Chapter III

EXPERIMENTAL

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Experimental

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3.1 Introduction

The synthesis of inorganic nanostructres with well defined size and shape, composition, crystanallity, and structure such as nanospheres, nanorods and nanocubes, has been active research area because of the unique size and shape – dependent properties [1- 5] of these compounds which are different from those of the bulk. These materials are important in the fields of catalysis, photography, electronics, photonics, data storage, optoelectronics, biological labelling, imaging, and biosensing [6 –11]. Cadmium stannate is ternary metal oxide semiconductor. The oxide can be prepared as a ceramic material or as in amorphous [12], and polycrystalline form [13]. Cardile et al. [14], Wu et al. [15], Shen et al. [?] reported spinnel cubic crystals in CTO films. Various deposition methods such as RF sputtering [5-6], Spray pyrolysis, Electrolessdeposition, co-precipitataion.methods were employed to prepare Cd_2SnO_4.

Reference missing

$CdO - SnO_2$ complex oxides ($CdSnO_3$ and Cd_2SnO_4) have been systematically studied as transparent conductive materials [16-18]. These compounds are n- type wide band gap semiconductors. The possible presence of structural defects such as oxygen vacancies and cadmium interstitials is responsible for conductivity [16,19]. The preparation and characterisation of the $CdO - SnO_2$ system were reported in the various papers [20, 21].

$CdSnO_3$ powder can be used as a gas sensing material for detecting various gases [22 –23]. Zhang et.al. prepared $CdSnO_3$ by solid phase synthesis (SnO_2 and $CdCO_3$ used as reactants) [23] and co – precipitation synthesis method that $SnCl_4$ and $CdSO_4$ were used as inorganic precursor and NH_4OH as precipitant. The characterization of Cd_2SnO_4 samples using co-precipitation technique is in view interest. The present chapter reports on the technical details about the material synthesis, structural, optical and electrical characterization of the Cd_2SnO_4 samples by XRD, SEM, dark electrical resistivity and dielectric measurement techniques.

3.2 Experimental

3.2.1 Preparation of samples:

The cadmium stannate samples were prepared by a chemical co-precipitation method using AR grade equimolar (0.1M) stannic chloride pentahydrate ($SnCl_4.5H_2O$) and cadmium chloride ($CdCl_2$) 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 400-1200°C 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.

Presintering/ Calcination: The purpose of Presintering is to decompose the precursors into metal oxides, resulting into end product. This process also helps to homogenise the material & controls the shrinkage that occurs in the final sintering. During presintering the amount of reaction depends upon the reactivity of the components & on the presintering temperature.

Milling: In this step reactivity of the powder is improved. The smaller particles are achieved so that the secondary grain growth is avoided during final sintering. After milling powder is dried & used for preparing the final product of required shape.

Sintering: Sintering is most important heat treatment process by which a mass of compact powder is transferred into a dense form. For good quality materials in bulk form, the grain size should be uniform. The final process achieves inter granular pores, continuous grain growth & develops microstructure. The sintering temperature, sintering time & atmosphere plays an important role in the development of microstructure. The factors like particle size, particle shape, particle size distribution, inter particle porosity, homogeneity in chemical composition, pore size distribution, temperature gradients are affected by the sintering process. The flow chart representation of the material synthesis route has been depicted in the Fig. 3.1.

