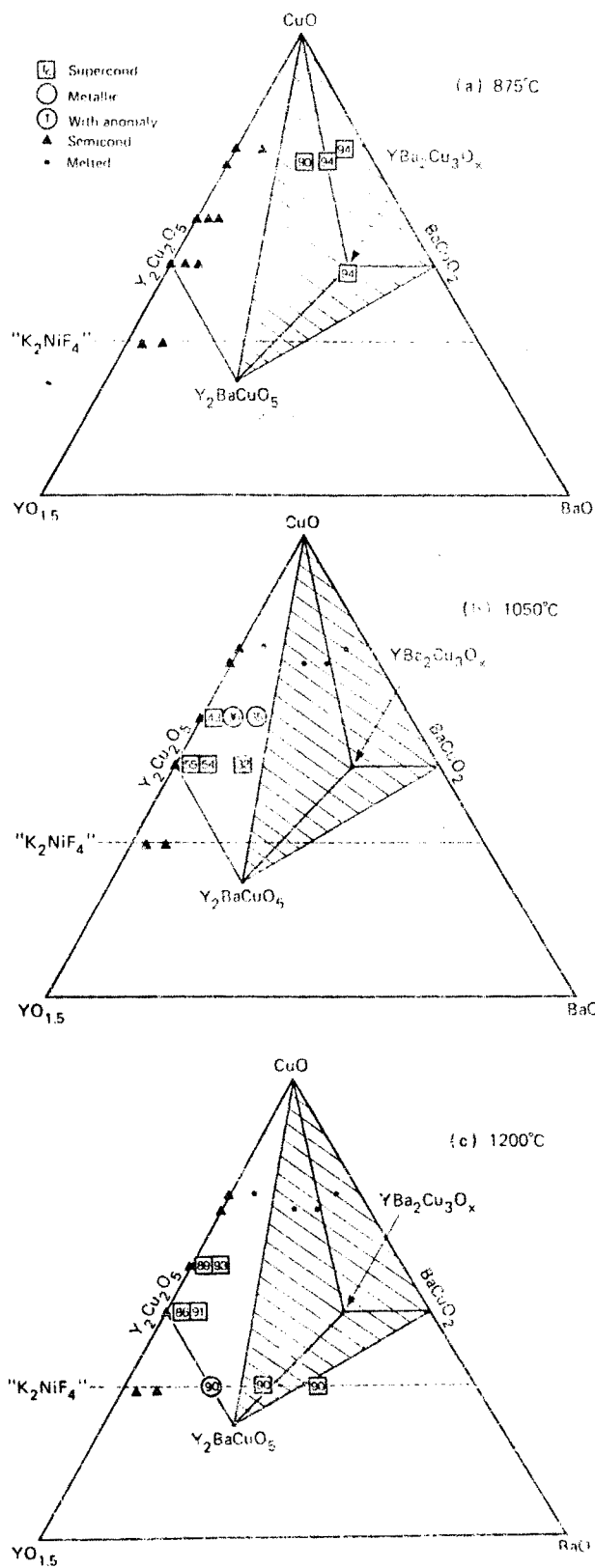
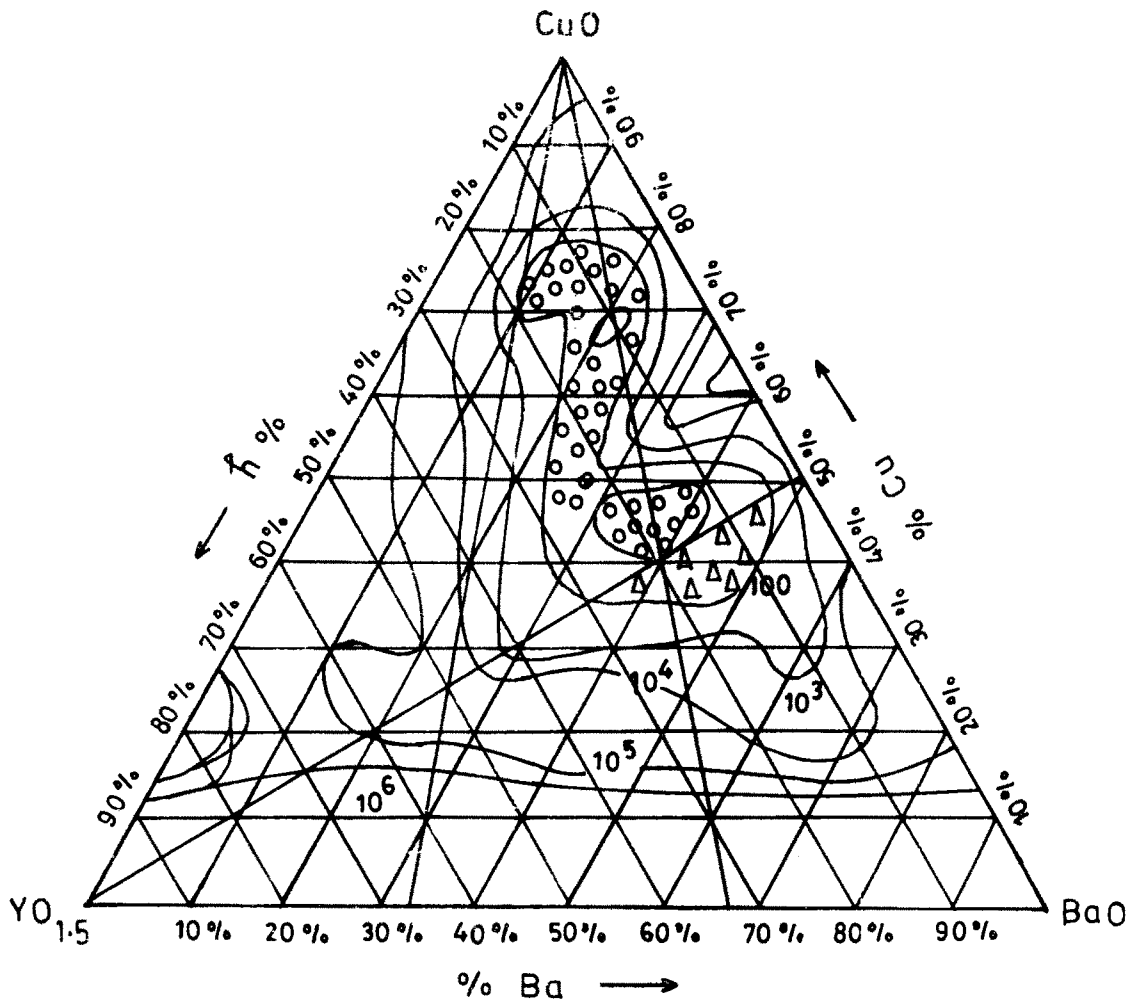


FIG. 4.1 — Compositions of Y-Ba-Cu-O system and summary of results for samples prepared at (a) 875° C and (b) 1050° C (c) 1200° C



- - SUPERCONDUCTING COMPOSITION .
- △ - SAMPLES SHOWING $T_c > 100$ K .

FIG. 4-2 — GIBBS TRIANGLE CONTOUR LEVELS IN ROOM TEMPERATURE RESISTIVITY (IN Ωcm) AS FUNCTION OF COMPOSITION .

-will be presented as is done in Fig. 4.2. Normally phase diagrams are not prepared for more than three components. It is difficult to determine data for all compositions corresponding to three components. However, such three component diagrams are immensely useful for proper understanding of 1,2,3 ceramics.

