

Preparation of indium tin oxide powder from low-grade metallic indium and tin

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Abstract—Preparation of indium-tin oxide(ITO) powder by oxalic acid from metallic indium and tin was investigated. The intermediate(indium-tin oxalate salt) was formerly prepared at various conditions, and thermal decomposition was followed to obtain ITO powder for ITO target. Optimum conditions for preparation of the intermediate were oxalic acid concentration 2.0 M, pH 8.0, reaction temperature 80 °C and reaction time 6 hours. The purity of the intermediate could be increased by recrystallization up to 99.99% (4 N). The phase transition temperature of the intermediate to ITO powder was analyzed by TGA. The purity, crystal structure and particle shape of ITO powder were examined by ICP-OES, XRD and TEM, respectively. ITO powder obtained was spherical, whose size was 20-50 nm.

Keywords: Indium-tin Oxalate Salt, Indium-tin Oxide (ITO), Oxalic Acid, Indium Metal, Tin Metal

INTRODUCTION

Owing to the rapid development of IT industry, portable information devices are becoming diversified. Touch screens, in particular, are receiving growing interest. Indium tin oxide (ITO) is an essential material for fabricating touch screens, because transparent electrode can be made of ITO. Therefore, the demand of ITO in the IT industry is significantly increasing [1].

ITO is a well-known transparent conducting oxide (TCO) that has a wide range of applications because of its excellent physical and chemical properties, such as transmittance in the visible light region, electric resistance, chemical and thermal stability, electrode pattern machinability, and infrared reflectivity [2].

For the continuous formation of transparent and conductive ITO film on substrate by sputtering, nodules should be formed on the surface of substrate. These nodules' formation frequently causes failure due to its low deposition rate, especially in case of long-term sputtering. To reduce failure of the nodule formation, it is necessary to fabricate high-density ITO targets. High-density ITO targets can be fabricated by atmospheric-pressure sintering. For the atmospheric-pressure sintering, the particle size of ITO powder should be minimized [3].

Because of the easy reaction control and low energy cost, sol-gel method [4], thermal decomposition [5], and solvothermal process [6] have been widely used for manufacturing nanoparticles of inorganic materials. In sol-gel method, indium and tin in the sol state are frequently used as starting materials for synthesizing metal-organic compounds.

Many investigators have reported on the preparation and characterization of ITO thin film by sol-gel method [7-10]. Most of them have used metal-organic compounds as starting materials.

Even though metal-organic compounds have a merit of acquiring uniform particle size, they still put restriction on industrialization because the compounds are expensive and organic components might behave as impurities.

In this study, indium-tin oxalate salt was formerly precipitated from low grade metallic indium and tin by oxalic acid. Low grade metallic indium and tin are cheaper than conventional starting materials, metal-organic compounds. Excess oxalate and trace metal ions in low-grade metallic indium and tin could be removed via chemical precipitation and recrystallization. Indium-tin oxalate salt was calcined to form spherical greenish-yellow ITO powder with

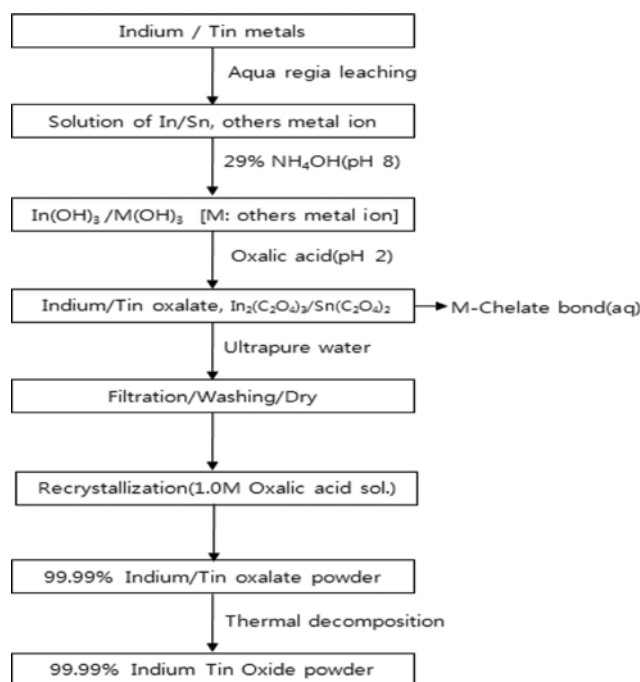


Fig. 1. Flow diagram for preparation of ITO powder.