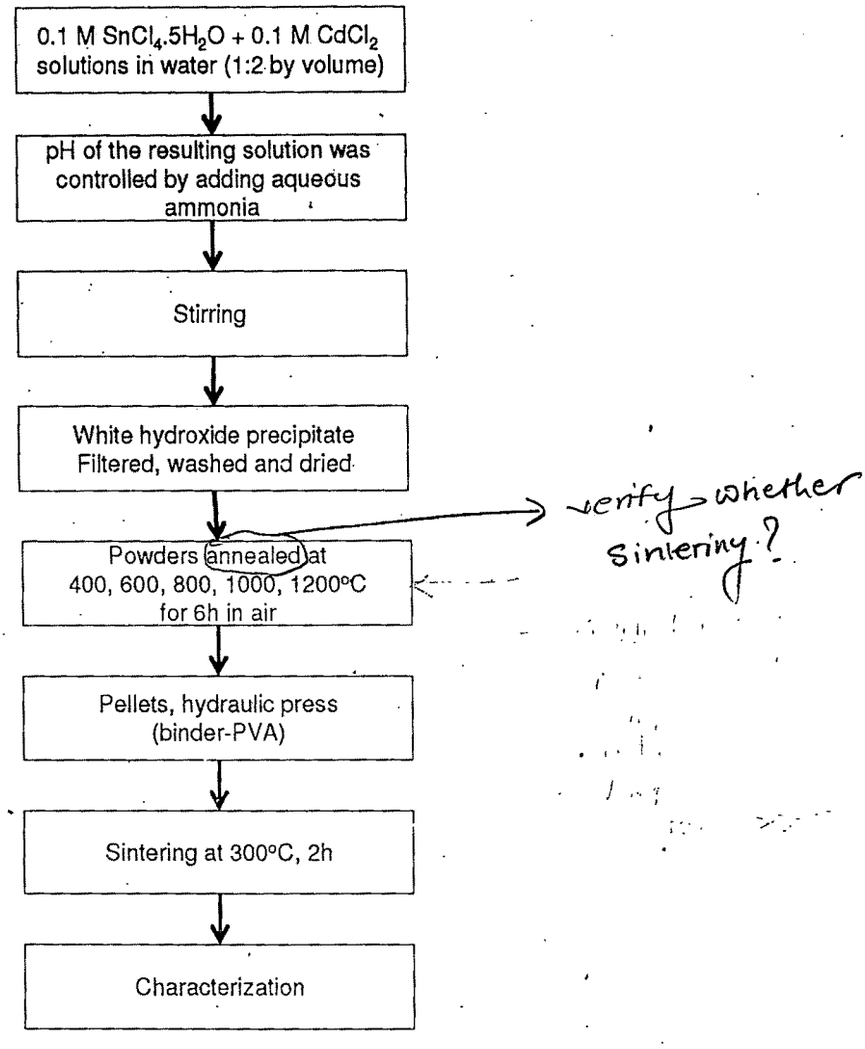

Fig. 3.1: Flow chart of material synthesis

3.2.2 X-ray diffraction

The samples were characterized by X-ray diffractometer (Philips, Model PW-3710) using Cu-K_α radiation (λ = 1.54056 A°) for crystal structure analysis. The X-ray machine was operated at generator tension of 40 kV and generator current of 30 mA. The XRD patterns of prepared cadmium stannate samples were recorded within the span of 10 - 100 ^{0} at the step size of 0.02° on computer controlled system (Fig. 3.2).