It is not impossible to go for multicomponent system $M > 3$. For example adding oxygen as the 4th component yielding information for entire range of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$ values. A system which is used for study of three component system is the use of a point for one component that is Y/Ba/Cu. A line will then represent all compositions starting with $A_{100}B_0$ at starting point to A_0B_{100} at the end point B and at any length of the line composition A_nB_{100-n} . Three such binary lines defining compositions A_n , B_m , B_nC_m and C_nA_m give an equilateral triangle. The plane area, within the triangle will represent $A_nB_mC_{100-n-m}$ composition. Such a triangular phase diagram is known as the Gibb's triangle. Each vertex represents a pure component. In an anticlockwise direction the linear displacement shows increasing proportion of the component towards which the point is moving. Lines drawn parallel to any chosen base represent compositions with fixed proportion of the vertex element. The Gibb's triangle and the way in which composition data is entered on the Gibb's triangle³⁰ is shown in fig. 4.2. A composition diagram on the basis of δ -value is prepared by

with respect to resistivity and is given in fig. 4.2. Various phases at equilibrium at a few chosen temperatures are given in fig. 4.1.a, 4.1b and 4.1.c. These standard data on compilation serve as a guide line in deciding the preparatory procedure. A more complex phase diagram with the 4th component will be a four dimensional trigonal prism. In the study of ceramic superconductors such a four dimensional diagram may not be useful at the level of todays knowledge of the structure. However, the 4th dimension can be added as temperature and a stack of Gibb's triangles at temperatures between 500° to 1200° will give a trigonal prism which will be immensely useful. Another variation which can be introduced in the diagram will be stacking of Gibb's triangles for compositions such as the one starting with $Y_1La_0Ba_2Cu_3O_{6.5}$ through known intermediate compositions to $Y_0La_1B_2Cu_3O_{6.5}$. Alternatively $YBa_2Sr_0Cu_3O_{6.5}$ as starting composition to $YBa_0Sr_2Cu_3O_{6.5}$ through known compositions will give trigonal prisms which will be a useful guideline for optimization of the experimental conditions. We intend to take up this work as the next part.

4.7 BONDING, STRUCTURE, STEREOCHEMISTRY, MOLECULAR ORBITALS AND ENERGY BAND SPECTRA

The copper ion under various electronic environments may take multitude of stereochemical patterns as follows :

- (1) $Cu-O_2$: a linear structure

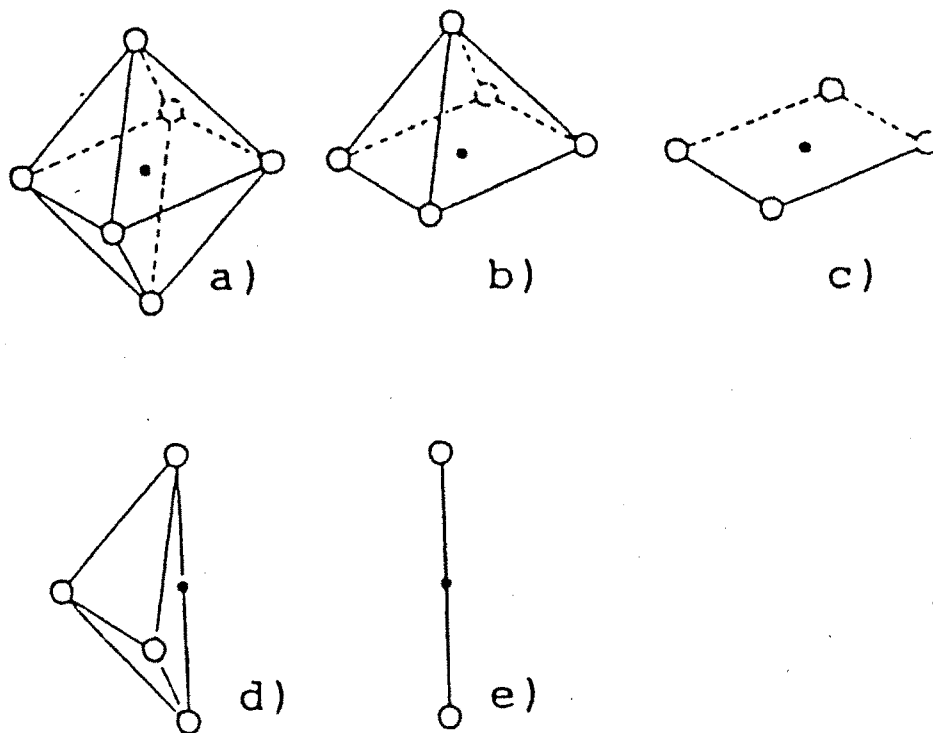


Fig.4.3.a.Coordination polyhedra

(2) Cu-O_4 structure : Central metal atom surrounded by four oxygens giving a perfectly square planar arrangement. In this structure all the five atoms are coplanar and Copper-oxygen distances are the same.

(3) Alternatively a trigonal pyramidal structure with 3 oxygens at the apices of an equilateral triangle with copper at the centre of the triangle, 4th oxygen occupying the apical position of the structure.

(4) Square pyramidal CuO_5 structure : 4-oxygens and copper form a perfect square plane and 5th oxygen occupies the apical position of the pyramid.

(5) Octahedral CuO_6 : Perfect AB octahedron with CuO_4 as a perfect square plane and two axial position occupied by two remaining oxygens. All Cu-O distances are identical.

The cuprate materials may be built up by using these elemental polyhedra with stacks or piles of the elemental units in many ways giving moderately complex to highly complex structural units. If the Z-axis is elongated and both equatorial axes are equal an elongated tetragonal geometry results whereas inequality of all three axes gives orthorhombic geometry. Deviations from these ideal geometries give distorted crystal habits.

Such geometries and their effect on electron density around copper atom can be studied by XRA and XPS. A comparison of model stereochemistries and 1,2,3 compound are in progress in our laboratory as a collaborative project.

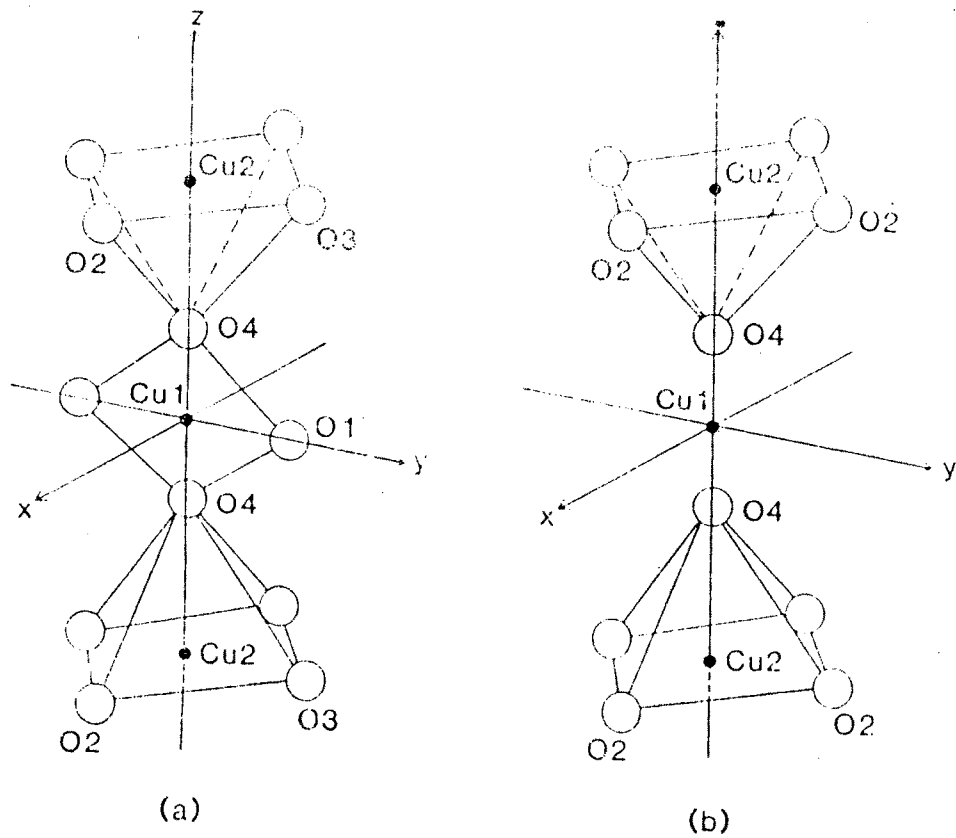


FIG. 4.3 - Local environments for the Cu₁ and Cu₂ atoms in (a) YBa₂Cu₃O₇ and (b) YBa₂Cu₃O₆ following the Y-Cu₂-Ba-Cu₁-Ba-Cu₂-Y ordering along Z.

