

Solvent effect on synthesis of indium tin oxide nano-powders by a solvothermal process

Jin-Seok Lee, Sung-Churl Choi*

Department of Ceramic Engineering, Hanyang University, Seoul 133-791, Republic of Korea

Received 15 May 2004; received in revised form 2 August 2004; accepted 15 August 2004

Abstract

Well-crystallized and nano-sized indium tin oxide (ITO) powders were prepared by a solvothermal process from a mixed solution consisting of indium nitrate and tin chloride. The characteristics of the solvothermally synthesized ITO powders were studied to investigate the contribution of the processing variables (solvent, working temperature, working pressure) on the physico-chemical properties.

The results of this study show that the nano-sized blue ITO powders with a single phase could be directly obtained by changing the medium from water to organic solvent. Comparison of the yellow ITO powders synthesized by the coprecipitation using calcination of precipitates and blue ITO powders synthesized by the solvothermal process indicated that the solvothermal process led to an in situ reduction reaction.

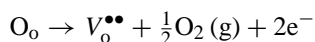
Solvent viscosity in the solvothermal process strongly influences both electrical and optical properties of ITO materials for transparent conducting oxides (TCOs). The size of synthesized ITO particles increased with increasing solvent viscosity due to steric hindrance. Moreover, the shape of the synthesized ITO particles became more square with increasing solvent viscosity, because the preferred orientation of ITO materials for crystallization is the fastest in the $\langle 100 \rangle$ direction.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Powders-chemical preparation; Defects; Electrical properties; Indium tin oxide (ITO); Solvothermal process; SnO₂

1. Introduction

Indium tin oxide (ITO) is an advanced ceramic material with many electronic and optical applications due to its excellent properties of high conductivity ($\approx 10^4 \Omega^{-1} \text{cm}^{-1}$) and high transparency (85–90%) to visible light.^{1,2} The high electrical property is originated from the creation of a conducting carrier–oxygen vacancy with the addition of dopant (Sn) to the matrix (In₂O₃). The oxygen vacancies act as doubly ionized donors and contribute at a maximum two electrons to the electrical conductivity as seen in the following equation:³



In₂O₃ exists in two different crystallographic structures, i.e. rhombohedral and cubic forms. High electrical conductivity is normally achieved by the stabilization of the cubic phase.^{4–6}

Among the various processing methods, one of the best techniques for making ITO films is magnetron sputtering, which uses either an In–Sn alloy or an In₂O₃–SnO₂ oxide as the sputtering target. The sputtering efficiency and the properties of the sputtered films are strongly dependent on the density of the sputtering target.³ Nanocrystalline powders ranging from 1 to 100 nm have a high driving force for densification due to their enormous surface area at relatively low temperature.⁷

Several chemical techniques, such as coprecipitation, sol–gel, hydrothermal method, etc., have been used to prepare nanocrystalline powders.⁸ Among these chemical techniques, the hydrothermal process has attracted a great deal of attention since particles with the desired characteristics

* Corresponding author. Tel.: +82 2 2290 0505; fax: +82 2 2291 6767.
E-mail address: choi0505@hanyang.ac.kr (S.-C. Choi).

can be prepared with this technique by controlling the solution pH, reaction temperature, reaction time, solute concentration and the types of solvent depending on the particular application.⁹ The main advantages of hydrothermal synthesis are related to homogeneous nucleation processes, ascribed to elimination of the calcinations step to produce very low grain sizes and high purity powders.¹⁰ Moreover, many inorganic materials can be prepared at substantially lower temperatures in hydrothermal reactions than in solid-state reactions due to shorter diffusion distances for reactants for crystallization. Shorter diffusion distances for reactants results in lower temperatures for crystallization which, in turn, alleviate stoichiometry problems associated with volatilization of high vapor pressure components.¹¹

In the conventional hydrothermal process, water can adversely affect the synthesis of the desired compounds due to the sensitivity of some precursors to water, the decomposition of some reactants in water and the inability of some reactions to occur in the presence of water. It is impossible to obtain ITO powders with cubic phase without an additional phase by conventional hydrothermal process since it does not have enough energy to break the bonds among the precursor molecules below the supercritical condition. To prepare crystallized ITO nano-powders with a single phase, Udawatte and Yanagisawa^{2,12,13} reported that it was necessary to do additional heat treatment on hydrothermally derived precursors. In order to apply ITO materials to transparent conducting thin films, annealing for ITO powders crystallized by calcinations should be conducted under reduced conditions to increase carrier concentration. And then, color of ITO powders changes from yellow to blue.

Yu¹¹ found that the solvent in a solvothermal process could be used as shape-controller of nanoparticles, since the solvent physico-chemical properties such as polarity, viscosity, and softness will strongly influence the solubility and transport behavior of the precursors.

The purpose of this study was to obtain blue ITO nano-powders with a single phase without an additional heat treatment and to compare with physico-chemical properties of solvothermally synthesized ITO powders in various organic solvents with different viscosities. The various characteristics of powders will influence to both electrical and optical properties of ITO thin films in application.

