

Cd₂SnO₄—its sol-gel preparation and materials properties

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Abstract. Cd₂SnO₄ powder has been synthesized through acrylamide sol-gel route for the first time. The gelation-calcination steps have been studied. Morphological examination of the network matrix and the calcined products has been done through SEM. XRD shows the orthorhombic structure of the Cd₂SnO₄ powder obtained. Arrhenius plots yield activation energies of 0.01 and 0.61 eV for the low and high slope regions, respectively. A semiconductor to metal transition is observed in the range 210–225°C.

Keywords. Cadmium tin oxide; sol-gel; acrylamide.

1. Introduction

Fine semiconductor oxides are important materials on account of their varied applications in sensors (Advani and Gordon 1980), rechargeable batteries (Hashemi *et al* 1988; Jayachandran *et al* 1993) and energy converting and conserving systems (Cardile 1991) to name just a few. Rapid progress has been made in the synthesis of semiconductor oxides through new techniques like the sol-gel method with many advantages over the conventional solid-state route. The sol-gel method enables the production of a wide range of fine particles of controlled size and morphology, high purity, molecular homogeneity and reduced processing temperature.

The currently well-known sol-gel processes (Hench and West 1990) employ the expensive metal-alkoxide precursors. In this report, an inexpensive but efficient organic polymer is used for gel formation. Here, an organic polymer such as polyacrylamide helps in the formation of submicron pores in the gel matrix (Tanaka 1981). Aqueous solutions are gelled by the *in situ* formation of an organic network and the reactions, in the trapped precursor inorganic salt solution, form hydrous oxides or hydroxides of metals. The subsequent direct calcination of the dried gel produces submicron size semiconductor oxide powders.

Cd₂SnO₄ has been synthesized by solid-state reaction (Smith 1960; Golestani-Fard *et al* 1983). For the first time, this compound has been synthesized by the organic sol-gel method by the present authors and a detailed account of the gelation-calcination processes and the materials properties of the synthesized powder is presented here.

2. Experimental

AR grade CdCl₂, SnCl₄, citric acid, acrylamide, N,N'-methylene-bis-acrylamide and ammonium persulphate were used. The gel formation and calcination steps are

explained in a later section. A programmable furnace, Heraeus Model No. K 1710, was used for heating. XRD analysis was carried out with a JEOL JDX 803-a X-ray equipment using $\text{CuK}\alpha$ radiation through a Ni filter. DTA measurements were made with a fabricated set-up consisting of a ceramic furnace which could go up to 1000°C , a chromel-alumel thermocouple, a ceramic sample holder and an X-Y-t recorder. SEM analysis was done using a scanning electron microscope, JSM 35 CF JEOL. Resistance vs temperature was measured by the two-probe method.

3. Results and discussion

The flow chart for the synthesis of Cd_2SnO_4 powder by the sol-gel route is given in figure 1. The precursor was prepared by mixing aqueous chlorides of cadmium and tin in the mole ratio of 2 : 1. Citric acid was used as the complexing agent and to avoid precipitation. Aqueous ammonia was used to adjust the pH at 2, 4, 5, 7 and 10.

