

Indium tin oxide nano-particles through an emulsion technique

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Abstract

Spheroidal indium tin oxide (ITO) nano-particles with In/Sn = 85:15 (at.%) were prepared by an emulsion technique under mechanical agitation without the aid of any surface-active agent. X-ray powder diffraction (XRD) indicated the stabilization of cubic ITO as the only phase at 250 °C. Particle size analysis showed a narrow distribution of 20–58 nm range particles with a mean size of 38 nm, thus, confirming their nano-structured nature. The pellets sintered at 1350 °C for 6 h were found to have 95–97% of theoretical density. Thus, well sinterable nano-particles of ITO powders were prepared at a significantly low temperature compared to that in the reported methods. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Indium tin oxide (ITO) films find wide applications in thin film solar cells and electroluminescent devices due to their highly conductive and transparent nature [1]. The high conductance is achieved by doping with Sn, and thereby enhancing the oxygen vacancies in the In₂O₃ lattice. In₂O₃ exists in two different crystallographic modifications, i.e. hexagonal and cubic forms. High electrical conductance normally is achieved by the stabilisation of the cubic phase. Many techniques such as evaporation, sputtering, chemical vapour dep-

osition and sol–gel methods are available to obtain good quality ITO films of desirable properties [2–4]. Recently, the work in our laboratory has also focused on obtaining good quality conductive ITO coatings on float glass by the relatively inexpensive sol–gel method [5]. However, recent developments on thin-film technology proved that compared with the films produced by the solution sol–gel process, better films can be produced by dip or spin coating of suspensions of nano-particles [6].

ITO powders are normally prepared by mixing dry powders of In₂O₃ and SnO₂ and calcining the mixture at temperatures above 1000 °C [7]. A few reports are available on the preparation of ITO powders by coprecipitation method or sol–emulsion technique by the use of a surfactant [7–9]. In the coprecipitation method with NH₄OH, the precipitated hydroxides had

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to be calcined at 1000 °C to produce hexagonal In₂O₃ [7]. In the sol–emulsion technique, due to the use of a surfactant, a minimum temperature of 700 °C was required to obtain phase pure ITO powders [8]. Here, we report a very simple emulsion technique without the use of any surfactant for the preparation of ITO nano-particles at a temperature as low as 250 °C.

2. Experimental procedure

2.1. Preparation of precursor materials

The starting materials for In₂O₃–SnO₂ powder were indium ingots (>99.9%, Sisco research laboratory) and SnCl₄·5H₂O (98% Loba Chemie). A stock solution of InCl₃ was prepared by dissolving shredded indium ingots in concentrated hydrochloric acid (35.4% AR, sd fine chem.) so as to obtain a concentration of 0.48 M In³⁺. For the preparation of 85:15 In/Sn oxide powders, a calculated quantity of SnCl₄·5H₂O was dissolved in the required amount of InCl₃ solution. The resulting mixed salt solution was added to 2-butanol or 2-propanol (AR, sd fine chem.). The volume ratio of the mixed salt solution/organic solvent was 1:7. This precursor was put under a mechanical agitation of 1000 rpm. Precipitation as a mixed hydrous oxide was effected at a pH of 8–9 with the addition of triethylamine (TEA) [10], an organic base under constant agitation. After complete precipitation, the entire mass was kept under agitation for 10 more minutes to ensure complete homogenisation. The precipitated material was collected by centrifugation at 6000 rpm, dispersed in acetone under stirring and again centrifuged at 6000 rpm. The process was repeated twice and the final precipitate was dried at 100 °C in air for 1 h to obtain the dried precursor. The above procedure was re-

peated under different experimental conditions. The details of selected experiments are given in Table 1. The dried powders were calcined at various temperatures viz. 250, 300, 400 and 500 °C for 6 h to examine the crystallization behaviour. The 300 °C calcined powders were pelletised at a pressure of 500 kg/cm² and sintered at 1350 °C for 6 h in air.