2. Experimental procedure

2.1. Powders preparation

Indium(III) nitrate *n*-hydrate ($\text{In}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, Kanto Chemical Co. Inc., Japan) and tin(IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, Kanto Chemical Co. Inc., Japan) were used as starting materials. Ammonia solution (28% NH_4OH , Junsei Chemical Co. Ltd., Japan) was used as the mineralizer.

Indium precursor and tin precursor were precipitated from 0.1 M $\text{In}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ solution and 0.1 M $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ so-

lution, respectively. The two solutions were mixed with the mole fraction of In:Sn of 92:8 under vigorous stirring. After the solution attained equilibrium, ammonia solution was added drop by drop into the mixed precursor solution until pH 11. Upon mineralizer addition, gelation of suspension rapidly occurred around pH 4 and the solution was agitated at 3000 rpm for 4 h. The precipitates formed from the solution were aged for a day. The supernatant solution was decanted and the wet precipitates were washed several times by centrifugation using water until the pH was remaining near neutral region. The precipitates were dried at 80 °C for 10 h to remove water molecules perfectly. Portions of each dried precipitate were redispersed under constant stirring in beakers with 300 ml organic solvent: ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, Kanto Chemical Co. Inc., Japan), polyethylene glycol 600 ($\text{H}(\text{OC}_2\text{H}_4)_n\text{OH}$, Kanto Chemical Co. Inc., Japan), and ethanol ($\text{C}_2\text{H}_5\text{OH}$, Kanto Chemical Co. Inc., Japan). The resulting suspensions were placed in 2000 ml stainless steel pressure vessels equipped with magnetic stirrers. The vessels were then heated up to 250 °C at a rate of 10 °C/min. The final products were repeatedly washed with ethanol and centrifuged several times and then dried at 80 °C for 24 h.

2.2. Powders characterization

The phase of final ITO powders was identified by X-ray diffraction (XRD, Rigaku, D/max-2C, Japan) using $\text{Cu K}\alpha_1$ radiation. XRD patterns of ITO powders were obtained in the 2θ range between 20° and 80° with a step of 0.01° and a scan speed of 5 °/min. The crystallite size of the ITO powders was calculated from the line broadening of the (2 2 2) diffraction line according to the Scherrer equation:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where D is the crystallite size (in angstroms), λ the wavelength of $\text{Cu K}\alpha_1$ radiation, and β the corrected half-width of the diffraction peak. Degrees of relatively preferred orientation were estimated by (4 0 0)/(2 2 2) intensity ratios from XRD patterns of each ITO powder. The size and shape of the crystallized ITO powders were observed by transmission electron microscopy (TEM, JEM-2010, JEOL, Japan). The degree of agglomeration between primary particles was examined by field emission-scanning electron microscopy (FE-SEM, JSM-6330F, JEOL, Japan). The electrical surface properties of samples were determined by electrokinetic sonic amplitude (ESA, 9800, Matec Applied Sciences, MA). Suspensions containing a solid-phase weight fraction of 1% with water as solvent were dispersed by ultrasonic treatment for 30 min. All titrations were performed by the addition of acid to the initially basic suspensions. The optical properties of ITO powders were characterized by room temperature photoluminescence (PL, 1000M, SPEX, USA) with a He–Cd laser as a light source using an excitation wavelength of 325 nm and a power of 30 mW.

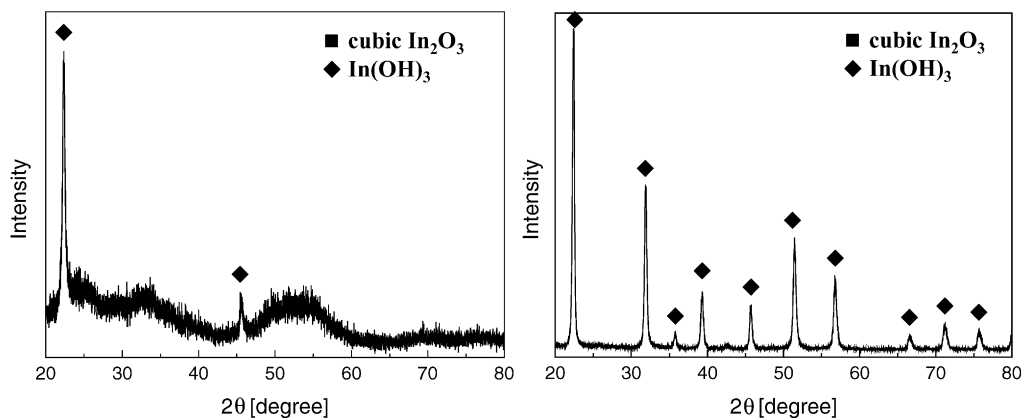


Fig. 1. XRD patterns of precipitates (left) and powders synthesized by the hydrothermal process.