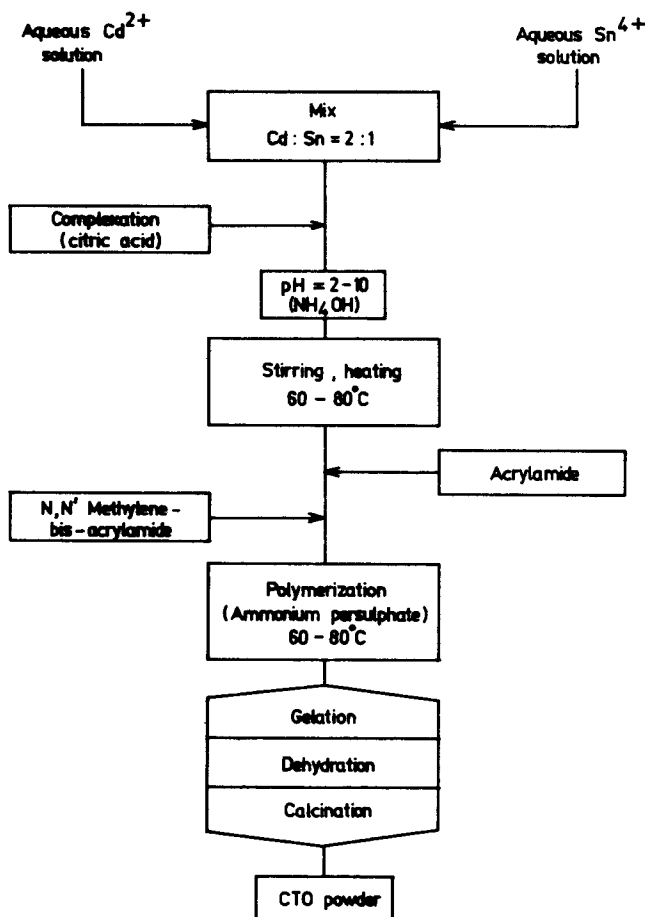


Figure 1. Flow chart of the sol-gel process.

The clear solution was heated to 60–80°C. 6 g of acrylamide and 1 g of N,N' methylene-bis-acrylamide were added gradually one after the other under continuous stirring and the solution temperature maintained for about 15 min. Then 0.05 g of ammonium persulphate was added as polymerization catalyst. In about 2–5 min gelation was complete and a translucent and non-sticky gel was formed.

Dehydration of the gel should be done carefully under controlled heating steps. If the temperature is lower than 50°C, it takes around a week for complete dehydration. At temperatures greater than 150°C, there is a very large increase in volume, even up to 20 times the initial volume, and the gel turns into a loose dark powdery residue which is undesirable. Dehydration at 100°C for 48 h is found to be optimum for getting a shrunken, white or light yellow coloured residue. The volume reduces to about a tenth of its initial volume due to the removal of the trapped water in the pores.

The thermal behaviour of the dried residue was examined by DTA and is shown in figure 2. The first endothermic peak at about 75°C is ascribed to the evaporation of water physically adsorbed on the gel. The second endothermic peak at about 230°C may be due to the removal of the functional groups (Byong-Ho Kim *et al* 1992) and the decomposition of hydroxides. The two exothermic peaks in the temperature range of 500–600°C might be attributed to the burnout of the carbon. The broad exothermic region from about 700 to 1000°C may be associated with the formation of CdO and SnO₂ and subsequent reaction to form Cd₂SnO₄, as seen from the XRD analyses. The process of Cd₂SnO₄ formation continues up to 900°C. The fall in the curve beyond 900°C may be due to the decomposition of the formed Cd₂SnO₄ into SnO₂ and CdSnO₃, as borne out by the XRD results.

Based on the DTA analysis, calcination was carried out under controlled heating steps. An initial slow heating rate (HR) had to be maintained to break the organic network. Up to 600°C the HR was maintained at 2, 5 and 10°C per min and then calcination was carried out at temperatures of 700, 800, 900 and 1000°C for different durations.

At 2°C per min HR, the reaction was too slow and the product was a powder with distinct black and yellow components. At 5°C per min HR, only yellow

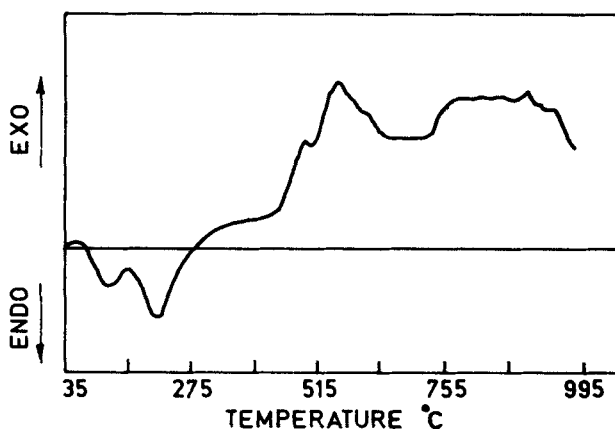


Figure 2. DTA curve of the dried gel residue.

