C H A P T E R - V

SUMMARY

CHAPTER - V

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5.1 INTRODUCTION

At the beginning of the 20th century liquefaction of helium and discovery of superconductivity associated with mercury and lead opened a new field of study of physics and chemistry at low temperatures. Later superconductivity was detected in binary compounds and alloys raising Tc from 4 to 27 K. In 1986 the real breakthrough came when superconductivity was detected in cuprate ceramics. Over a period of four years, thousands of compositions have been screened and attempts are made to attribute or correlate superconductivity to certain structural parameters. Much headway has been crossed in preparatory solid state techniques in connection with many novel materials like spinels, ferrites, garnets, zeolites and ceramics. It has been now realized that attempts must be done to get desired physical state of intermediates through novel chemical routes. Precursor synthesis and its subsequent course of thermal decomposition and thermal formation needs extensive studies. We have introduced for the first time preparation of precursor oxalates through precipitation from homogeneous solution (PHFS) by using hydrolytic formation of oxalate ion from diethyl oxalate.

We have also studied the precursor route using metal acetylacetonates. A study of formation of precursors, formation of mixed oxides as intermediates, formation of cuprate ceramics from the intermediates and the necessary preliminary testing and structure of the ceramic materials which are candidate HTSC materials has been done.

5.2 FORMATION OF OXALATE PRECURSOR BY PHFS TECHNIQUE

Ceramic oxidic compositions are generally prepared from metal compounds such as oxides, hydroxides, carbonates, nitrates or carboxylates. Amongst the carboxylates, oxalate ion is suitable. Metal oxalates generally form carbonates on heating at medium temperatures ($\sim 300^{o}C$) and carbonates so formed decompose into oxides below $1000^{o}C$ Alkaline earth carbonates require heating over long periods and also temperatures 1200-$1400^{o}C$.

The formation of pure and fine grained precipitate is necessary for getting chemically pure materials. Occlusion or adsorption of impurities must be avoided. Oxalate ion is generally preferred over hydroxide ion for this purpose. However, oxalate precipitates of rare earth are gelatinous and hence some improved precipitation technique must be used. PFHS using diethyl oxalate has been studied at single element level and as ternary or quaternary mixtures of ions. The nature of precipitate and their thermal degradation is presented in second chapter. Although clean and granular precipitates of oxalates and mixed oxalates are obtained by this method, there remains a difficulty with respect to carbonate decomposition. The X-ray diffractograms and IR band at 1650 cm^{-1} are used to decide upon heating conditions and duration to eliminate carbonate ion. The 1,2,3 HTSC phase is metastable and sintering without fusion is desirable to get HTSC material. The issue of presence of carbonate ion is a major obstacle.

5.3 ACETYLACETONATE COMPLEXES AS PRECURSORS

Metal acetylacetonates prepared as given in chapter three are not valatile and yield oxides without involving an intermediate carbonate step. This method gives extremely fine grained oxidic materials. It is convenient for the formation of HTSC ceramics. We have carried out the characterization of individual and mixed metal acetylacetonate and studied their thermal degradation. Use of acetylacetonate complex precursor route is therefore, proper technique in HTSC synthesis.

5.4 FURTHER STUDIES OF OXIDIC MATERIALS

The oxidic material obtained from decomposition of oxalate and acetylacetonates are further processed to get candidate HTSC materials. The process of sintering, annealing and soaking in oxygen are carried out and the resulting materials are analyzed for metal and δ-oxygen content. X-ray diffractograms are analyzed for the presence of orthorhombic phase, IR absorption spectra and Tc are reported. The material has been prepared and preliminary characterization has been done. This covers the topic of the present dissertation. Further studies of physical properties are in progress and will be published separately.