3. Results and discussion

According to previous reports on the electrical properties of ITO materials,^{7,8,14} the size of the ITO crystalline lattice showed a minimum at approximately doping contents of 8 mol%, which corresponded to the optimum ratio where the lowest resistivity was obtained. Most of the hydrothermal crystallization is known to proceed via a dissolution–reprecipitation mechanism reaction, which is applicable to this study.^{14–16} The decrease in the crystallite size is followed by an increase in pH, since the nucleation rate is more rapid than the grain growth rate due to the predominant condensation reaction under basic conditions.¹⁷ Agli et al.¹⁸ also reported that crystallite size decreased and the degree of crystallization increased with higher concentrations of NH_4OH , where $-\text{OH}$ ligands derived from NH_4OH make the metal hydroxide precursor. It is suitable to accelerate Ostwald ripening, which more quickly dissolve the smaller grains. It is proposed that solvothermal treatment is an Ostwald ripening process and the dissolution process can control the kinetics of the growth of larger grains.¹⁹

Fig. 1 shows the XRD patterns of precipitates and powders synthesized by the hydrothermal process. It was observed that precipitates consisted primarily of amorphous and indium hydroxide. These precipitates were used as precursors for the synthesis of ITO powders in this study.

Powder synthesized by the hydrothermal process consisted of only indium hydroxide without oxide phases. Despite hydrothermal treatment from 200 to 270 °C for 6–120 h, no oxide phases were observed in the XRD patterns. Because the hydrothermal process does not have enough energy to break the bonds of the precursors. In order to prepare hydrothermally crystallized ITO nano-powders with a single phase below the supercritical condition, Udawatte and Yanagisawa^{2,12,13} reported that it was necessary to subject the hydrothermally derived precursors to an additional heat treatment.

In order to avoid additional heat treatment, organic solvents such as ethanol, ethylene glycol, and polyethylene glycol were used instead of water. Conventional hydrothermal

process is confined to conditions in which some reactants will decompose in the presence of water or the precursors are very sensitive to water, or some reactions will not happen while water exists, resulting in the failure in synthesis of the desired compounds. Thus, by substituting non-aqueous solvents for water, a solvothermal process has been developed which can prepare various nanocrystalline compounds and which can initiate some conventional solid-state reactions in organic media under mild conditions.¹¹

Fig. 2 shows XRD patterns of synthesized ITO powders by the solvothermal process with ethylene glycol as a function of the working temperature. Below 250 °C, powders consisted of mixed phases such as cubic In_2O_3 , $\text{In}(\text{OH})_3$, and InOOH . Since, there was not sufficient energy to completely break the precursor bonds to allow crystallization by the dissolution–reprecipitation mechanism. However, ITO powders synthesized by the solvothermal process just at 250 °C had patterns identified with the cubic structure without additional phases. In the solvothermal process with ethylene glycol as the solvent, it was observed that 250 °C was the critical temperature for forming a single oxide phase. Table 1 summarizes the physical properties of ITO powders synthesized by calcining the precipitates at 600 °C for 1 h in air

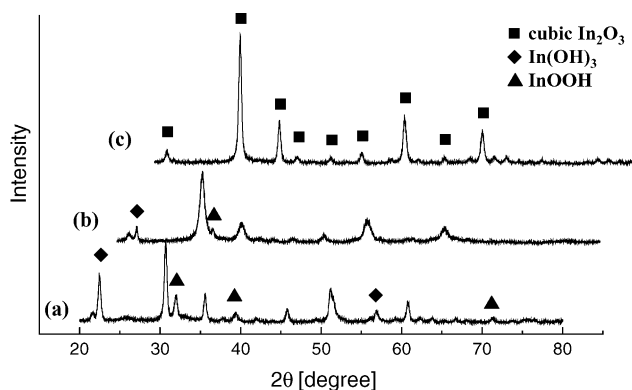


Fig. 2. XRD patterns of ITO powders synthesized by the solvothermal process with ethylene glycol as solvent: (a) at 210 °C, (b) 230 °C, and (c) 250 °C for 6 h, respectively.

Table 1

Physical properties of ITO powders synthesized by calcining the precipitates at 600 °C for 1 h in air and by the solvothermal process with ethylene glycol as solvent at various temperatures and pressures for 6 h, respectively

Sample name	Temperature (°C)	Pressure (psi)	Powders color	Crystal structure
ITO1	600	Atmosphere	Yellow	Cubic In ₂ O ₃
ITO2	210	180	Khaki	Cubic In ₂ O ₃ + In(OH) ₃ + InOOH
ITO3	230	270	Khaki	Cubic In ₂ O ₃ + In(OH) ₃ + InOOH
ITO4	250	410	Blue	Cubic In ₂ O ₃

and by the solvothermal process with ethylene glycol as the solvent at various temperatures for 6 h.

