Chapter V

SUMMARY AND CONCLUSIONS

CHAPTER - V

Summary and Conclusions

Co-precipitation has wide spread applications in chemical analysis and radiochemistry. Besides its applications in chemical analysis and in radiochemistry, co-precipitation is also "potentially important to many environmental issues closely related to water resources, including acid mine drainage, radionuclide migration in fouled waste repositories, metal contaminant transport at industrial and defense sites, metal concentrations in aquatic systems, and wastewater treatment technology". Co-precipitation method is also used for the preparation of layered double hydroxide. The search for new ternary metal oxides appropriate to gas sensing applications is of particular importance. Cadmium stannate (Cd_2SnO_4) is ternary metal oxide semiconductor, which has received a great attention as a gas sensing material. Considering the importance and scope of the subject in the present investigation, the studies are made on preparation and physico-chemical characterization of cadmium stannate. Samples were prepared from aqueous media by chemical co-precipitation technique. The present work is divided into five parts.

Chapter-I opens with general preface of the subject matter. Extensive literature survey on Cd_2SnO_4 prepared by physical and chemical methods is discussed. The purpose of the present research work is stated at the end of the chapter.

Chapter-II includes with introduction of different methods available for the preparation of samples in the bulk form. The theoretical background of various characterization techniques such as X-ray diffraction (XRD), Scanning electron microscopy (SEM), dielectrical measurements viz. electrical resistivity, is outlined in detail. Basics of the co-precipitation and mechanism of co-precipitation have been discussed. **Chapter-III** opens with the experimental details of co-precipitated samples

of Cd_2SnO_4 from aqueous medium and optimization of preparative parameters The cadmium stannate samples were prepared by a chemical co-precipitation method using AR grade equimolar (0.1M) stannic chloride pentahydrate (SnCl4.5H2O) and cadmium chloride (CdCl2) as precursors in 1:2 composition by volume in solution. The preparation conditions were carefully controlled. Double distilled and deionized water was used for solution preparation. Solution pH, considered using the relation between pH and concentrations of both the solutions was adjusted to neutral by adding aqueous ammonia to preserve the hydroxide phases of Cd and Sn. The homogeneous solution was prepared by thoroughly mixing both the solutions. White gelatinous precipitate formed, was filtered using Whatmann filter paper No.17. The precipitate was washed thoroughly until traces of Cl were removed. It was further dried at ambient temperature and sintered at different temperatures within 400-1200oC for 6 hr in air atmosphere. These compositions were further mixed with polyvinyl alcohol as a binder and pressed into pellets of 15mm diameter and 2–3mm thickness using a hydraulic press. Also the experimental details of various characterization techniques such as LCR meter, X-ray diffraction, Scanning electron microscope, Electrical resistivity, Dielectrical measurements etc. are explained. Various preparative parameters are argued in detail.

Chapter IV deals with results and discussion. Various characterizations have been discussed viz. X-ray diffraction (XRD), Scanning electron microscope (SEM), Electrical resistivity, Dielectrical measurements. Structural analysis of the Cd_2SnO_4 samples are carried out using XRD patterns, recorded by varying diffraction angle (2θ) from 10 to 100°. X-ray diffraction patterns of cadmium stannate samples sintered at different temperatures are shown in figure 4.1. The samples are polycrystalline and fit well with the rhombohedral and spinel cubic crystal structures with preferred characteristic temperatures. The intensity and number of diffraction peaks depend on