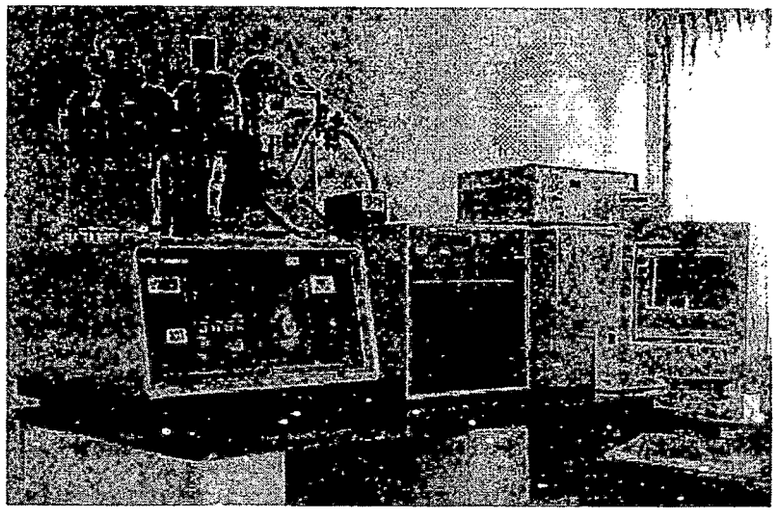

Fig. 3.2: Philips make X-ray diffractometer

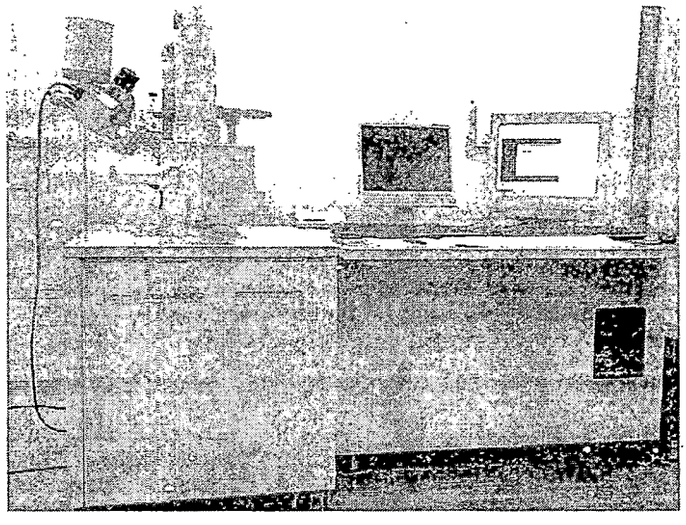

Fig. 3.3: JEOL, Japan make scanning electron microscope (SEM)

3.2.3 Scanning Electron Microscopy

Surface morphology was studied using JEOL, Japan, JSM-6360, scanning electron microscope (SEM) (Fig. 3.3). The samples were coated with gold(Au) of thickness 150 Å using Polaron SEM sputter coater E-2500. The SEM images were taken with computer controlled machine at accelerating voltage of 15kV, magnification of ×20,000 and spot size of ~ 50 μm.

3.2.4 Dielectric measurements

The AC parameters such as capacitance (C) and dissipation factor (tan δ) of the samples were measured in the frequency range 20Hz to 1MHz using LCR meter (HP 4284 A) (Fig. 3.4). HP4284A is based on the auto-balancing bridge method which offers high accuracy over wide impedance range and relatively wide frequency coverage (20 Hz to 1 MHz). It enables both online and offline graphical presentation of measured data. The dielectric constant (ε') was calculated using the relation

$$\varepsilon' = \frac{C_p t}{\varepsilon_0 A} \tag{3.1}$$

where C_p is the capacitance of the pellet, t the thickness of the pellet, A the area of cross section of the pellet and ε_0 is the permittivity of free space (8.854×10^{-12} Fm^{-1}).

The AC conductivity of the samples was estimated from the dielectric parameters. As long as the pure charge transport mechanism is the major contributor to the loss mechanism, the AC conductivity (σ_{AC}) may be calculated using the relation

$$\sigma_{AC} = \omega \varepsilon' \varepsilon_0 \tan\delta \tag{3.2}$$

where, ω the angular frequency and tanδ is the dissipation factor.

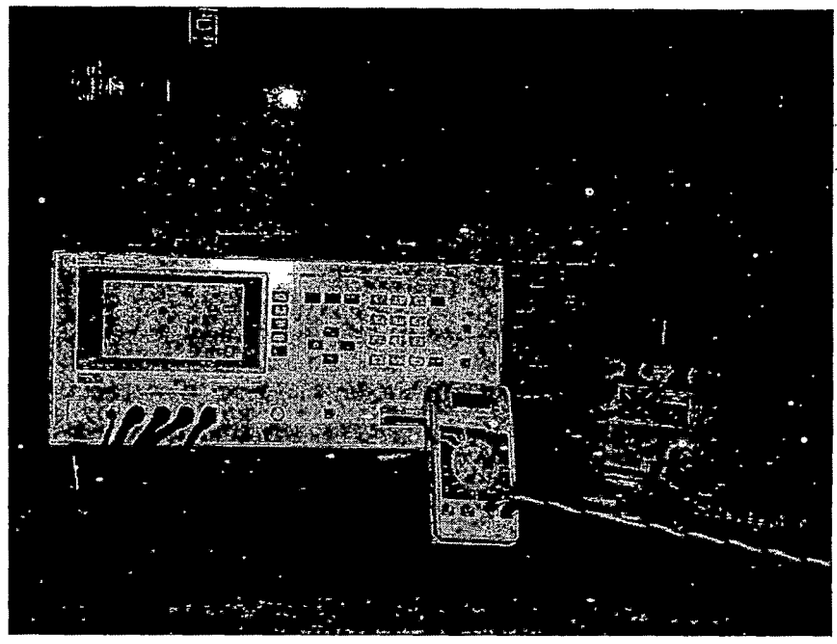

Fig. 3.4: LCR meter (HP 4284 A)