2.2. Physical characterization of the powders

Thermal characteristics of the precursor material were studied on a Netzsch TG/DTA (409c) unit at a heating rate of 10 °C/min. The calcined powders were further characterised by particle size analysis (Autosizer IIC Malvern) and powder X-ray diffraction (XRD) on Philips PW-1730 with Ni-filtered CuK_α radiation at a scan rate of 2°/min. Unit cell parameter was calculated from the observed 'd'-spacing, which was accurately measured with the help of silicon as an internal standard. Particle size and morphology of the synthesized powders were further monitored with the help of a transmission electron microscope (TEM), (JEOL, JEM-200X). Scanning electron microscope (SEM) and Energy dispersive X-ray analysis (EDAX) work on the calcined powders were performed on a Leo 430i scanning electron microscope.

3. Results and discussion

The mean particle size of the ITO powders given in Table 1 indicates that compared to the type of the organic solvents used, the concentration of the cations present in the starting solutions is more significant, when other parameters are unaltered. Experimental parameters for Run no. 2 of Table 1 therefore, proved to be the optimum for obtaining ITO nano-

Table 1
Experimental details for the preparation of different precursor materials

Run no.	Concentration of the metal ions in the starting solution		Organic solvent (OS)	Dielectric constant of OS	Particle size mean (nm)
	In	Sn			
1	0.48	0.08	2-butanol	15.8	770.6
2	0.24	0.04	2-butanol	15.8	38.4
3	0.24	0.04	2-propanol	18.3	620.7

particles in the present investigation. Because of the relatively high dielectric constant and miscibility in aqueous medium [11] of 2-propanol, the interfacial tension at the solvent/solution interface is expected to be low compared to that of 2-butanol. Thus, considering the Laplace equation [12],

$$\Delta p = 2\gamma/a \quad (1)$$

where Δp =pressure difference, γ =interfacial tension, and a =radius of the droplet, under identical conditions of precipitation, the droplet size, and hence, the final particle size [12] is expected to be small for 2-propanol, causing more agglomeration. In fact, after the addition of the mixed salt solution to 2-propanol under agitation, a clear solution was obtained visually. Precipitation with TEA in such bulk medium leads to nucleation and subsequent growth of the particles in an uncontrolled way [13], generating large particles with wide size distribution (Table 1, Fig. 1). The use of lower alcohols, i.e. ethanol, methanol with high dielectric constant causing high miscibility with the mixed salt solution is also unsuitable for monodispersed ITO nano-particle preparation. Based on the above arguments, 2-butanol with comparatively low dielectric constant, and low miscibility [11] in the aqueous medium is expected to produce larger droplet size, and hence, the final particle size with less agglomeration. In addition to this, concentration of metal ions in the solution is also an important factor in determining the final particle size. In fact, generation of a cloudy solution (without any precipitate formation) during the addition of the aqueous salt solution to 2-butanol under mechanical agitation suggested the formation of emulsion of aqueous

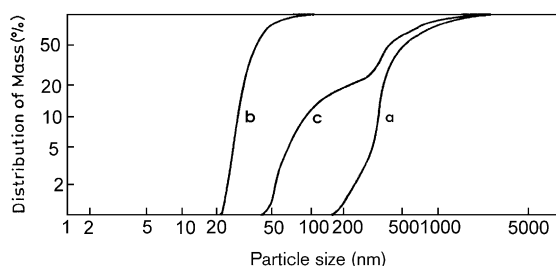


Fig. 1. Particle size distribution curve of 300 °C ITO powders prepared in (a) Run no. 1, (b) Run no. 2, and (c) Run no. 3.

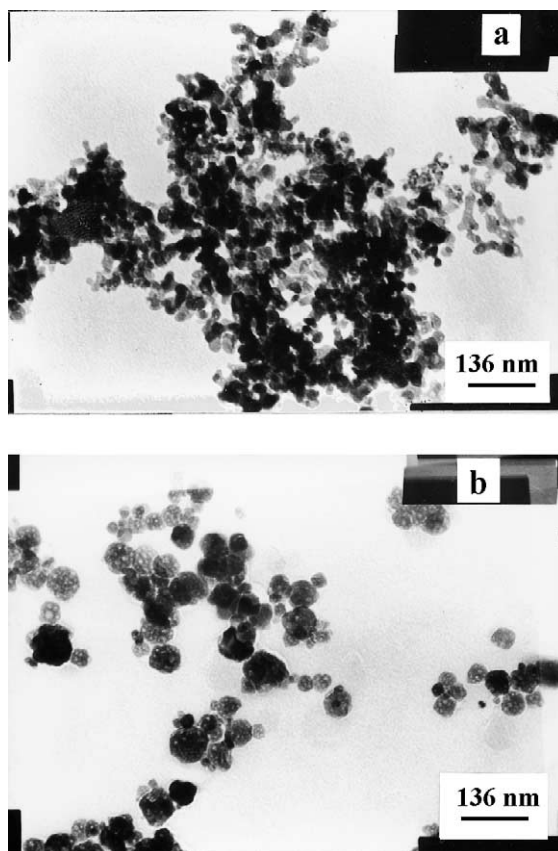
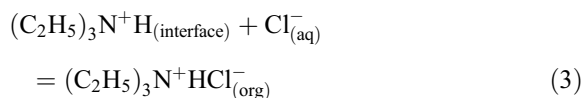
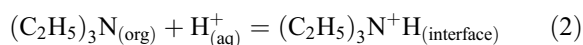