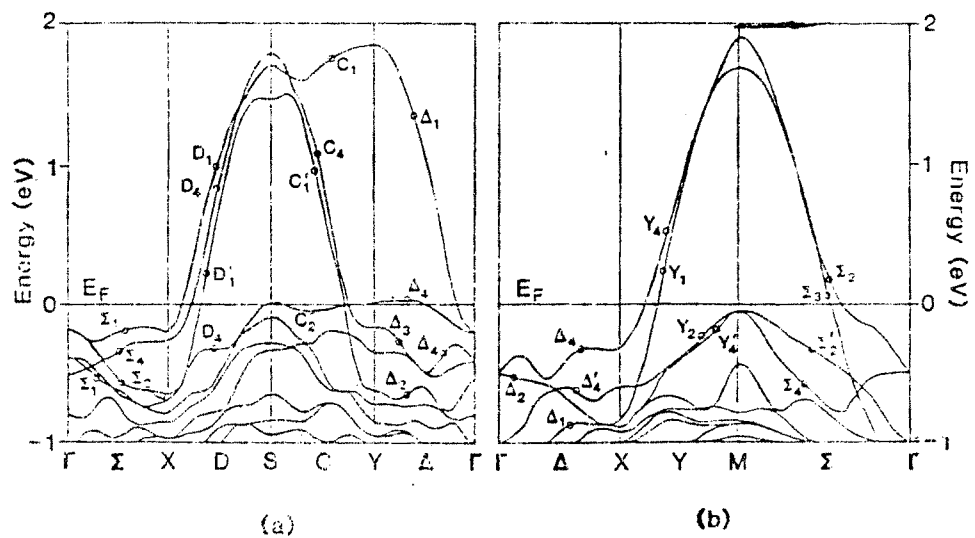


FIG. 4.4 - Energy bands of (a) YBa₂Cu₃O₇ and (b) YBa₂Cu₃O₆ near E_F.

The changes mentioned above are with respect to copper as central atom. The valence fluctuation of copper has already been mentioned as also the variation of crystal system from tetragonal to orthorhombic as function of δ -value.

The stacking of copper stereochemistries to give $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_6$ is given in fig. 4.3.

Energy band spectra of the corresponding compositions and structures have been extensively studied and the energy band spectra of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_6$ are given in figure 4.4. The prominent change of the 3d electronic structure from $\text{YBa}_2\text{Cu}_3\text{O}_7$ to $\text{YBa}_2\text{Cu}_3\text{O}_6$ clearly indicates its relation to lowering or absence of superconductivity. The energy band spectra are of only orthorhombic phases of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ where $\delta > 0.5$.

4.8 X-RAY DIFFRACTION STUDIES

X-rays, with wavelengths of the order of a few \AA , match with atomic and ionic sizes in molecular and crystal systems and therefore, the crystal lattices with constant interatomic distances function as diffraction centres and the diffracted patterns give a very powerful method for getting the direct information about crystal lattice and interatomic distances in molecular systems. It is possible to examine every starting material or all possible intermediates, as well as every stage of reaction yielding final

product in ceramic synthetic methods. The non-superconducting 1,2,3 or analogous systems with $AB_2Cu_3O_{6.5}$ is tetragonal and on absorption of oxygen gives rise to orthorhombic perovskite structure. This is a very crucial and critical stage. The thermodynamic consideration reveal that for the synthesis of ceramic materials highest possible temperature for sintering (without melting) must be used but at higher temperature the product will be unstable. Hence optimization of preparatory processes using prolonged sintering $950^{\circ}C$ followed by oxygenation at $\sim 650^{\circ}C$ has to be followed. The conformation of the desired phase, formation of desired crystal structure or absence of undesirable phases can only be monitored by using XRD. The XRD data from JCPDC file for copper oxide, barium oxide, strontium oxide, yttrium oxide and lanthanum oxide, binary cuprates and ternary cuprate phases are compiled for the comprehensive ready reference (Appendix 2). The XRD profiles of all the preparations of ceramic materials using hydrolytic oxalate formation precursor method and the acetylacetonate precursor route are also studied. The method of calculation of structural parameters is given as Appendix-1.

The thermal instability of 1,2,3 compound indicates that a large number of binary and ternary compounds are simultaneously formed and it is often seen that they are segregated in certain edges. Depending on the oxygen content, whole or part may be orthorhombic or tetragonal

and X-ray profiles taken at various stages of synthesis indicate the degree of success in getting desired product. It has been reported that alkaline earth carbonates especially barium carbonate decomposes only above 1360°C in air³¹. Retention of barium carbonate is indicated by the presence of X-ray lines³² at 24, 34, 42, 45 degrees of $2-\theta$ values.

The XRD data of most of the observable phases are scattered in the literature and is conflicting also. The XRD data for several observed compositions have been collected from literature and given in this Chapter. The samples were prepared from oxalate route. The presence of carbonate was verified by an IR line corresponding to the carbonate ion at 1425 cm^{-1} , 825 cm^{-1} .³³ Quite poor orthorhombic samples were obtained in the present study. XRD of one preparation showing presence of unreacted copper oxide and many other spurious lines and partial formation of 1,2,3 phase is also shown. It has been observed as shown by XRD patterns of samples prepared through acetylacetonate route that the resultant material is in almost all cases in the desired phase and hence acetylacetonate route is preferred.

The X-ray diffractograms reported in this work were taken on Rigaku Geigerflex III-D computerized X-ray diffractometer using copper tube. Two diffractograms, each of candidate materials prepared through oxalate precursor route

Table 4.3 XRD data for $\text{LaBaSrCu}_3\text{O}_{5.9}$ (Oxalate route)

No.	2θ	Intensity	d values	width	I/I_0
1	22.694	417	3.915	0.229	13
2	22.934	370	3.824	0.229	12
3	29.366	187	3.039	0.306	6
4	30.818	534	2.899	0.387	17
5	32.39	3129	2.761	0.351	100
6	32.714	2889	2.735	0.306	92
7	33.788	280	2.65	0.378	9
8	35.42	2030	2.532	0.423	65
9	37.706	219	2.383	0.315	7
10	38.624	2458	2.329	0.396	79
11	39.968	333	2.253	0.328	11
12	40.394	192	2.231	0.333	6
13	41.33	326	2.182	0.396	10
14	45.206	82	2.004	0.261	3
15	46.496	567	1.951	0.423	18
16	46.97	478	1.932	0.351	15
17	47.768	96	1.902	0.297	3
18	48.632	729	1.87	0.432	23
19	50.168	85	1.816	0.261	3
20	52.406	114	1.744	0.297	4
21	52.976	141	1.722	0.27	5
22	53.366	278	1.715	0.342	9
23	55.802	96	1.646	0.306	3
24	56.528	203	1.626	0.288	6
25	57.89	695	1.591	0.405	22
26	58.508	628	1.576	0.441	20
27	59.204	156	1.559	0.369	5
28	61.472	395	1.502	0.351	13
29	64.298	87	1.447	0.234	3
30	65.708	226	1.419	0.342	7
31	66.176	326	1.41	0.288	10
32	67.988	529	1.377	0.441	12
33	68.726	213	1.364	0.324	7
34	69.47	89	1.351	0.297	3