XRD patterns of ITO powders synthesized by calcining the precipitates at 600 °C for 1 h and by the solvothermal process in various solvents at 250 °C for 6 h shown in Fig. 3, indicate that all of the powders consisted of cubic In₂O₃ without additional phases. However, the color of synthesized ITO powders varied according to the process. Solvothermally synthesized powders were blue and the powders synthesized by coprecipitation using calcination were yellow. It is known that blue ITO powders have a higher carrier concentration than yellow ITO powders, due to more creation of the oxygen vacancies.²⁰ This indicated that the solvothermal process has an in situ reduction conditions. This is very advantageous for the preparation of blue ITO nano-powders, because the increase of carrier concentration and crystallization of precursors are simultaneously achieved in a single step.

Fig. 3 shows variations in crystallite size and (400)/(222) intensity ratio could be observed as a function of the types of solvent. Table 2 summarizes the physical properties including crystallite sizes calculated by the Scherrer equation in reference to the (222) XRD lines. It was observed that the higher solvent viscosity, the larger particle size, since nucleation rate is faster than crystalline growth rate in solvents with a lower viscosity. In addition, as can be seen in identical glycol group solvent, higher degree of polymerization caused larger particle size due to the steric hindrance of solvent, which retarded nucleation reaction.²¹

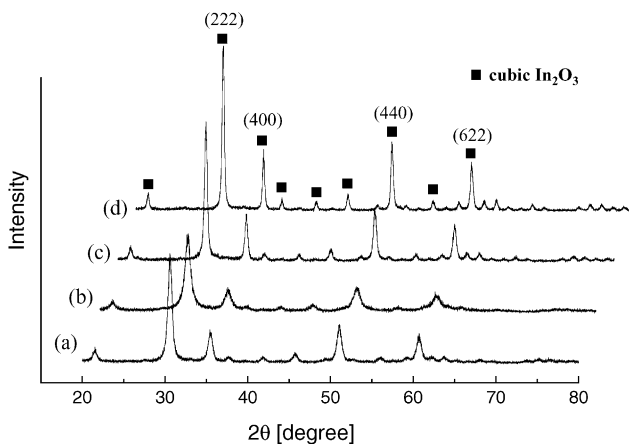


Fig. 3. XRD patterns of synthesized ITO powders at various conditions: (a) by calcining the precipitates at 600 °C for 1 h; by the solvothermal process in (b) ethanol, (c) ethylene glycol, and (d) polyethylene glycol 600 at 250 °C for 6 h, respectively.

Table 2

Physical properties of ITO powders synthesized by calcining the precipitates at 600 °C for 1 h and by the solvothermal process with various organic solvents at 250 °C for 6 h, respectively

Process	Solvent	Temperature (°C)	Crystallite size (nm)	Powder color
Calcination	None	600	15.24	Yellow
	EtOH	250	10.86	
Solvothermal	EG	250	19.12	Blue
	PEG	250	25.02	

The XRD intensity ratios provide information about the degree of relatively preferred orientation of synthesized ITO powders by the various processes. Powders with higher intensity ratios have higher Hall mobility and lower resistivity.^{3,22–24} Kamei and coworkers^{25,26} reported that (111) ITO films, whose dominant growth direction is along (111), accommodate larger amount of interstitial oxygen atoms into the films due to the non-uniform distribution of oxygen vacancies. The (111) ITO films always show a smaller density of free electrons compared to the (100) films despite being synthesized by the same process, since the interstitial oxygen atoms extinguish free electrons when combined with substitutional Sn atoms. Hence, preparation of ITO nano powders having a higher density of free electrons must involve retardation of the crystalline growth along (111) orientation. In general, it can be observed to relative density of free electron from (400)/(222) intensity ratios.

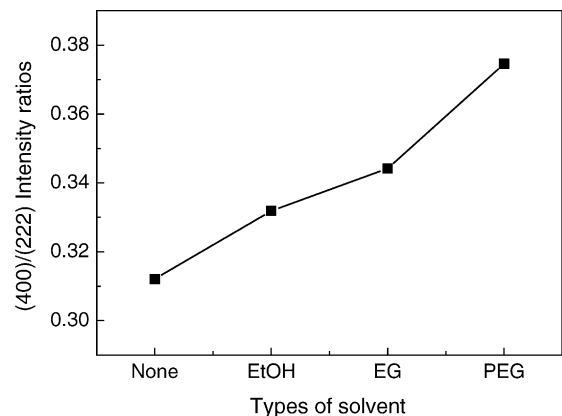


Fig. 4. (400)/(222) intensity ratios from XRD patterns of ITO powders synthesized by the coprecipitation using calcinations of precipitates (expressed as none in here) and by the solvothermal process in the various organic solvents.