powder resulted after calcination. At 10°C per min HR, a white coloured mass resulted. These observations lead to the conclusion that the optimum HR was 5°C per min to obtain yellow coloured powder after calcination as shown in figure 3a. The typical colour of Cd₂SnO₄ powder was yellow.

Calcination was done at temperatures of 700, 800, 900 and 1000°C for a duration of 3 h. The optimum calcination temperature was found to be 900°C at which, only yellow coloured powder was obtained as shown in figure 3b. At 700 and 800°C, the powder appeared to have both white and yellow components. At 1000°C only white coloured powder resulted. It is presumed that other phases of cadmium tin oxide are formed at temperatures higher than 900°C. The effect of calcination duration was studied by calcining for 1, 3 and 5 h. Pure yellow coloured powder was obtained for a calcination duration of 3 h as shown in figure 3c.

The calcined powders were subjected to XRD analysis. A multiplot of XRD patterns of the dried gels and the calcined products obtained at different temperatures in air is shown in figure 4. The dried gel is amorphous. Sharp XRD peaks are noticed for the powders obtained at all the calcining temperatures, which shows that crystallization is there even at 700°C, the lowest temperature of calcination.

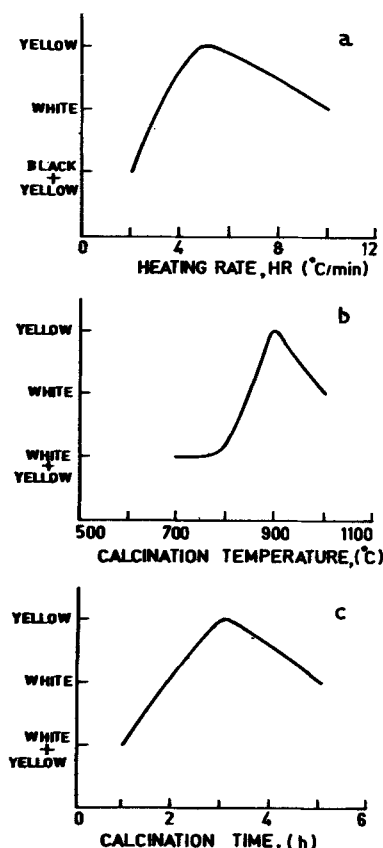


Figure 3. Colour changes of the calcined product under different preparative parameters of (a) heating rate (HR), (b) calcination temperature and (c) calcination time.