Table 4.4 XRD data for Orthorhombic $\text{LaBa}_2\text{Cu}_3\text{O}_{6.9}$ (Oxalate route)

No.	2θ	Intensity	d values	Width	I/I ₀
1	22.622	722	3.927	0.36	14
2	30.752	153	2.905	0.477	3
3	32.258	5256	2.772	0.396	100
4	32.576	2621	2.746	0.315	51
5	35.426	972	2.531	0.459	18
6	37.34	164	2.406	0.387	3
7	38.654	961	2.327	0.432	18
8	39.806	588	2.262	0.387	11
9	40.22	319	2.24	0.351	6
10	46.304	1151	1.959	0.459	22
11	46.79	643	1.939	0.369	12
12	48.668	225	1.869	0.351	4
13	52.19	226	1.751	0.558	4
14	52.796	165	1.732	0.306	3
15	57.626	1269	1.598	0.549	24
16	58.232	622	1.583	0.459	13
17	61.46	250	1.507	0.387	5
18	65.714	139	1.419	0.225	3
19	66.164	138	1.411	0.27	3
20	67.628	454	1.383	0.648	9
21	68.348	250	1.371	-	5

Table 4.5 XRD data for $\text{LaBaSrCu}_3\text{O}_{6.89}$ (acetylacetonate route)

No.	2θ	Intensity	d values	Width	I/I_0
1	22.784	138	3.899	0.333	10
2	23.318	87	3.811	0.279	7
3	24.524	100	3.626	0.297	8
4	26.432	83	8.369	xxx	6
5	31.058	370	3.877	xxx	28
6	31.97	270	2.797	0.405	36
7	32.456	1314	2.756	0.459	100
8	33.14	141	2.701	0.252	11
9	33.542	136	2.669	0.306	10
10	38.468	95	2.338	0.459	7
11	38.816	100	2.318	0.788	8
12	40.082	156	2.247	0.513	12
13	40.73	57	2.213	0.252	4
14	41.456	107	2.126	0.459	8
15	42.482	136	2.126	0.45	10
16	43.508	77	2.078	0.441	6
17	46.628	375	1.946	0.432	28
18	47.546	45	1.91	xxx	3
19	48.23	92	1.885	xxx	7
20	49.67	44	1.834	xxx	3
21	50.21	73	1.815	xxx	6
22	52.472	70	1.742	0.234	5
23	54.122	73	1.693	xxx	6
24	54.674	72	1.622	0.243	5
25	56.258	70	1.633	0.234	5
26	57.974	606	1.589	0.603	46
27	61.934	447	1.497	xxx	4
28	62.642	57	1.481	0.261	4
29	64.994	91	1.433	0.433	7
30	66.944	61	1.396	0.243	5
31	58.228	151	1.373	0.522	11

Table 4.6 XRD data for $\text{LaBa}_2\text{Cu}_3\text{O}_{6.9}$ (Acetylacetonate route)

No.	2θ	Intensity	d values	Width	I/I ₀
1	22.748	66	3.905	0.297	7
2	23.39	98	3.8	0.261	11
3	24.464	105	3.635	0.297	11
4	26.456	75	3.366	0.387	8
5	26.756	66	3.329	xxx	7
6	27.89	47	3.196	xxx	5
7	31.112	405	2.872	0.387	44
8	31.952	558	2.798	0.405	61
9	32.534	915	2.749	0.711	100
10	33.158	108	2.699	0.216	12
11	33.524	178	2.67	0.324	19
12	34.196	46	2.62	xxx	5
13	35.468	100	2.528	0.279	11
14	38.804	162	2.318	0.387	18
15	40.076	114	2.248	0.369	12
16	40.808	55	2.209	xxx	6
17	41.558	2.171	0.387	13	
18	42.512	164	2.124	0.36	18
19	43.52	111	2.077	0.306	12
20	44.342	51	2.041	xxx	6
21	46.706	256	1.943	0.342	28
22	47.012	262	1.931	0.36	29
23	48.236	108	1.885	0.351	12
24	50.354	47	1.81	xxx	5
25	52.592	59	1.738	0.234	6
26	54.152	67	1.692	xxx	7
27	54.692	73	1.626	0.351	8
28	56.24	75	1.634	xxx	8
29	58.058	456	1.587	0.729	50
30	58.658	122	1.572	0.261	13

...2



Table 4.6 contd.

No.	2θ	Intensity	d values	Width	I/I_0
31	62.552	59	1.483	0.22	6
32	64.916	90	1.435	0.229	10
33	66.986	67	1.395	0.27	7
34	68.246	126	1.373	0.441	14
35	68.582	101	1.367	0.252	11

Table 4.7 XRD data of orthorhombic matching d values for $\text{LaBaSrCu}_3\text{O}_{6.9}$ (Oxalate route)

$a = 3.878$ $b = 3.918$ $c = 11.754$

h	k	l	Calculated d values	Observed d values
0	1	0	3.901	3.915
1	0	0	3.824	3.824
0	0	4	2.965	2.922
0	1	3	2.759	2.761
1	1	0	2.731	2.735
1	1	1	2.65	2.65
0	0	5	2.34	2.32
1	1	3	2.253	2.53
1	1	4	1.996	2.004
0	0	6	1.951	1.951
2	0	0	1.912	1.902
0	1	6	1.745	1.744
1	2	1	1.719	1.722
2	0	3	1.716	1.715
1	1	6	1.587	1.591
2	1	3	1.571	1.576
0	1	8	1.370	1.364
0	2	6	1.379	1.377

Table 4.8 XRD data of matching d values for orthorhombic
 $\text{LaBa}_2\text{Cu}_3\text{O}_{6.9}$ (oxalate route)

a = 3.824 b = 3.902 c = 11.706

h	k	l	Calculated d values	observed d values
0	1	0	3.918	3.922
0	1	3	2.770	2.772
1	0	3	2.561	2.746
1	1	3	2.254	2.262
0	2	0	1.959	1.959
2	0	0	1.939	1.939
0	2	3	1.792	1.751
1	2	1	1.729	1.732
1	1	6	1.59	1.598
2	1	3	1.588	1.583

Table 4.9 XRD data of matching d values for $\text{LaBaSrCu}_3\text{O}_{6.89}$
 (Acetylacetonate route)

a = 3.811 b = 3892 c = 11.687

h	k	l	Calculated d values	Observed d values
0	0	3	3.899	3.859
1	0	0	3.811	3.811
0	0	4	2.921	2.877
0	1	3	2.753	2.756
0	0	5	2.337	2.338
0	2	0	1.946	1.946
2	0	0	1.905	1.91
0	1	6	1.741	1.742
2	0	3	1.71	1.69
1	1	6	1.584	1.589
0	1	3	1.367	1.373

Table 4.10 XRD data of matching d values for orthorhombic
 $\text{LaBa}_2\text{Cu}_3\text{O}_{6.9}$ (Acetylacetonate route)

a = 3.8

b = 3.862

c = 11.715

h	k	l	Calculated d values	Observed d values
0	0	3	3.905	3.905
1	0	0	3.8	3.8
1	0	2	3.187	3.196
0	1	3	2.745	2.749
1	1	0	2.708	2.699
1	1	1	2.639	2.62
0	1	4	2.335	2.318
0	0	6	1.952	1.943
0	2	0	1.931	1.931
0	2	3	1.730	1.38
1	1	6	1.583	1.587
1	2	3	1.575	1.572
0	1	8	1.389	1.373

FIG. 4.5 - XRD OF $\text{LaBa}_2\text{Cu}_3\text{O}_{6.9}$ OXALATE ROUTE .