Fig. 2. TEM picture of 300 °C calcined ITO powder (prepared in Run no. 2) dispersed in (a) Acetone and (b) Polyvinyl butyral.

microdroplets. These aqueous microdroplets in contact with TEA caused the precipitation of mixed hydrous oxide (within the droplets) according to the following two step mechanism [10], and avoiding the uncontrolled precipitation of the particles.



Appearance of spheroidal monodispersed ITO nanoparticles in the TEM picture in Fig. 2 suggests the formation of monodispersed spheroidal precursor material, which retained the same morphology after calcination. Based on the above discussion, it can be con-

cluded that organic solvents, including higher alcohols with low dielectric constants (compared to 2-butanol) will also be unsuitable for ITO nano-particle formation in the absence of any surface-active agents. Increase in the cation concentration in the aqueous microdroplets caused increased precipitation of the hydrous oxides thereby causing the formation of particles of increased size after calcination (Table 1) for Run no. 1. SEM picture in Fig. 3 indicates the formation of larger particles after the calcination of the precursor collected in Run no. 1. As discussed earlier, lower concentration of metal ions in Run no. 2 resulted in nano-particles of hydrous oxides and oxides. Note that to avoid the formation of undesirable carbon particles during calcination, the experiments were performed without the aid of any surface-active agents. Complete removal of the carbon particles necessitates high temperature, causing additional growth of the particles [8,9].

TG/DTA analysis of a typical precursor powder from Run no. 2 indicated a gradual weight loss of $\sim 17\%$ up to $250\text{ }^{\circ}\text{C}$, accompanied by a very sharp endotherm around $240\text{ }^{\circ}\text{C}$, due to the evolution of solvents unremoved during centrifugation. The presence of a weak endotherm below $100\text{ }^{\circ}\text{C}$ indicates that the amount of adsorbed water associated with these precursor powders is almost negligible. Crystallization of ITO phase was indicated by an exothermic peak around $263\text{ }^{\circ}\text{C}$.

Fig. 4 depicts the XRD patterns of the ITO powder synthesized by the calcination of the precursors at $250\text{ }^{\circ}\text{C}$

a -

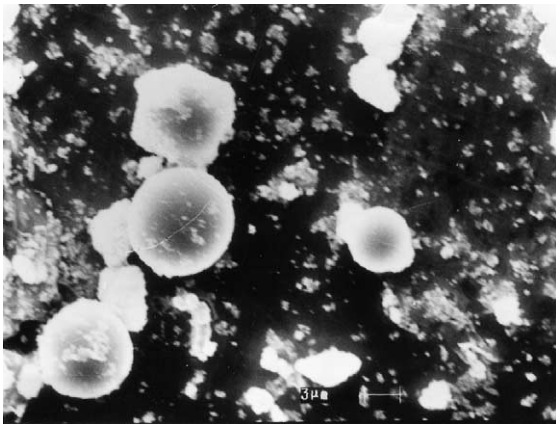


Fig. 3. SEM picture of $300\text{ }^{\circ}\text{C}$ calcined ITO powder (prepared in Run no. 1) showing large particles.

