

Development of nano indium tin oxide (ITO) grains by alkaline hydrolysis of In(III) and Sn(IV) salts

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Abstract. Indium tin oxide (ITO) nano powders of different compositions (In : Sn = 90 : 10, 70 : 30 and 50 : 50) were prepared by heat treatment (300–450°C) of mixed hydroxides of In(III) and Sn(IV). The hydroxides were obtained by the reaction of aq. NH₃ with mixed aq. solutions of In(NO₃)₃ and SnCl₄. FTIR and TG/DTA studies revealed that powders existed as In(OH)₃·H₂O–SnO₃H₂·H₂O in the solid state and then they transformed to In₂O₃–SnO₂ via some metastable intermediates after 300°C. Cubic phase of In₂O₃ was identified by XRD for the oxides up to 30% of Sn. Particle size measurements of the solid dispersed in acetone and SEM study for microstructure showed that the oxides were in the nano range (55–75 nm) whereas the size range determined from Debye–Scherrer equation were 11–24 nm.

Keywords. ITO nanoparticles; alkaline hydrolysis; thermal analysis; FTIR and XRD studies.

1. Introduction

As the indium tin oxide (ITO) is an advanced ceramic material with many electronic and optical applications due to its high electrical conductivity and transparency to light (Vossen 1977) in the visible region, its preparation not only in thin film form but also in bulk form has received much current interest (Woodhead and Segal 1985; Segal and Woodhead 1986; Bradley 1989; Segal 1989; Caulton and Hubert-Pfalzgraf 1990; Vanderslung and Sttelberger 1990; Yanagisawa and Udawatte 2000). In most of the cases, results have been reported for the preparation of ITO in the bulk form (Vojnovich and Bratton 1975; Gehman *et al* 1992; Nadaud *et al* 1994; Lee *et al* 1996; Yanagisawa and Udawatte 2000; Denoy and Pradeep 1997) with low Sn content (In : Sn ≥ 90 : 10). The present work deals with preparation and characterization of nano indium tin oxide (ITO) powders with relatively high content of Sn (In : Sn ≤ 90 : 10).

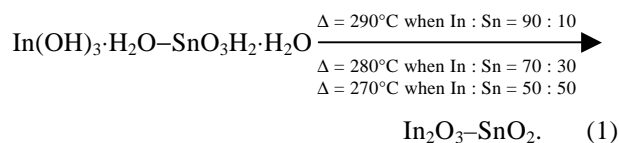
2. Experimental

2.1 Preparation of nano indium tin oxide powders

Indium tin oxide (ITO) nano powders of different compositions (In : Sn = 90 : 10, 70 : 30 and 50 : 50) were prepared from the starting materials, aqueous indium nitrate (prepared from In-metal ingots, SRL, Mumbai) and SnCl₄·5H₂O (Loba Chemi, Mumbai) (scheme 1).

3. Results and discussion

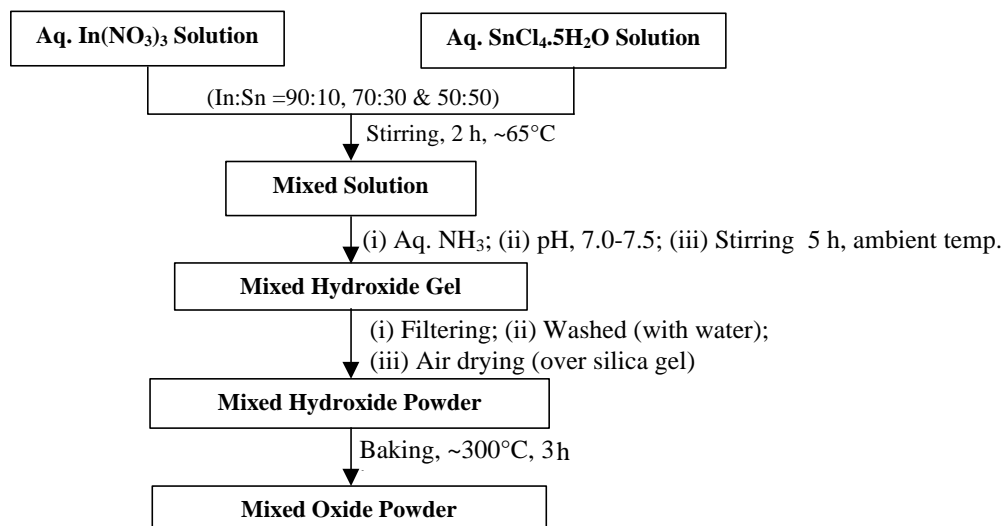
A systematic weight loss of the air-dried powders up to 1200°C was analysed by TG and DTA (NETZSCH-Geratebau GmbH instrument, model STA 409C) study. The results of TG and DTA showed that the transformation temperature of mixed-hydroxides to their mixed-oxides gradually decreased with increase in Sn content (1).