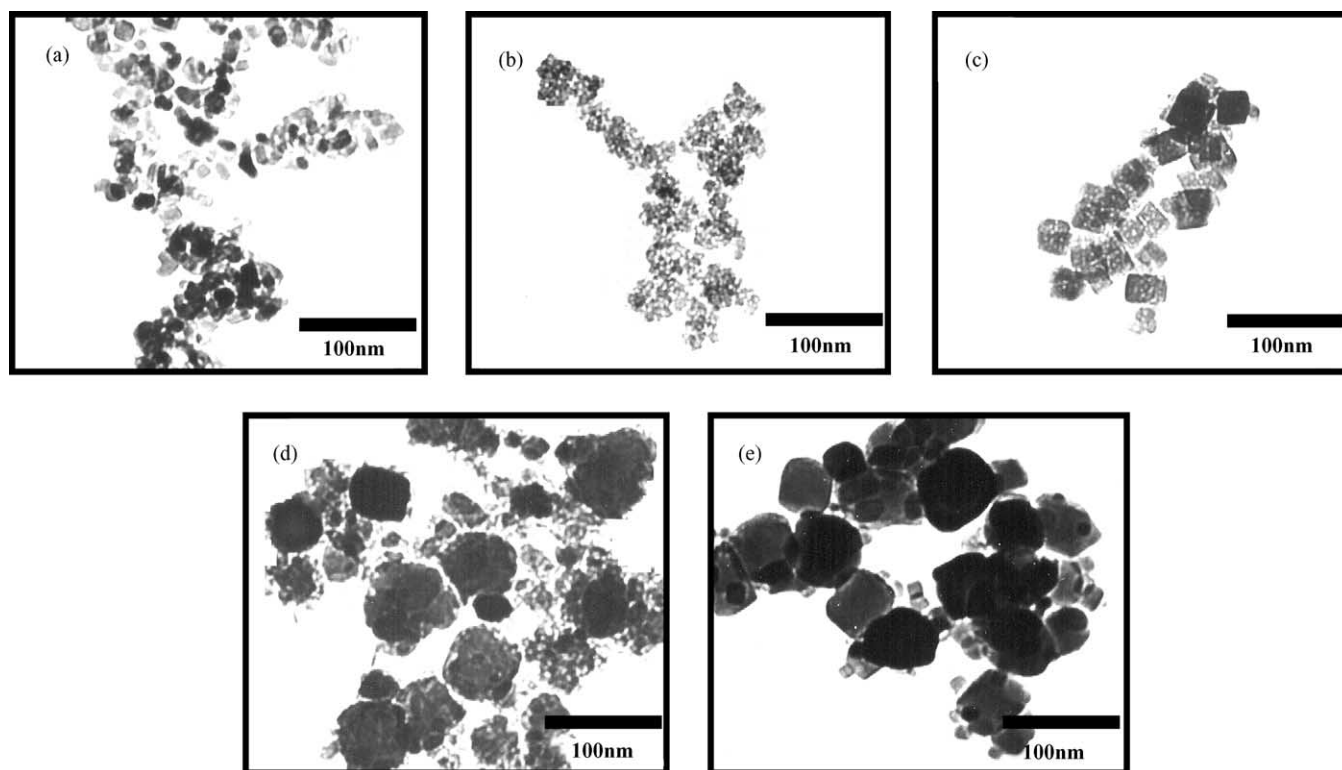


Fig. 5. TEM images of synthesized ITO powders at various conditions: (a) by calcining the precipitates at 600 °C for 1 h; by the solvothermal process in (b) ethanol, (c) ethylene glycol, (d) polyethylene glycol 600 at 250 °C for 6 h, and (e) polyethylene glycol 600 at 250 °C for 12 h, respectively.

Fig. 4 shows (400)/(222) intensity ratios from XRD patterns of synthesized ITO powders with various solvents. Intensity ratios of powders synthesized by the solvothermal process were larger than those synthesized by calcining the precipitates. And, in the solvothermal process, the intensity ratios of synthesized powders were larger in solvent with higher solvent viscosities, due to the crystalline growth in the preferred orientation along (100) direction.

Fig. 5 shows the transmission electron micrographs of the ITO powders by coprecipitation method using calcination of precipitates and the solvothermal process. It reveals that the shape and distribution of the synthesized particles by coprecipitation were nearly spherical and uniform, respectively. These micrographs show that the average size of the particles ranged from 10 to 20 nm, which agrees with the estimated crystallite size from XRD analysis. The shape and distribution of the particles synthesized by the solvothermal process in ethanol with the lowest viscosity of solvent used in this study were relatively spherical and uniform, respectively. However, synthesized ITO particles with glycol solvents, which had higher viscosities than the alcohol solvent, were square. This indicated that in high solvent viscosity the crystalline growth rate was faster than nucleation rate, resulting in the square shape of synthesized ITO particle, since the preferred orientation of ITO materials in the (100) direction is the fastest.²⁵ Moreover, in the glycol group solvents, it was found that synthesized ITO powders with higher polymerization number of used organic solvent tended to widen parti-

cles size distribution resulting from the relatively accelerated crystalline growth rate²¹ (see Fig. 5c and d). In polyethylene glycol 600 solvent, particles size and distribution were more influenced by solvent viscosity rather than holding time (see Fig. 5d and e).