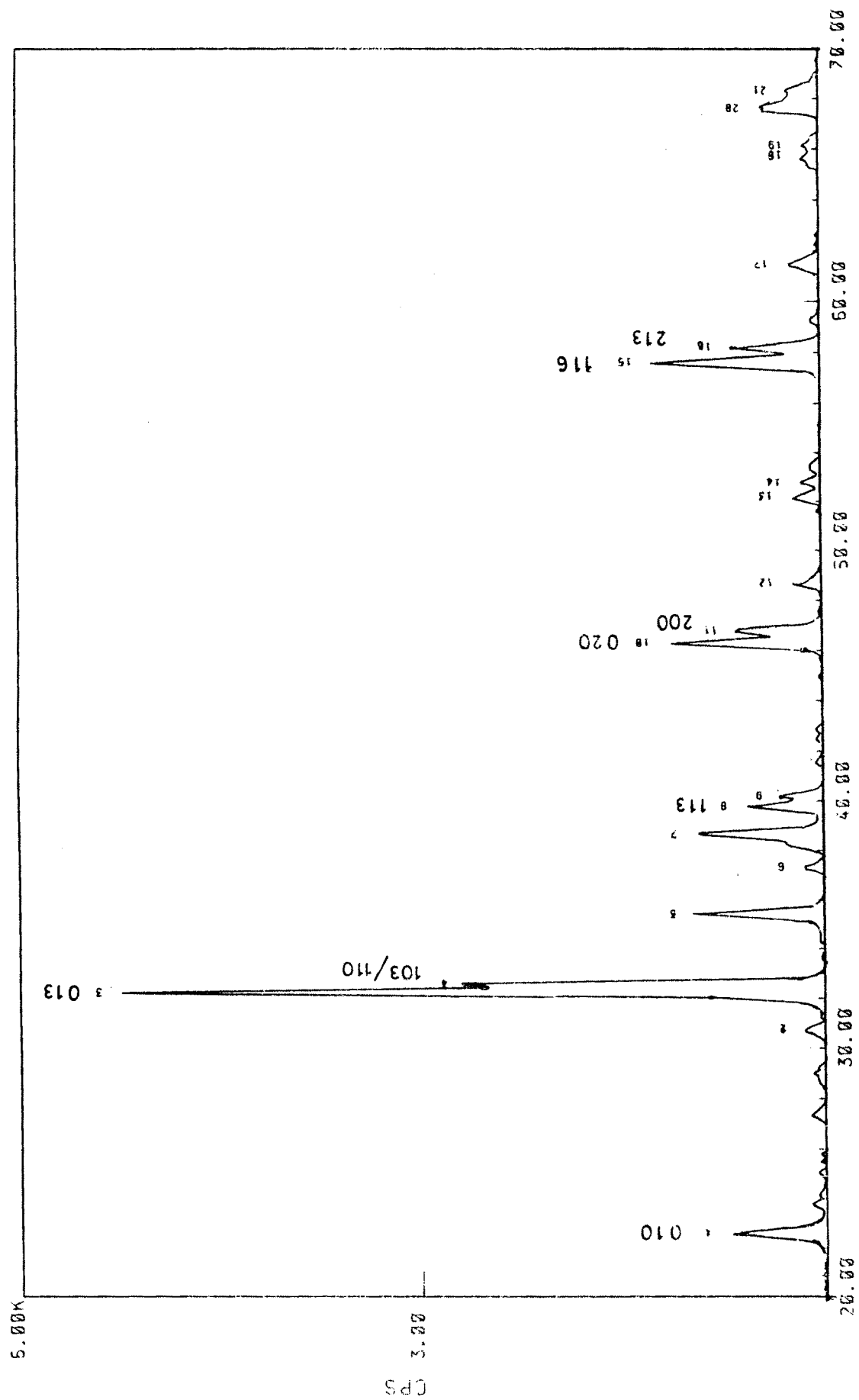


FIG. 4-6 — XRD OF $\text{LaBaSrCu}_3\text{O}_{6.9}$ OXALATE ROUTE .