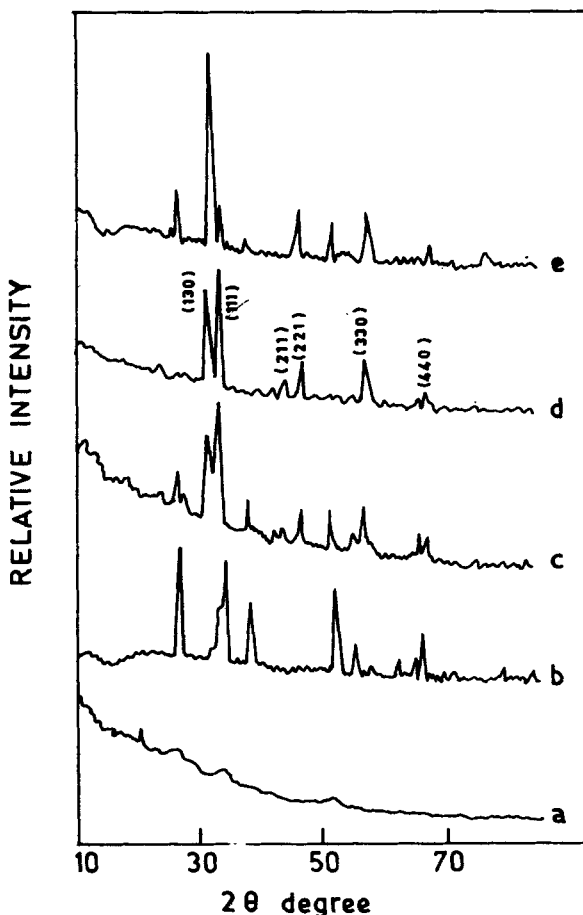


Figure 4. XRD patterns of (a) dried gel, (b) calcined at 700°C, (c) calcined at 800°C, (d) calcined at 900°C and (e) calcined at 1000°C.

On the basis of the XRD analyses, a synthesis mechanism of Cd_2SnO_4 powder can be proposed as given in table 1.

The Cd-Sn hydroxide gel first decomposes leading to the formation of CdO and SnO_2 . As the temperature increases CdO reacts with SnO_2 leading to a gradual formation of Cd_2SnO_4 till all CdO is used at 900°C. The product assumes a yellow colour completely indicating the completion of the formation of Cd_2SnO_4 phase. However, the Cd_2SnO_4 obtained contains a little amount of SnO_2 as a secondary phase. When the calcination temperature reaches 1000°C, Cd_2SnO_4 reacts with the residual SnO_2 and disintegrates to produce $CdSnO_3$ and SnO_2 as the predominant phases together with some Cd_2SnO_4 .

These results are somewhat contrary to earlier observations (Golestani-Fard *et al* 1983) for Cd_2SnO_4 formation by the solid state reaction of 2:1 CdO, and SnO_2 . They observed Cd_2SnO_4 phase at 1050°C and at higher temperatures, it decomposed to CdO and $CdSnO_3$ phases. The absence of CdO in the sol-gel derived Cd_2SnO_4 powders calcined at above 900°C for prolonged duration was due to the fact that CdO sublimation in dynamic air began at about 900°C (Cardile 1991).

Table 1. A correlation of the XRD studies and the possible chemical reactions' in the sol-gel synthesis of cadmium tin oxide (5 g batches).

Calcination temperature (°C)	Chemical reaction	Phases observed in XRD pattern
700	$\text{Cd}(\text{OH})_2 \rightarrow \text{CdO} + \text{H}_2\text{O}$ $\text{SnO}_2 \cdot x\text{H}_2\text{O} \rightarrow \text{SnO}_2 + x\text{H}_2\text{O}$	CdO SnO ₂
800	$\text{CdO} + \text{SnO}_2 \rightarrow \text{Cd}_2\text{SnO}_4 + (\text{SnO}_2) + (\text{CdO})$	CdO SnO ₂ Cd ₂ SnO ₄
900	$\text{CdO} + \text{SnO}_2 + \text{Cd}_2\text{SnO}_4 \rightarrow \text{Cd}_2\text{SnO}_4 + (\text{SnO}_2)$	Cd ₂ SnO ₄ SnO ₂
1000	$\text{Cd}_2\text{SnO}_4 + \text{SnO}_2 \rightarrow \text{CdSnO}_3 + (\text{SnO}_2) + (\text{Cd}_2\text{SnO}_4)$	CdSnO ₃ SnO ₂ Cd ₂ SnO ₄