3.2.5 Electrical resistivity

One can use four – probe and two– probe method for resistivity measurement. Two–probe method using large plates for contact was used for making resistivity measurements. The nano sized powder of samples was pressed into pellets of the size 1cm diameter and thickness approximately 2–3mm by applying pressure of 75 Kbar for 10 min duration. The two opposite sides of the pellet were painted with silver paste for making good ohmic contacts after making necessary physical measurements. A second coat of silver paint was applied on the pellet after drying of the first coat. The pellet was placed between the well-cleaned discs of the equipment that form the two electrodes of measuring system. The schematic block diagram shows the circuit arrangement made for the measurements. The electrode assembly with the sample that forms the part of the circuit was then placed in furnace for making the necessary measurements.

The constant potential of 2V was applied across the sample. Variation in current with temperature was recorded from room temperature to 500°C. The temperature measurements were made with the help of temperature controller, which uses chromel–alumel thermocouple for the same. The resistance of the sample was calculated using Ohm's law and hence the resistivity of the sample at different temperatures calculated by using the formula $R = \rho t/A$, where 't' is the thickness of the conductor; 'A' is area of the cross section & ρ is resistivity. The same procedure was applied for other samples. Figure 3.5 depicts the schematic representation of the pellet sample holder used in dc resistivity measurement experiment.

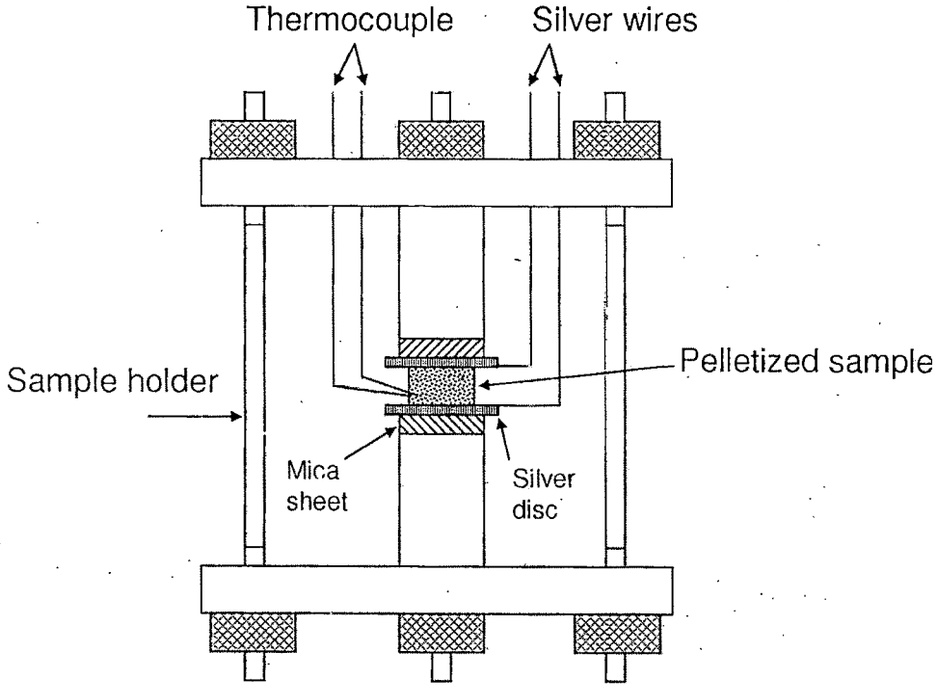

Fig. 3.5: Schematic representation of the pellet sample holder used in dc resistivity measurement experiment

Table 3.1 Preparative parameters

Sr. No	Parameter	Specification
1	pH	7.0
2	Precursors	$CdCl_2$, $SnCl_4.5H_2O$
3	Concentration of Precursors	0.1 M
4	Solvent	Deionised water
5	Sintering period	6 hr
6	Sintering temperature	400, 600, 800, 1000, 1200°C

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