It was anticipated that ITO powders with crystalline growth in the (100) direction would have higher conductivity of final ITO films due to the generation of free electrons resulting from the uniform distribution of the oxygen vacancies.^{25,26}

Fig. 6 shows the field emission scanning electron micrographs of the ITO powders crystallized by calcination and solvothermal process. Yellow ITO powders synthesized by the coprecipitation using calcination had high degree of agglomeration among the primary particles and non-uniform agglomerates' distribution than blue ITO powders synthesized by the solvothermal process. This indicated that it was very available to solvothermal process for synthesis of nano-sized ITO powders.

Fig. 7 illustrates the solvent effect on the electrokinetic behavior of ITO as a function of suspension pH at a particle weight fraction of 1%, where suspensions were prepared with ITO powders crystallized in various organic solvents and water as solvent.²⁷ This verifies that the degree of reduction varies depending on diverse types of solvent in the solvothermal process. The isoelectric points of all suspensions exhibited nearly in a neutral region between pH 7 and 8. It was observed that surface charges of all samples were

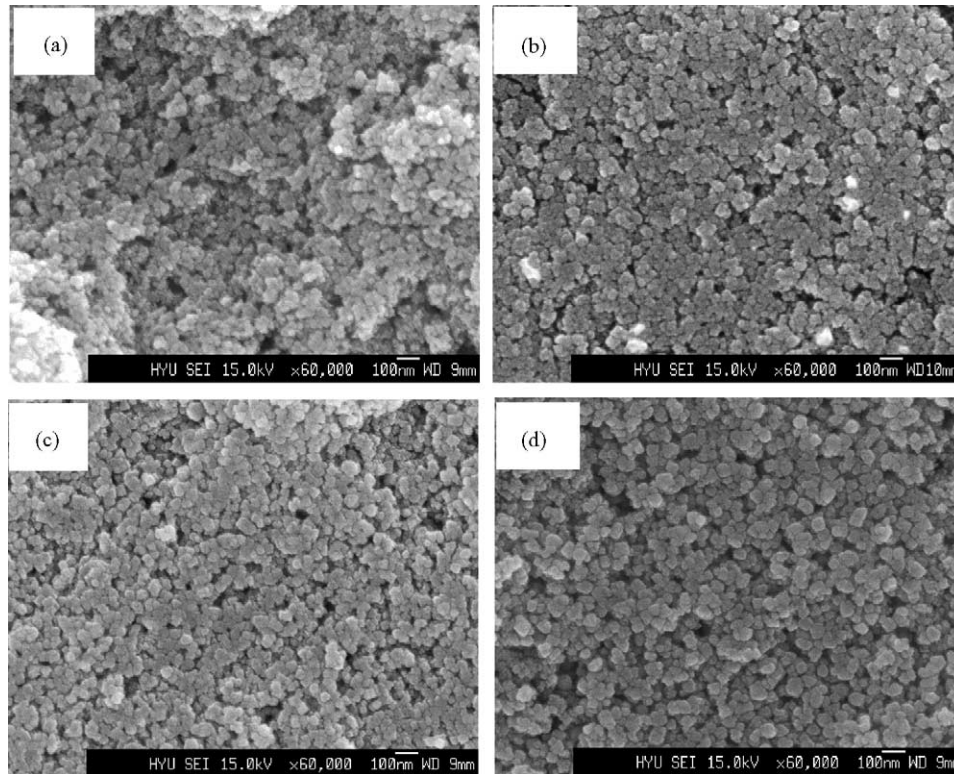


Fig. 6. FE-SEM images of synthesized ITO powders at various conditions: (a) by calcining the precipitates at 600 °C for 1 h; by the solvothermal process in (b) ethanol, (c) ethylene glycol, and (d) polyethylene glycol 600 at 250 °C for 6 h, respectively.

positive (positive dynamic mobility) in the acidic pH range. The ITO surface generally exhibits oxygen.²⁸ The reduction process creates oxygen vacancies in both the surface and lattice of ITO materials. The high degree of reduction causes a decrease in the total potential charge of the ITO surface due to the partial removal oxygen on the surface. In the solvothermal process for the synthesis of ITO powders, the difference in the dynamic mobility of each powder indicated varying degrees of reduction resulting the change in the total surface charge. This showed that the degree of reduction depended on viscosity of the solvent used, which corresponded to the crystalline growth orientation of ITO materials. Solvother-

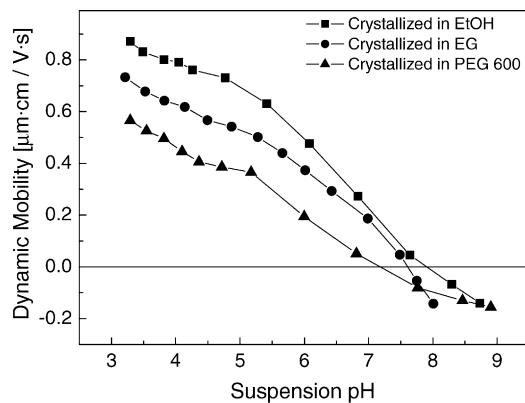


Fig. 7. Electrokinetic behavior of ITO powders synthesized by the solvothermal process as a function of the types of solvent and suspension pH.

mally synthesized ITO powders in polyethylene glycol 600 with the highest viscosity used in this study exhibited the lowest dynamic mobility. This means that a higher viscosity solvent causes higher degree of reduction, which is in a good agreement with analysis of (4 0 0)/(2 2 2) intensity ratios from the XRD patterns.