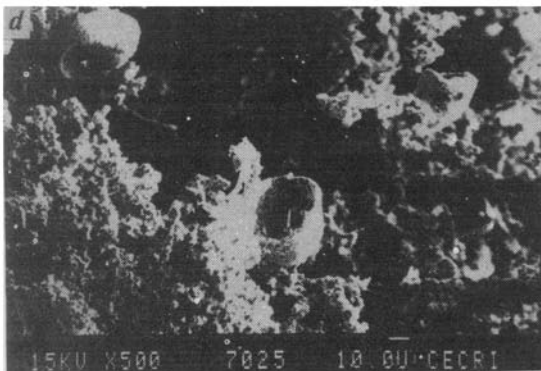
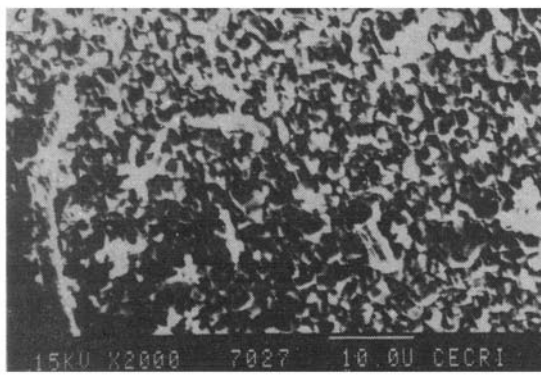
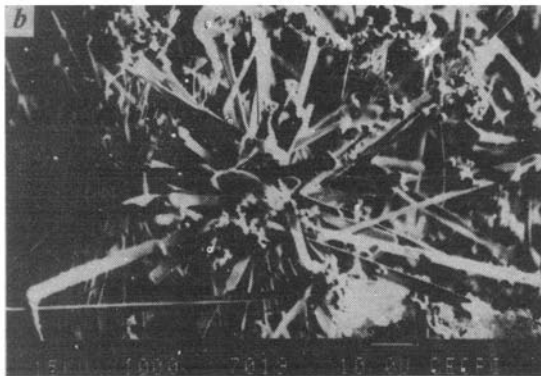
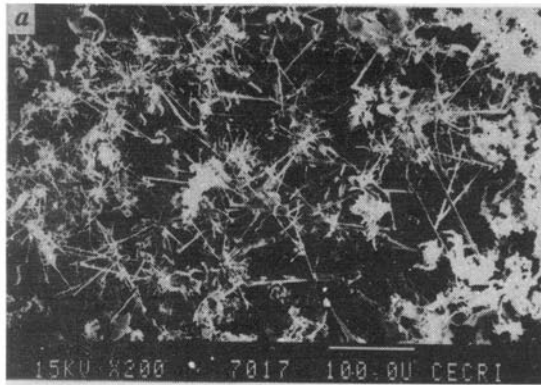
Morphology of the calcined residue and the crushed powder was studied by SEM. The acrylamide sol-gel matrix was a polymeric network with pores of about 1–5 µm diameter (Tanaka 1981). The sol containing the precursors, was trapped in the pores. When dehydration and calcination were carried out, the polymer network evaporated leaving the oxide powder in the form of a loosely held network. This network structure is shown in figure 5a. It is interesting to note that cob-web like formations scattered all over the mass. These structures were interconnected with needles with a diameter of about 1 µm. Figure 5b provides a closer view of an individual cob-web structure. The branches from the centre of the clusters extend to the neighbouring clusters which is the characteristic feature of the acrylamide gel with interconnected pores.

Figure 5c depicts the SEM picture of ground Cd₂SnO₄ powder. It shows an agglomerated mass of grain size about 2 µm. The product obtained at 1000°C shows a different morphology with some cup-like structures made up of fine particles as shown in figure 5d.

The synthesized powder was orthorhombic with lattice parameters $a = 5.560 \text{ \AA}$, $b = 9.894 \text{ \AA}$ and $c = 3.218 \text{ \AA}$ and these compare well with the reported values of $a = 5.563 \text{ \AA}$, $b = 9.892 \text{ \AA}$ and $c = 3.192 \text{ \AA}$ (Bowden and Cardile 1990).