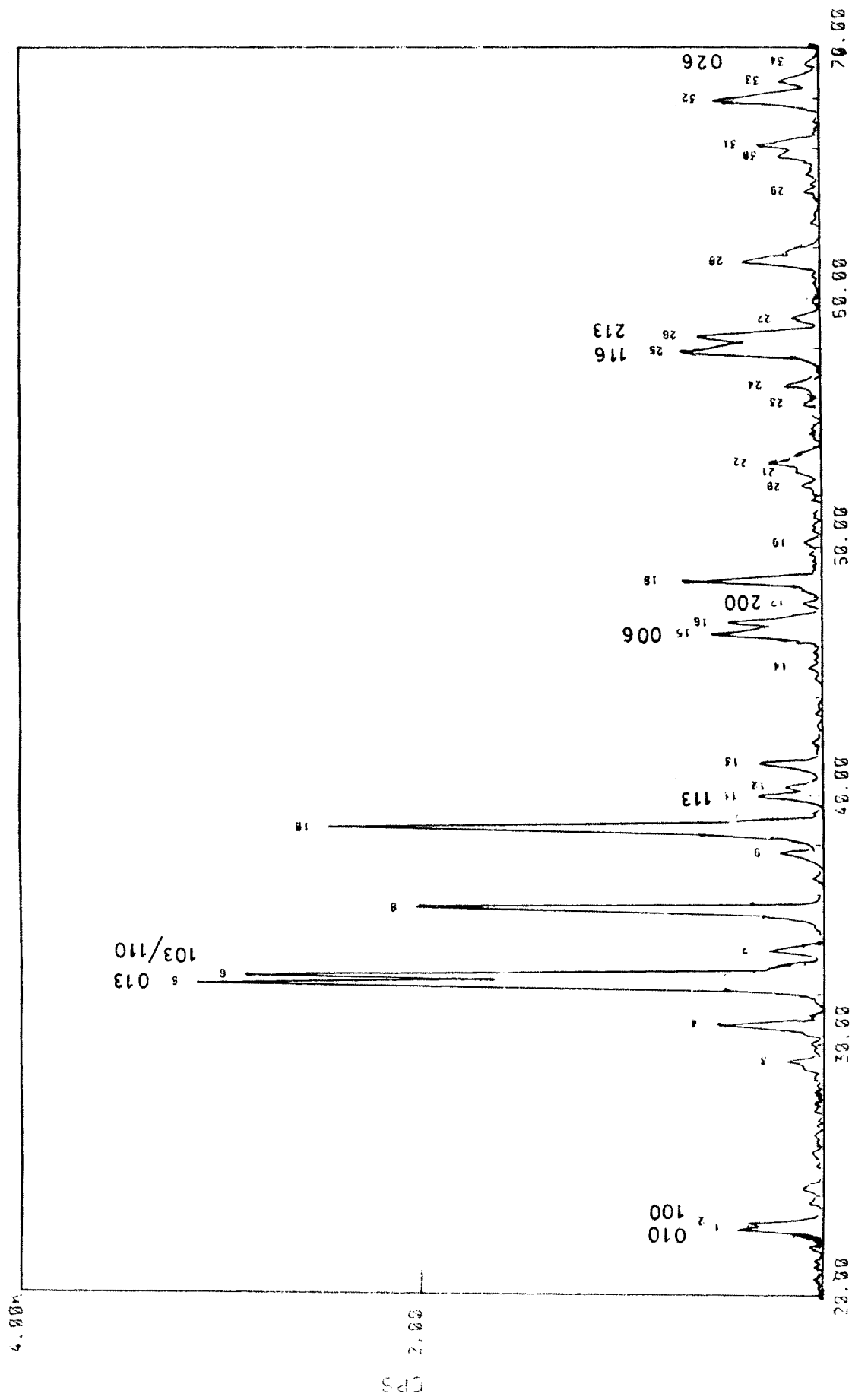
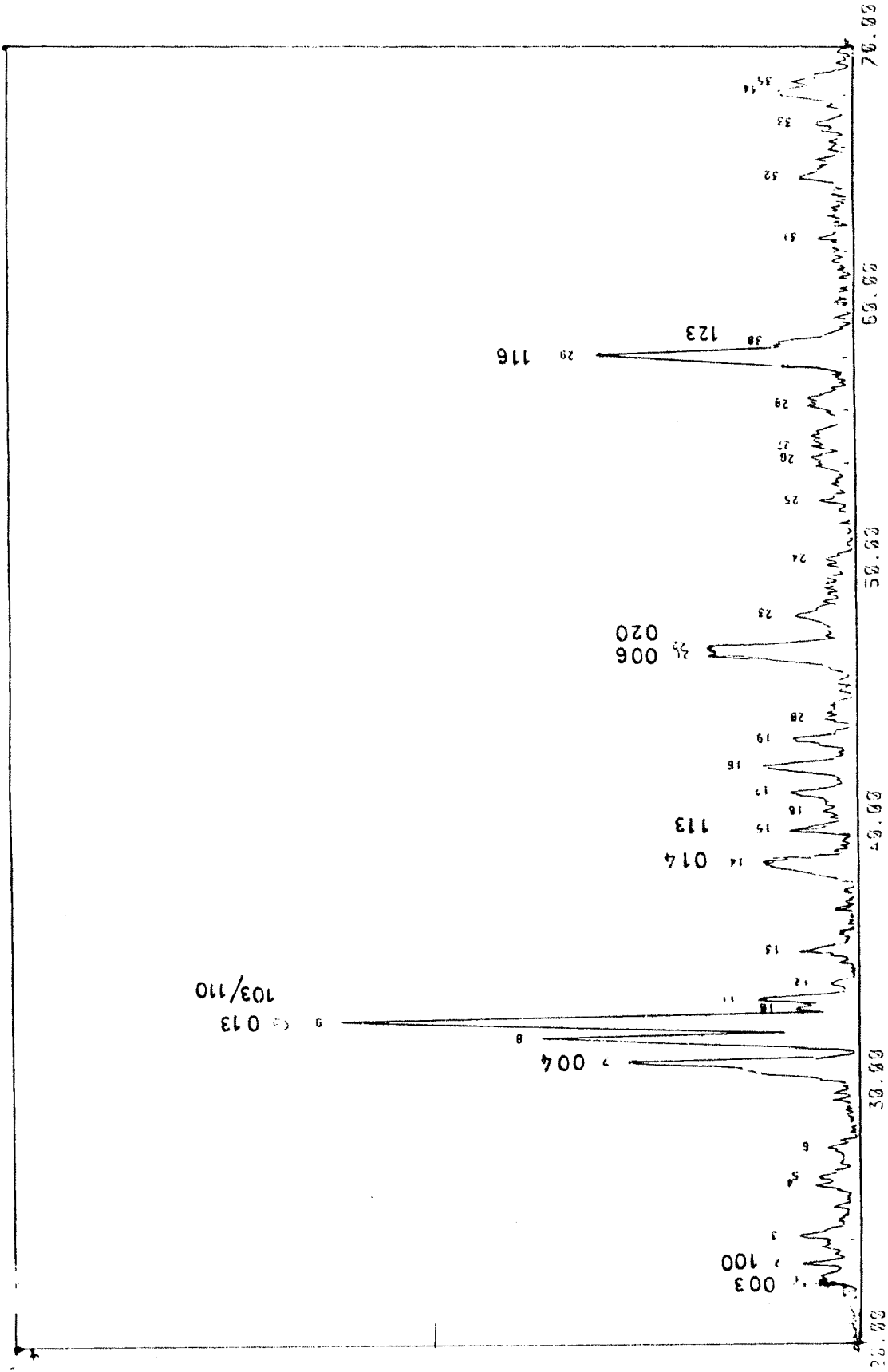


FIG. 4.7 - XRD OF $\text{LaBa}_2\text{Cu}_3\text{O}_{6.9}$ ACETYLACETONATE ROUTE .



and acetylacetonate precursor route are given in Fig. 4.5 to 4.8.

From the diffraction pattern lines were attributed to the orthorhombic-tetragonal structures. It is seen that the data fits in conformity orthorhombic structure. The materials are orthorhombic and a, b, c values in each case is given at the beginning of each table 4.3 to 4.10 along with all other recorded and calculated values. The lines are attributed various planes as shown on the diffractograms. Spurious lines indicate presence of certain percentage of allied phases or crystalline forms, such as tetragonal, 2,3 compounds intermediates like $\text{La}_2\text{Cu}_2\text{O}_5/\text{BaCuO}_2$ or CuO . The line shapes are analyzed by many workers and the relative profile of a couple adjacent lines has been proposed as an index of a structural feature. Beyer et al.³⁴ indicated that if δ is less than 0.5 generally orthorhombic structure is present and 006/020 line is stronger than 200 line. In tetragonal phase 200 line is stronger than 006 line.³⁴

Orthorhombic to tetragonal phase transition observed in $\text{YBa}_2\text{Cu}_3\text{O}_7$ at 650°C .^{36,37} While it exists $\sim 350^\circ\text{C}$ in case of $\text{LaBa}_2\text{Cu}_3\text{O}_7$.³⁸ CNR Rao³⁹ observed X-ray diffraction patterns of $\text{YBa}_2\text{Cu}_3\text{O}_7$ sample annealed in N_2 is more distorted than that annealed in O_2 . X-ray diffraction patterns of the $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7+\delta}$ clearly show a gradual change over from the orthorhombic to tetragonal structures with increase

in x. The absence of 1 0 3 and 0 0 6 reflection distinguishes tetragonal structure.⁴⁰

The X-ray diffractograms of several impurity phases are collected from literature and given in Appendix-2. The presence barium carbonate-strontium carbonate impurity is shown by a pair of lines occurring at 2θ value of 24 and 24.5°. In acetylacetonate route carbonate formation is not observed. Carbonate line do not appear in samples prepared by using oxalate route because sufficiently long heat treatment has been given to these samples to eliminate barium carbonate-strontium carbonate.

4.9 INFRARED SPECTRA OF INTERMEDIATES AND END PRODUCTS

Infrared spectra of starting material are already discussed. The infrared absorption spectra of intermediate phases $\text{La}_2\text{Cu}_2\text{O}_5$, $\text{Y}_2\text{Cu}_2\text{O}_5$ and BaCuO_2 are given in Fig. 4.9 and Table 4.12. Two samples which are fully oxygenated, i.e. sample No.1 and 8 are chosen for infrared study and are recorded in fig. 4.10 and table 4.12.