Fig. 8 illustrates the room temperature PL emission spectra and PL maximum intensities of each ITO powder syn-

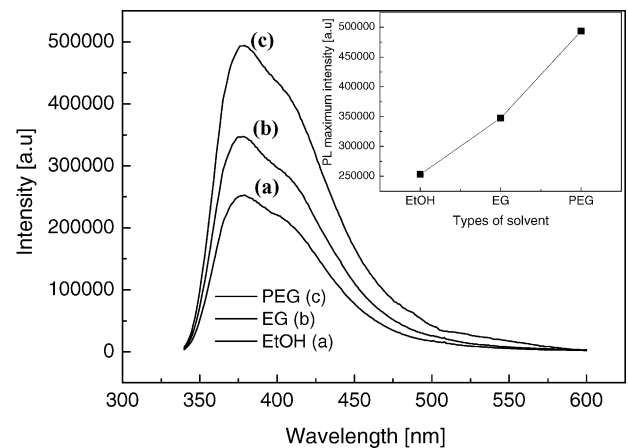


Fig. 8. PL emission spectra of each sample synthesized by the solvothermal process in: (a) ethanol, (b) ethylene glycol, and (c) polyethylene glycol 600 at 250 °C for 6 h, respectively. PL maximum intensities of each ITO powder synthesized by the solvothermal process plotted as a function of the types of solvent (inset).

thesized by the solvothermal process as a function of types of solvent. PL spectra were recorded under exactly the same conditions for all samples. It is shown that the main emission peak was at about 360 nm, which indicated suitable optical property for transparent conducting oxides (TCOs) materials. The most notable feature of Fig. 8 was that PL intensities increased with increasing solvent viscosity, which meant that increasing solvent viscosity influenced the generation of more free electrons resulting from the creation of oxygen vacancies.²⁹ These results were in a good agreement with results from XRD, TEM, and ESA. Therefore, it could be confirmed that solvothermally synthesized ITO powders in polyethylene glycol with the highest viscosity in this study would have higher conductivity of final ITO thin films, resulting from larger density of free electron.

4. Conclusions

Well-crystallized and nano-sized ITO powders were prepared by a solvothermal process from a precursor solution containing indium nitrate and tin chloride without an additional heat treatment. The results of this study show that the blue ITO nano-powders with only cubic phase could be directly obtained by using organic solvent instead of water. Comparison of the yellow ITO powders synthesized by the coprecipitation method using calcination of the precipitates and blue ITO powders synthesized by the solvothermal process indicated that the solvothermal process led to an in situ reduction reaction, which was confirmed with powders colors.

Solvent viscosity in the solvothermal process strongly influenced both physico-chemical and electrical properties of ITO powders. The synthesized ITO particles increased with increasing solvent viscosity in size, since high solvent viscosity relatively accelerates the crystalline growth rate in comparison with the nucleation rate with steric hindrance. So, the shape of synthesized ITO particles was subjected to be square, because the preferred orientation of ITO materials in the $\langle 100 \rangle$ direction is the fastest. It was anticipated that ITO powders with the crystalline growth along the $\langle 100 \rangle$ direction would have higher conductivity of final ITO thin films originated in increasing density of free electrons closely relating to the uniform distribution of the oxygen vacancies.