The FTIR spectra (Nicolet 5PC FTIR spectrometer) confirmed the existence of hydrated powders as In(OH)₃·H₂O–SnO₃H₂·H₂O by characteristic vibrations at 1100–1160, 550 and 520 cm⁻¹ for *d*(OH) of In(OH) (Nakamoto 1970), *n*(Sn–O) of Sn(OH) (Orel *et al* 1994) and *n*(In–O) of In(OH) (Hamberg and Granqvist 1986; White and Keramida 1972), respectively.

The X-ray diffraction pattern, measured on Phillips PW-1730 X-ray powder diffractometer (*I* = 1.5418 Å), of the air-dried samples (In : Sn = 90 : 10, 70 : 30) are matching with the pattern of the cubic In(OH)₃ (JCPDS card no. 16-161). Cubic In₂O₃ phase (Swanson *et al* 1955) was obtained when the samples were heated at ≥ 300°C under different atmospheric conditions [air and H₂(5%)–Ar(95%)], while a cassiterite phase of SnO₂ (Baur 1956; McCarthy and Welton 1989) was obtained in the case of In : Sn = 50 : 50 (figure 1). The resistivity (*r*) of the bulk material with relatively low Sn content (In : Sn = 90 : 10) measured by two-probe system was ~ 0.6 Ω·cm. The crystallite size of the oxide powders,

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Scheme 1. Schematic representation of preparation of indium tin oxide powders.

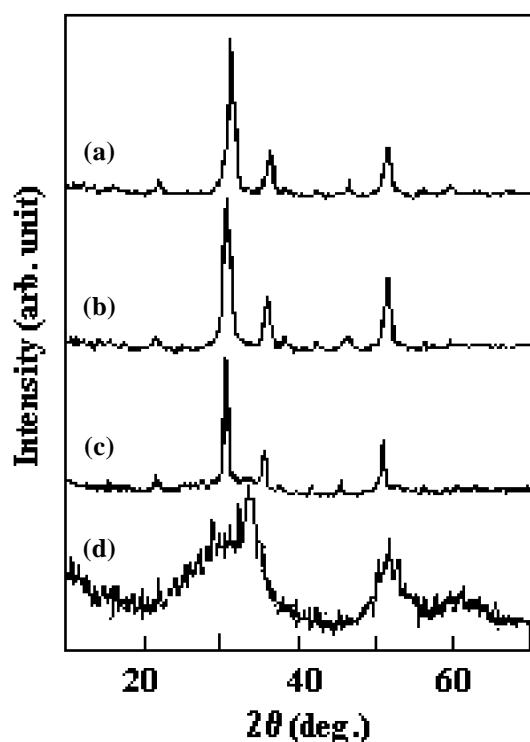


Figure 1. X-ray diffraction pattern of the oxide powders with different compositions (In : Sn atomic ratio): (a) 100 : 0, (b) 90 : 10, (c) 70 : 30 and (d) 50 : 50.

Table 1. Crystallite size of the ITO powders obtained under different heating conditions.

Composition (In : Sn atomic ratio)	Crystallite size (nm)		
	300°C/air	450°C/air	450°C/H ₂ (5%)– Ar(95%)
90 : 10	11	13	18
70 : 30	19	23	24

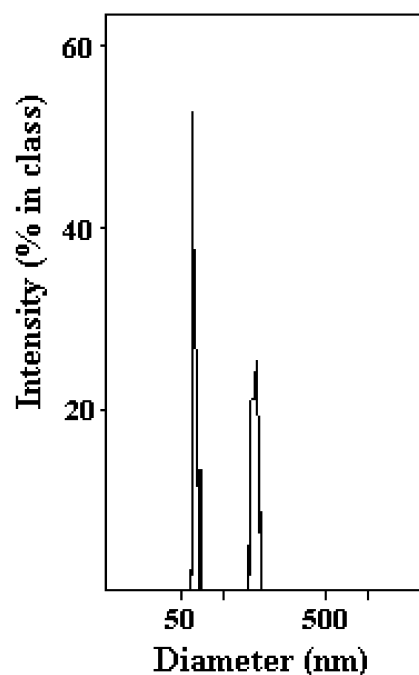


Figure 2. Particle size distribution of ITO powder (In : Sn = 90 : 10), dispersed in acetone by ultrasonication for 2–3 min.

calculated from Debye–Scherrer equation (Segal and Woodhead 1986), was in the range 11–23 nm (table 1). The powders were dispersed in acetone and size of the particle was determined by dynamic light scattering method (Zetasizer 1000HS). A bimodal narrow-size distributions (55–75 nm) were obtained (figure 2). Microstructure revealed by SEM (Leo 400c) also depicts the existence of nano-particles in the generated powders. Particles of higher size range (150–170 nm) were also observed which are probably due to the partial agglomeration of the nano particles as evidenced by SEM (figure 3).