These were recorded in KBr pellet on Perkin Elmer model 783 infrared spectrophotometer within the range 300-800 cm^{-1} . Infrared absorptions due to Cu-O, Sr-O and Ba-O vibrations can only be detected, whereas La-O and Y-O vibrations lie in still low wave number range. The Cu-O vibrations are generally observed at 360 and 580 cm^{-1} . These bands show increased intensity of absorption with increasing

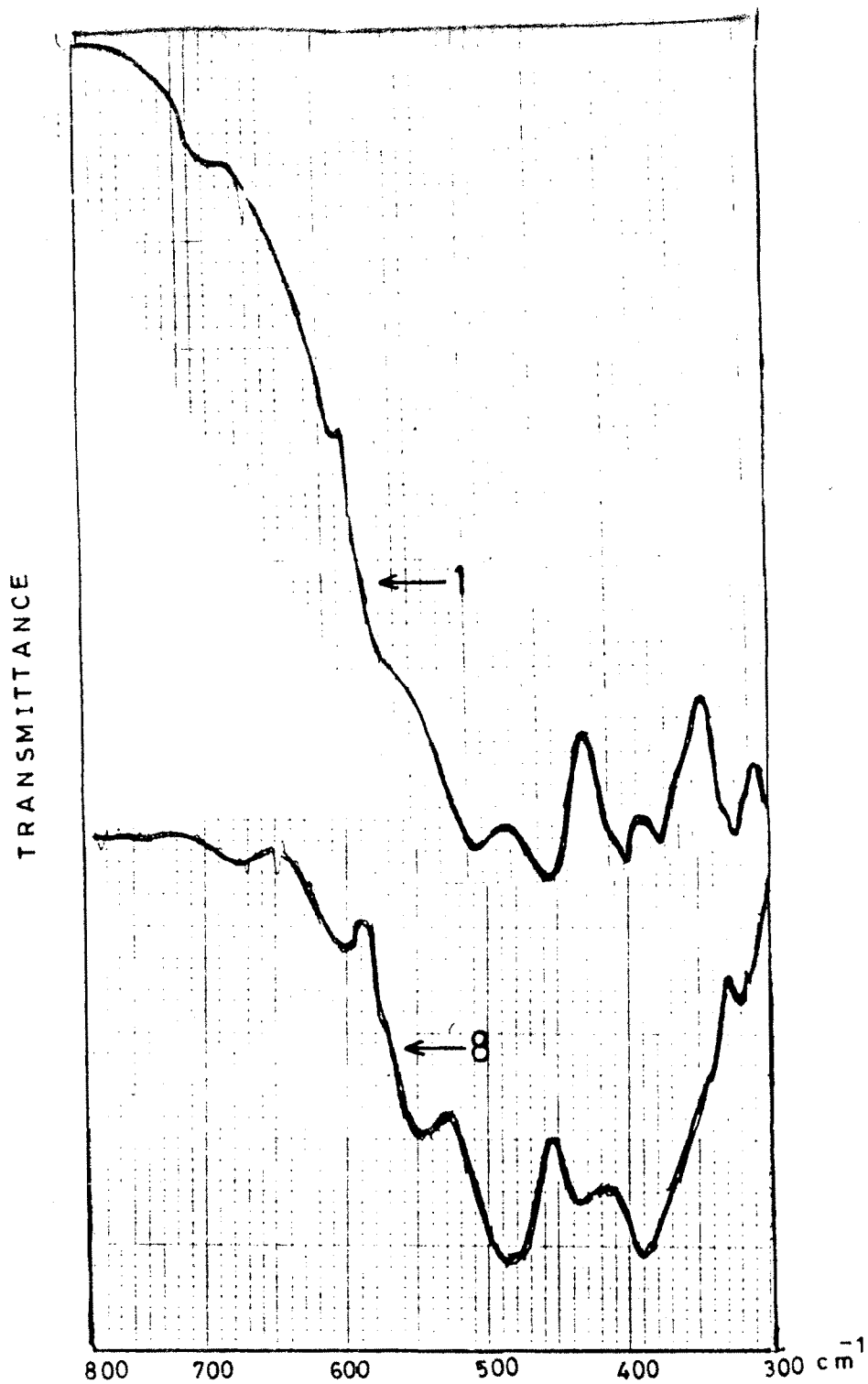
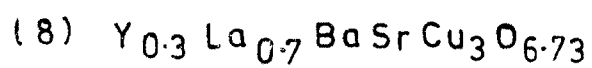


FIG. 4.9 — INFRARED ABSORPTION

SPECTRA OF —



TRANSMITTANCE

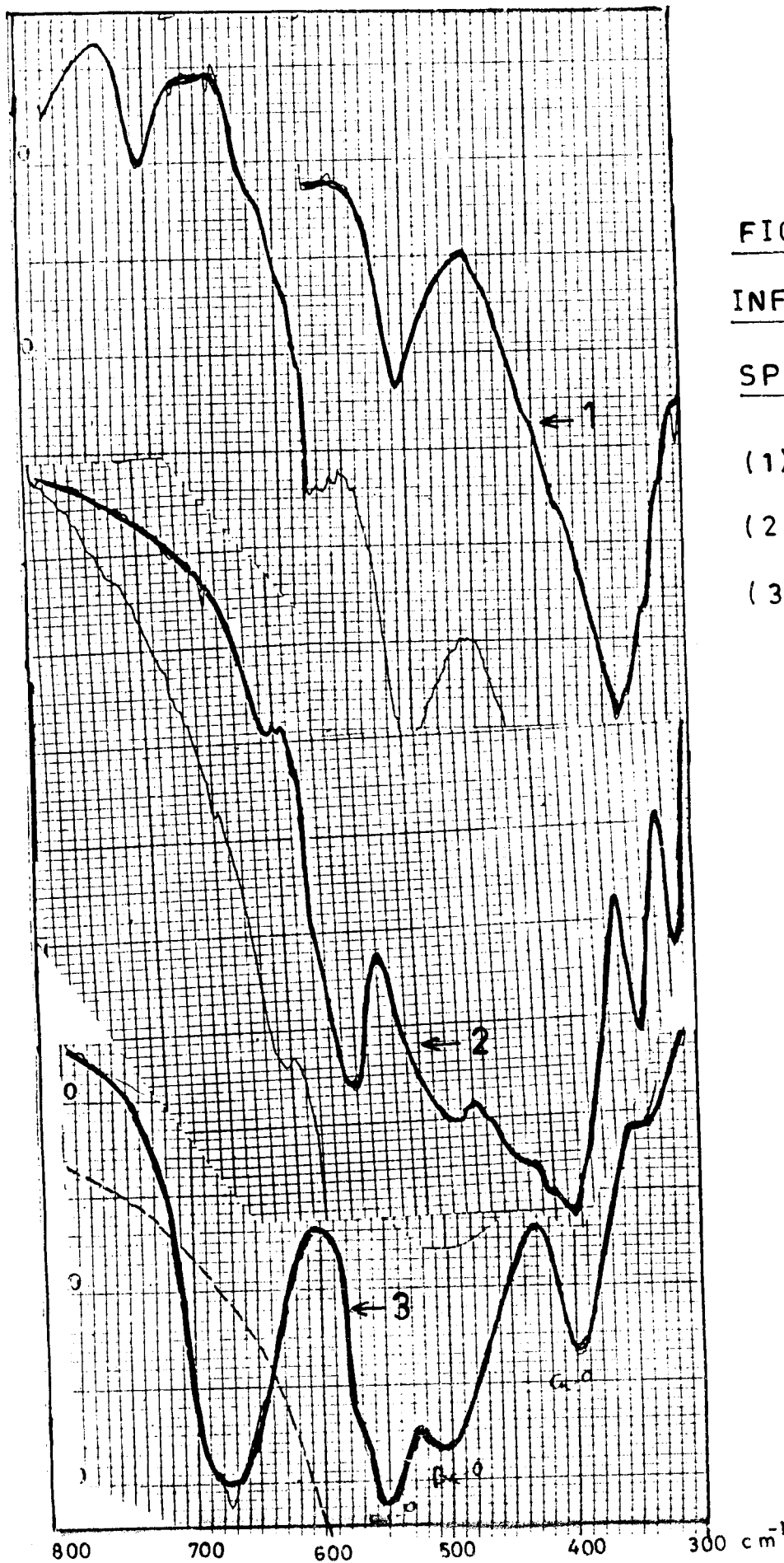


FIG. 4.10 —

INFRARED ABSORPTION

SPECTRA OF

(1) $\text{La}_2\text{Cu}_2\text{O}_5$

(2) $\text{Y}_2\text{Cu}_2\text{O}_5$

(3) BaCuO_2

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carrier concentration with δ . Due to additional oxygen atom O(1) which is at an infrared active lattice site show for some modes definite frequency shifts and the oscillator strength value also increased. It is found that the bands are shifted towards the low frequency side which may be attributed to the shielding by free carriers and the increase of the oscillator strength for Cu(1) - O(1) stretching mode which starts at $O_{6.1}$ at 515 cm^{-1} in the fully reduced system and ends at $O_{6.9}$ at 585 cm^{-1} in the fully oxidized form⁴¹⁻⁴³.