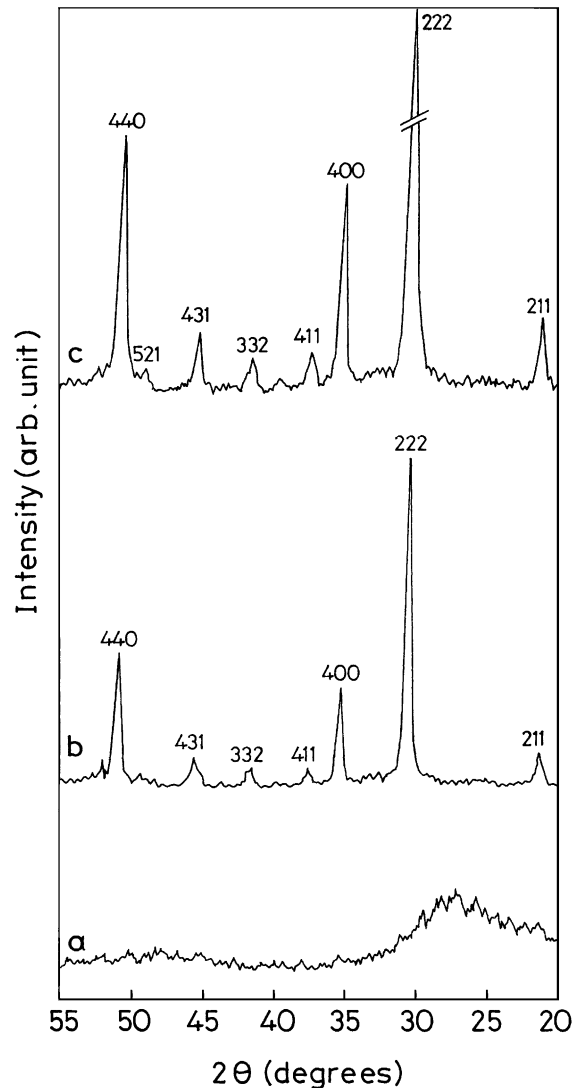


Fig. 4. Powder x-ray diffraction pattern of ITO powder prepared from Run no. 2 (a) Precursor powder (b) Calcined at $250\text{ }^{\circ}\text{C}$ and (c) Calcined at $400\text{ }^{\circ}\text{C}$.

nd $400\text{ }^{\circ}\text{C}$ along with that of the uncalcined precursor material. It is very interesting to note that the white precursor hydrous oxide is amorphous to X-rays while on calcination at $250\text{ }^{\circ}\text{C}$, the same changes its colour to the characteristic pale yellow colour of In_2O_3 followed by the crystallization of the doped In_2O_3 at this very low temperature. The sharp diffraction peaks for the sample calcined at $250\text{ }^{\circ}\text{C}$, indicating a high degree of crystallization, is notable. If one concen-

trates on the very intense peak at $30.2^\circ 2\theta$, it is evident that with an increase in the calcination temperature, the intensity of the peak increases significantly along with a reduction in the peak half width indicating the growth of ITO particles with the calcination temperature. The peaks observed in the XRD pattern of 250°C calcined sample match well with the cubic In_2O_3 peaks reported in the Joint Committee for Powder Diffraction Standards (JCPDS 6-416). The calculated lattice parameter for cubic ITO phase is $10.13 \pm 002 \text{ \AA}$ when compared to the reported lattice parameter of undoped In_2O_3 which is 10.118 \AA . Intensities of the three most important peaks of In_2O_3 namely $\langle 222 \rangle$, $\langle 400 \rangle$ and $\langle 440 \rangle$ reflections do not deviate from the PDF intensities, implying random non-oriented arrangement of the ITO particles. The major peaks due to SnO_2 , at 26.5° and 35.5° and SnO , at $33.2^\circ 2\theta$ were absent in the observed pattern, indicating complete miscibility of In and Sn in the proposed composition. No other crystalline phases were observed in the diffraction pattern. The observed crystallization temperature is significantly low when compared to that of the conventional powder preparation techniques.

Fig. 1b indicates the particle size distribution of the powder from Run no. 2 which was calcined at 300°C for 6 h and dispersed in acetone. It is clear that the particles are very uniformly distributed with a mean diameter of 38.4 nm. The 300°C calcined powders were dispersed in acetone and also a polymeric solution of poly vinylbutyral (PVB) to understand the nature of particles and their morphology. Morphological characterization of the powders from TEM revealed that (Fig. 2a and b) they are of nearly spherical shape, however, they apparently look like well-dispersed hexagonal microcrystallites of nano-ITO particles. The nano-particles are more agglomerated in the acetone media (Fig. 2a), while they are finely dispersed and well separated in the polymeric solution (Fig. 2b). EDAX analysis on the 300°C calcined powders showed the presence of In, Sn and O in the matrix.