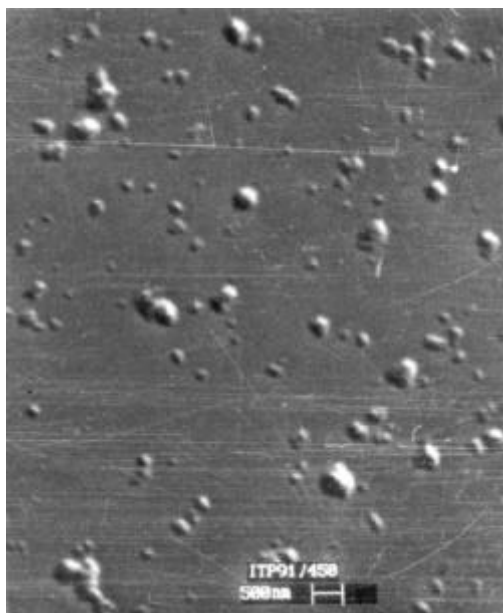


Figure 3. SEM of the ITO powder (In : Sn = 90 : 10) obtained on heating at $\sim 450^\circ\text{C}$ for 2 h in air.

4. Conclusions

Indium tin oxide (ITO) nanoparticles containing relatively high Sn-content (In : Sn = 90 : 10, 70 : 30 and 50 : 50) were prepared from In(III) and Sn(IV) salts. TG/DTA and X-ray diffraction studies showed that the transformation of hydroxides to their corresponding oxides occurred at $\sim 300^\circ\text{C}$, which were found to be in the nano size range (55–75 nm).

Acknowledgements

One of the authors (NCP) is grateful to CSIR, New Delhi for providing the financial support under CSIR-RA scheme. Authors are thankful to Dr H S Maiti, Director,

CGCRI, Kolkata, for his constant encouragement to carry out this work. Thanks are due to Dr (Ms) M Chatterjee, Sol-Gel Division, CGCRI, Kolkata, for her helpful suggestions. Thanks are also due to the colleagues of the X-ray Division, SEM and Membrane Section, CGCRI, Kolkata, for their assistance in material characterization.

References

- Baur W 1956 *Acta Crystallogr.* **9** 515
 Bradley D C 1989 *Chem. Rev.* **89** 1317
 Caulton K G and Hubert-Pfalzgraf L G 1990 *Chem. Rev.* **90** 969
 Denoy M D and Pradeep B 1997 *Bull. Mater. Sci.* **20** 1029
 Gehman B L, Jonson S, Rudolf T, Scherer M, Weigert M and Werner R 1992 *Thin Solid Films* **220** 333
 Hamberg I and Granqvist C G 1986 *J. Appl. Phys.* **60** 123
 Lee D H, Vuong K D, Contrate R A Sr. and Wang X W 1996 *Mater. Lett.* **28** 179
 McCarthy G and Welton J 1989 *Powder Diffraction* **4** 156
 Nadaud N, Nanot M and Boch P 1994 *J. Am. Ceram. Soc.* **77** 843
 Nakamoto K 1970 *Infrared and Raman spectra of inorganic and coordination compounds* (New York: John Wiley)
 Orel B, Lavrencic-Stanger U, Crnjak-Orel Z, Bukovec P and Kosec M 1994 *J. Non-Cryst. Solids* **167** 272
 Segal D 1989 *Chemical synthesis of advanced ceramic materials* (Cambridge, UK: Cambridge University Press)
 Segal D L and Woodhead J L 1986 *Proc. Br. Ceram. Soc.* **38** 245
 Swanson H E, Gilfrich N T and Ugrinic G M 1955 *Natl. Bur. Stand. (US) Circ.* **539** 26
 Vanderslung W G and Sttelberger A P 1990 *Chem. Rev.* **90** 1027
 Vojnovich T and Bratton R 1975 *J. Ceram. Bull.* **54** 216
 Vossen J L 1977 *Phys. Thin Films* **9** 1
 White W B and Keramida V G 1972 *Spectrochim Acta* **A28** 501
 Woodhead J L and Segal D L 1985 *Proc. Br. Ceram. Soc.* **36** 123
 Yanagisawa K and Udawatte C P 2000 *J. Mater. Res.* **15** 1404