the amount of corresponding phases. The data was analyzed by making use of JCPDS card Nos. 34-0758 (rhombohedral CdSnO3), 80-1469 (spinel cubic Cd2SnO4) and 73-0973 (spinel cubic Cd1.33Sn1.33O4). At 400°C sample shows an amorphous as well as the nanocrystalline $CdSnO_3$ phase. At 600°C the XRD pattern shows rhombohedral crystal structure with only $CdSnO_3$ phase and all the peaks could be easily identified. Sample sintered at 800°C shows strong presence of $CdSnO_3$ phase. But the presence of (220), (222) and (511) peaks from Cd_2SnO_4 phase confirms that it is changing to Cd_2SnO_4 phase. At higher temperatures viz. 1000 and 1200°C the sample show mixed phases of $CdSnO_3$, Cd_2SnO_4 and $Cd_{1.33}Sn_{1.33}O_4$. The (222) and (511) planes of Cd_2SnO_4 spinel cubic structure are observed to be strongest in the sample sintered at 1000°C (d_{222}=2.6359□Å) and 1200°C (d_{511}=1.7672□Å) respectively. The shifting of strongest plane in the sample sintered at 1200°C sample with respect to that of the one sintered at 1000°C is due to change in single crystal d value. The other planes such as (311), (331), (400), (444), (622), (642), (731) and (800) are observed for Cd_2SnO_4 phase. Another new phase $Cd_{1.33}Sn_{1.33}O_4$ having (442), (620) and (733) planes is observed in spinel cubic crystal structure. As the sintering temperature increases up to 800°C the peak intensity of $CdSnO_3$ phase increases. In case of Cd_2SnO_4 phase it increases as the temperature is raised up to 1000°C because of enhancement in crystallinity. It then decreases due to the crystal reorientation effect.

The SEM study reveals the compact morphology with large number of trapezoidal single crystals. This may be the unique feature of this material and those large numbers of small particles are formed when sintering of material occurs.

The two point resistivity measurement shows that the prepared Cd_2SnO_4 samples have resistivity in the order of 10^4-10^5 Ωcm. The variation of logρ with reciprocal of temperature shows that resistivity decreases with increase in temperature

and supports the semiconductor nature of Cd_2SnO_4. The activation energy is found to be 1.132 eV, which is very near to the value reported (1.18 eV) for single crystal. The result supports formation of perfect or nearly perfect stoichiometric compound (Cd_2SnO_4). The variation of dielectric constant with frequency at room temperature shows that dielectric constant (ε') decreases abruptly at lower frequencies and remains constant at higher frequencies showing dispersion of dielectric constant at lower frequencies. The dielectric constant varies with applied frequency due to charge transport relaxation time. The large value of dielectric constant at lower frequencies is explained on the basis of space charge polarization due to inhomogeneous dielectric structure and resistivity of the sample. These inhomogeneities in the present system are caused due to voids, dislocation and grain structure.

The variation of dielectric loss with frequency shows that at lower frequencies $\tan\delta$ is large and it decreases with increasing frequency. The $\tan\delta$ is the energy dissipation in the dielectric system, which is proportional to the imaginary part of dielectric constant. At higher frequencies the losses are reduced and the dipoles contribute to the polarization. The loss factor curve is attributed to domain wall resonance. At higher frequencies, losses are found to be low if domain wall motion is inhibited and magnetization is forced to change by rotation. The plots of $\log\sigma_{ac}$ versus $\log\omega$ are observed to be almost linear indicating that the conduction increases with increase in frequency. The linearity of the plots confirms small polaron mechanism of conduction. The slight decrease in conductivity is attributed to conduction by mixed polarons. In ionic solids the electrical conductivity is due to migration of ions and the ionic transport depends on angular frequency. Thus, the ac conductivity (σ_{ac}) is proportional to the angular frequency and it is confirmed here by linear plots of conductivity with angular frequency. Relatively higher value of dielectric constant, loss

tangent and ac conductivity in case of the sample sintered at 1000°C might be due to dominance of Cd_2SnO_4 phase in the formed composite.

It is concluded that cadmium stannate can be prepared using cost effective chemical co-precipitation technique. By tuning the calcining temperature the phase of Cd-Sn-O system can be tuned. Future prospect of the work would be use of cadmium samples in gas sensor application. The sensitivity of the gas sensor may be improved further by optimizing the preparative parameters of co-precipitation technique.