The sintered pellets of ITO powders from all the three runs were found to have 95–97% of theoretical density in air after sintering at 1350°C for 6 h. Fig. 5 illustrates the SEM picture of the fracture surface of the sintered pellets of sample nos. 1, 2 and 3 of Table 1, respectively. Substantial amount of grain growth with well-connected plate like grains are clearly seen

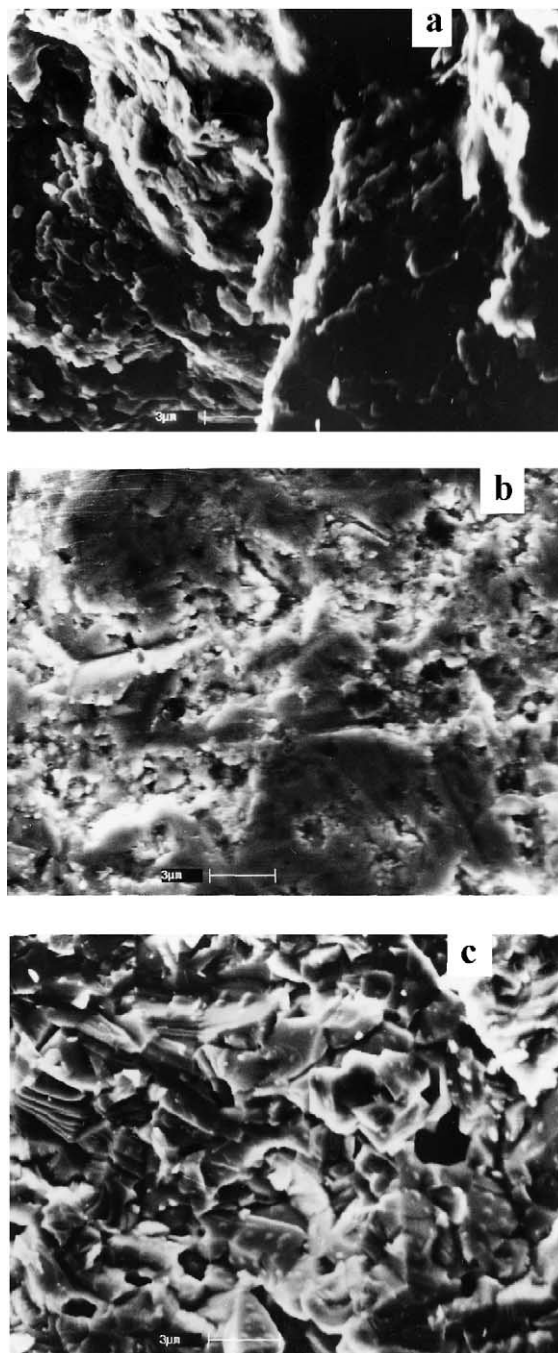


Fig. 5. SEM picture of the surface (S)/fracture surface (FS) of the sintered pellets of ITO powders from (a) Run no. 1 (FS), (b) Run no. 2 (S) and (c) Run no. 3 (FS).

on the fracture surface of sample no. 3 (Fig. 5c) when compared to sample nos. 1 (Fig. 5a) and 2 (Fig. 5b). The difference in grain growth in all probability is associated with the difference in particle morphology and size of the starting powders.

4. Conclusions

Unlike the coprecipitation method, where In_2O_3 crystallised in the hexagonal form along with SnO_2 as a secondary phase on calcination at $550\text{ }^\circ\text{C}$ [7], in the present method, the cubic In_2O_3 phase was found to crystallize at a temperature as low as $250\text{ }^\circ\text{C}$ in all the cases. Earlier observations on ITO powder preparations claimed that the solubility of tin in cubic In_2O_3 is only up to (6 ± 2) at.%. By this emulsion method, we were able to prepare cubic In_2O_3 with doped Sn apparently up to 15 at.% at a substantially low temperature compared to the conventional method or the coprecipitation method. In addition to preparing uniform conductive coatings for device applications, these powders can also be used as oxygen electrodes in high-temperature fuel cells.

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