References

- Hwang, J. H., Edward, D. D., Kammler, D. R. and Mason, T. O., Point defects and electrical properties of Sn-doped In-based transparent conducting oxides. *Solid State Ionics*, 2000, **129**, 135–144.
- Udawatte, C. P. and Yanagisawa, K., Sintering of additive free hydrothermally derived indium tin oxide powders in air. *J. Solid State Chem.*, 2000, **154**, 444–450.
- Tahar, R. B. H., Ban, T., Ohya, Y. and Takahashi, Y., Tin doped indium oxide thin films: electrical properties. *J. Appl. Phys.*, 1997, **83**(5), 2631–2645.
- Devi, P. S., Chatterjee, M. and Ganguli, D., Indium tin oxide nanoparticles through an emulsion technique. *Mater. Lett.*, 2002, **55**, 205–210.
- Nadaud, N., Lequeux, N. and Nanot, M., Structural studies of tin-doped indium oxide (ITO) and $\text{In}_4\text{Sn}_3\text{O}_{12}$. *J. Solid State Chem.*, 1998, **135**, 140–148.
- Pramanik, N. C., Das, S. and Biswas, P. K., The effect of Sn(IV) on transformation of co-precipitated hydrated In(III) and Sn(IV) hydroxides to indium tin oxide (ITO) powder. *Mater. Lett.*, 2002, **56**, 671–679.
- Kim, B. C., Lee, J. H., Kim, J. J. and Ikegami, T., Rapid rate sintering of nanocrystalline indium tin oxide ceramics: particle size effect. *Mater. Lett.*, 2002, **52**, 114–119.
- Kim, B. C., Kim, S. M., Lee, J. H. and Kim, J. J., Effect of phase transformation on the densification of coprecipitated nanocrystalline indium tin oxide powders. *J. Am. Ceram. Soc.*, 2002, **85**(8), 2083–2088.
- Lee, J. S. and Choi, S. C., Crystallization behavior of nano ceria powders by hydrothermal synthesis using a mixture of H_2O_2 and NH_4OH . *Mater. Lett.*, 2004, **58**, 390–393.
- Piticescu, R. R., Monty, C., Taloi, D., Motoc, A. and Axinte, S., Hydrothermal synthesis of zirconia nanomaterials. *J. Eur. Ceram. Soc.*, 2001, **21**, 2057–2060.
- Yu, S. H., Hydrothermal/solvothermal processing of advanced ceramic materials. *J. Ceram. Soc. Jpn.*, 2001, **109**(5), S65–S75.
- Udawatte, C. P. and Yanagisawa, K., Fabrication of low-porosity indium tin oxide ceramics in air from hydrothermally prepared powder. *J. Am. Ceram. Soc.*, 2001, **84**(1), 251–253.
- Yanagisawa, K. and Udawatte, C. P., Preparation and characterization of fine indium tin oxide powders by a hydrothermal treatment and postannealing method. *J. Mater. Res.*, 2000, **15**(6), 1404–1408.
- Tomonaga, H. and Morimoto, T., Indium-tin oxide coatings via chemical solution deposition. *Thin Solid Films*, 2001, **392**, 243–248.
- Štefanić, G., Popović, S. and Musić, S., Influence of pH on the hydrothermal crystallization kinetics and crystal structure of ZrO_2 . *Thermochim. Acta*, 1997, **303**, 31–39.
- Tomaszewski, H., Weglarz, H. and Gryse, R. D., Crystallization of yttria under hydrothermal conditions. *J. Eur. Ceram. Soc.*, 1997, **17**, 403–406.
- Hirano, M. and Kato, E., Hydrothermal synthesis of nanocrystalline cerium(IV) oxide powders. *J. Am. Ceram. Soc.*, 1999, **82**(3), 786–788.
- Agli, G. D., Colantuono, A. and Mascolo, G., The effect of mineralizers on the crystallization of zirconia gel under hydrothermal conditions. *Solid State Ionics*, 1999, **123**, 87–94.
- Wu, N. C., Shi, E. W., Zheng, Y. Q. and Li, W. J., Effect of pH of medium on hydrothermal synthesis of nanocrystalline cerium(IV) oxide powders. *J. Am. Ceram. Soc.*, 2002, **85**(10), 2462–2468.
- Shimada, S. and Mackenzie, K. J. D., A novel method for crystal growth of indium oxide, In_2O_3 , from the vapour phase. *J. Cryst. Growth*, 1981, **55**, 453–456.
- Wang, C., Deng, Z. X., Zhang, G., Fan, S. and Li, Y., Synthesis of nanocrystalline TiO_2 in alcohols. *Powder Tech.*, 2002, **125**, 39–44.
- Kim, D., Han, Y., Cho, J. S. and Koh, S. K., Low temperature deposition of ITO thin films by ion beam sputtering. *Thin Solid Films*, 2000, **377/378**, 81–86.
- Thilakan, P. and Kumar, J., Studies on the preferred orientation changes and its influenced properties on ITO thin films. *Vacuum*, 1997, **48**, 463–466.
- Terzini, E., Thilakan, P. and Minarini, C., Properties of ITO thin films deposited by RF magnetron sputtering at elevated substrate temperature. *Mater. Sci. Eng.*, 2000, **B77**, 110–114.
- Kamei, M., Shigesato, Y. and Takaki, S., Origin of characteristic grain-subgrain structure of tin-doped indium oxide films. *Thin Solid Films*, 1995, **259**, 38–45.
- Kamei, M., Enomoto, H. and Yasui, I., Origin of the crystalline orientation dependence of the electrical properties in tin-doped indium oxide films. *Thin Solid Films*, 2001, **392**, 265–268.

27. Wäsche, R., Naito, M. and Hackley, V. A., Experimental study on zeta potential and streaming potential of advanced ceramic powders. *Powder Tech.*, 2002, **123**, 275–281.
28. Chaney, J. A., Koh, S. E., Dulcey, C. S. and Pehrsson, P. E., Surface chemistry of carbon removal from indium tin oxide by base and plasma treatment, with implications on hydroxyl termination. *Appl. Surf. Sci.*, 2003, **218**, 258–266.
29. Lee, S. W., Song, D. G., Lee, J. W., Kim, S. T., Park, I. Y. and Won, M. S., Enhancement of luminescence efficiency of ZnS:Cu nanocrystals by pH control. *Mater. Sci. Eng.*, 2003, **B103**, 241–245.