The powder exhibits *n*-type behaviour as observed by the hot-probe method. The log *R* vs temperature variation for the powders prepared at pH 2, 4, 5, 7 and 10 is shown in figure 6. All the curves show a variation in slope in the temperature region of 85–105°C which is in accordance with the reported transition temperature of 84°C for the screen printed Cd₂SnO₄ layer with orthorhombic structure (Setty 1989). The resistance goes on decreasing up to a point and then increases. This continuous decrease in resistance can be ascribed to an increase in the number of electrons which can be attributed to the release of chemisorbed and bound oxygen

Figure 5. Scanning electron micrographs of the (a) uncrumbled network, (b) closer view of an individual cob-web structure, (c) agglomerated mass and (d) powder calcined at 1000°C.



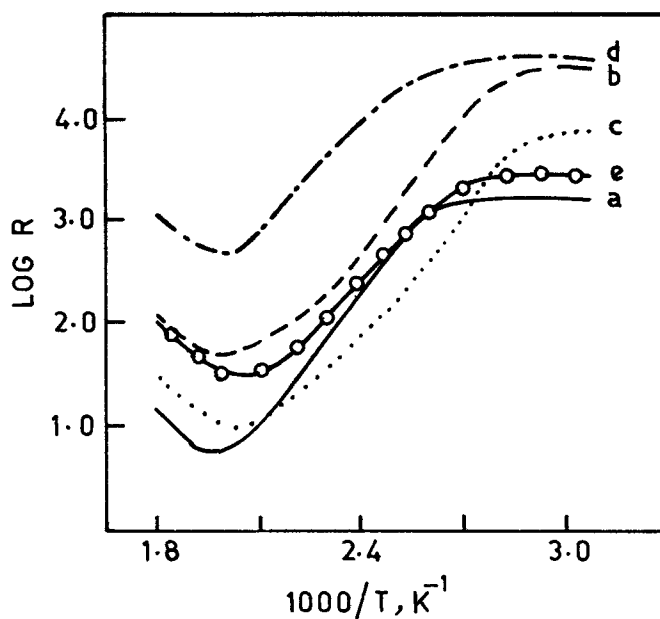
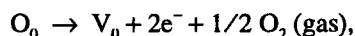


Figure 6. Plot of $\log R$ vs $1000/T$ for powders prepared at (a) pH 2, (b) pH 4, (c) pH 5, (d) pH 7 and (e) pH 10.

Table 2. The optimized process parameters for the synthesis of Cd_2SnO_4 powder by acrylamide for sol-gel method (5 g batches).

Sol pH	5
Gelation temperature	60–80°C
Gelation time	2–5 min
Dehydration temperature	100°C
Dehydration time	48 h
Heating rate	5°C/min
Calcination temperature	900°C
Calcination time	3 h
Colour of the powder	Yellow

species on heating the powder. This process contributes more electrons by the desorption process



resulting in enhanced conduction.

Beyond this point, there is an increase in resistance. The continuous supply of electrons reaches saturation imparting a metal like behaviour to the Cd_2SnO_4 powder. This semiconductor to metal-like transition is observed in the range 210–225°C which is comparable to the range 215–227°C reported earlier (Setty 1989). The calculated activation energy values corresponding to the low and high slope regions are about 0.01 and 0.61 eV respectively which are again comparable to the reported values of 0.01 and 0.76 eV (Setty and Sinha 1986; Setty 1989).

4. Conclusions

A detailed investigation of the synthesis of Cd_2SnO_4 powder through the acrylamide sol-gel route has been presented. It has been possible to synthesize Cd_2SnO_4 powder at a lower temperature of $900^\circ C$ by this sol-gel route. The optimized process parameters to obtain orthorhombic Cd_2SnO_4 powder are given in table 2. A small amount of SnO_2 is present in the product. The synthesized powder is composed of particles with a narrow size distribution of $1-3 \mu m$. The particles appear to be agglomerated. The product exhibits *n*-type conductivity and shows a semiconductor to metal transition around $210-225^\circ C$, which property makes it useful for thermal switching applications.

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