The infrared spectra also show characteristic features for orthorhombic and tetragonal phases as reported by Hariharan et al.⁴⁴ The orthorhombic phase is characterised by a strong band at $\sim 575 \text{ cm}^{-1}$. Whereas the tetragonal phase show bands at ~ 590 and 640 cm^{-1} . The 575 cm^{-1} band in orthorhombic phase arises from Cu(1), O(1) antisymmetric stretching vibrations,⁴⁵ and the band $\sim 590 \text{ cm}^{-1}$ in tetragonal phase indicates defect vibrations in the vicinity of O4 site.⁴⁶

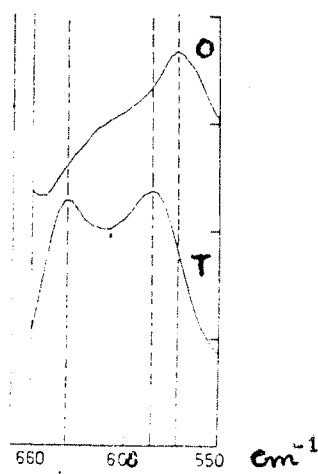


Fig. 4.11 Infrared absorption spectra of O and T phases after a background correction.

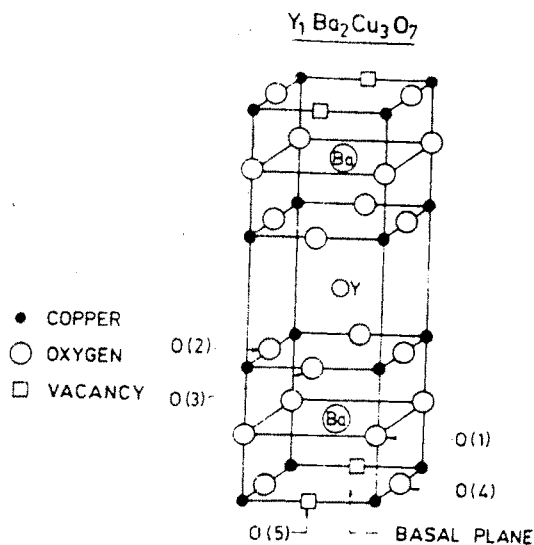


Fig. 4.12 Lattice of 1,2,3 compound

The reported vibrational infrared absorption bands for $YBa_2Cu_3O_{6.5+\delta}$ reported in earlier literature are tabulated below.

Table 4.11 IR vibrational modes for $YBa_2Cu_3O_{6.5+\delta}$ and from earlier literature and calculated frequencies.⁴⁷

Mode frequency	Calculated assignment and normal coordinate
115	109 B_{1u} vs rest axial
155 \pm 5	161 B_{1u} vs Ba axial
195 \pm 5	199 B_{1u} vs rest axial
275 \pm 5	238 B_{2u} vs Cu(2) in plane x,y
320 \pm 7	361 B_{3u} vs rest in plane x
570 \pm 8	555 B_{1u} vs O(1) axial
610 \pm 10	575 B_{2u} vs rest in plane y

Table 4.11b. Frequencies of IR vibrational modes for La_2CuO_4 in cm^{-1} 48

TO	LO	Assignment and normal coordinate	
163	183	La Vs CuO(1) O(2)	in plane
220	250	CuO Vs LaO (2)	in plane
363	390	CuLa Vs O(1) (2)	in plane
671	683	Cu Vs O(1)	in plane
	550	Plasmon frequency	
240 (320)	463	CuLa Vs O(1) O(2)	axial
501	574	Cu Vs O(1) asym	axial

4.10 CRITICAL TEMPERATURE, T_c

The preliminary check of samples was carried out by finding out the resistance of the thin pellet. Those samples which showed resistance of the order of 1 K ohm were selected and those with resistance was rejected in preliminary sorting T_c for the samples prepared in the present study are expected to be between 89 and 91 K. The sequence of testing was as follows :

Those samples which showed greenish colour or a redish colour were found to contain green or red microcrystals and were rejected. Those samples which were dark black in colour were analyzed for the chemical composition of the bulk by chemical methods and δ values were confirmed by thermal

Table 4.12 - Infrared absorption spectral data.

$\text{La}_2\text{Cu}_2\text{O}_5$	Predominant mode
320	-
335	-
360	-
400	-
420	La_2O_3
525	CuO
600	CuO
635	La_2O_3
725	-
$\text{Y}_2\text{Cu}_2\text{O}_5$	Predominant mode
315	Y_2O_3
345	Y_2O_3
400	CuO
425	Y_2O_3
445	-
495	-
470	-
620	CuO

BaCu_2O_2	Predominant mode
340	-
400	CuO
500	-
550	-
580	-
480	BaO

$\text{Y}_{1.0}\text{Ba}_2\text{Cu}_3\text{O}_{6.40}$	Predominant mode
320	BaO
330	Y_2O_3
370	-
400	CuO
455	-
570	CuO
570	Y_2O_3
590	-
680	-

$\text{Y}_{0.3}\text{La}_{0.7}\text{BaSrCu}_3\text{O}_{6.73}$	Predominant mode
320	BaO
345	Y_2O_3
385	-
440	-
485	-
550	-
600	CuO
675	-

analysis and photometric method. These samples which showed δ values ~ 0.25 i.e. samples with $O \sim 6.75$ to $O \sim 6.95$ were probably the best preparation and their XRD analysis was carried out by using SmCo_5 magnet and liquid nitrogen. Levitation test was carried out on very thin pellets of the material. Finally only the successful levitated material with clear XRD indication of the desirable phase were tested for T_c by foreprobe resistivity method using PREMA make nanovoltmeter.

In all the cases T_c values were ~ 80 K as per expectation for these compositions. Due to more intimate mixing at molecular level formation single phase material is more likely and hence studies of critical current will be more interesting. It has been found that the room temperature resistivity can be used as an indicator parameter and the phase diagram is given earlier (Fig. 4.1).

4.11 CONCLUSION

The aim of the present project was to critically examine the role of preparatory techniques in final form and purity of the end products with a comparative outlook as shown by ceramic solid state preparation and the chemical precursor rout. Details of chemical precursor routes are discussed in the second and third chapters and the material is subjected to preliminary testing for superconductivity

as presented in this chapter. The reporting here is confined to only structural characterization of the products and qualitative physical testing of superconductivity. The scope of the present project was confined to only this much selected area and further detailed investigations of magnetic and other properties will be published elsewhere as the next part of the project. The studies have indicated that by using chemical precursor route followed by less elaborate sintering procedure, pure homogeneous ceramic materials are obtained as indicated by very low value of room temperature resistivity of the finished pellets. Acetylacetonate precursor route is therefore recommended as a reliable method for preparation of 1,2,3 or 1,1,1,3 or any intermediate composition based on the use of rare earth oxide, alkaline earth oxide and copper oxide ceramic HTSC materials.

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