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Table 1. Impure trace metal ions in metallic indium and tin analyzed by ICP-OES

Unit	(ppm, mg/L)											
Item	In	Sn	Cu	Cd	Co	Fe	Na	Ni	Pb	Zn	Mn	Cr
In metal	-	4482	1688	7	3.8	92.5	1.8	1382	328	125	-	-
Sn metal	8241		79	-	10.4	304	-	-	55.6	-	2.2	10

particles sizes of 20-50 nm. The procedure is shown in Fig. 1.

EXPERIMENTAL

0.059 M indium (99.189%, GMS21 Co. Ltd.) and 0.006 M tin (99.131%, GMS21 Co. Ltd.) metals were completely dissolved in 30 mL aqua regia; the acid concentration of 9.5 wt% was achieved by adding ultrapure water to make the mother liquid. During the dissolution process of metals, the temperature of solution was increased to 120 °C due to heat of dissolution.

The impure trace metal ions in metallic indium and tin were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, Optima 5300DV, Perkin Elmer, USA) and listed in Table 1. For aqua regia solution, HNO₃ (69%, JUNSH) was mixed with HCl (35%, JUNSH) at a volumetric ratio of 3 : 1.

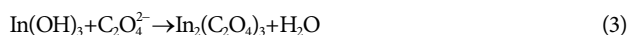
Initially, colloidal particles of In(OH)₃ and Sn(OH)₄ were formed by slow addition of precipitant, ammonia water (NH₄OH, 29%, JUNSEI), until pH of mother liquid became 8.0. The addition of oxalic acid (H₂C₂O₄·2H₂O, 99%, SAMCHUN) was followed to precipitate indium-tin oxalate salt. Indium tin oxalate salt precipitates were collected by vacuum filtration and washed with ultrapure water. Cake of indium tin oxalate salt was then dried in an oven at 80-100 °C for eight hours. To obtain high purity, the salt was dissolved and re-crystallized in oxalate solution. Finally, the salt was thermal decomposed in furnace at 600 °C to make indium tin oxide.

Ultrapure water was used to prepare all solutions in this experiments. The purity of prepared indium tin oxide was analyzed by ICP-OES. Crystalline and qualitative analysis were carried out by X-ray diffractometry (XRD, Rigaku D/MAX 2500, Japan), and the particle shape was analyzed by transmission electron microscopy (TEM, HITACHI LTD, H-7500, Japan).

RESULTS AND DISCUSSION

1. Effects of Oxalic Acid Concentration

Oxalic acid has been used for the precipitation of rare earth metal oxides [11], synthesis of polyhydroxy metal oxalates by auto-oxidation, and fabrication of open-framework tridimensional structures [12-14]. The chemical reactions for the precipitation of a metal-oxalate by oxalic acid are as follows:



During the precipitation of indium tin oxalate salt, it is expected that the trace metallic ions in the low grade metallic indium and tin can be removed because they do not form oxalate salt. If it is

possible, low grade metallic indium and tin can be used as starting materials and the cost will be reduced.

To examine the effect of concentration of oxalic acid on the removal of the trace metallic ions, the precipitation of indium tin oxalate salt proceeded for 6 hours with different oxalic acid concentrations. The precipitation temperature was fixed at 80 °C and the result is shown in Fig. 2. As shown, the removal rates of trace metallic ions generally increased with oxalic acid concentration; however,

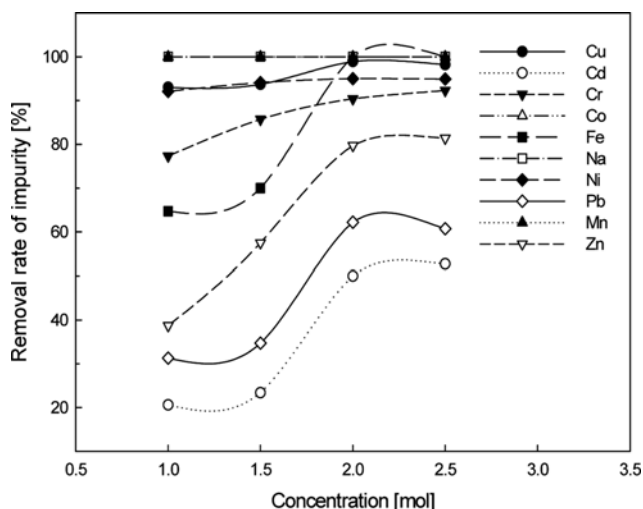


Fig. 2. Variation of removal rates of trace metallic ions with oxalic acid concentration at 80 °C.

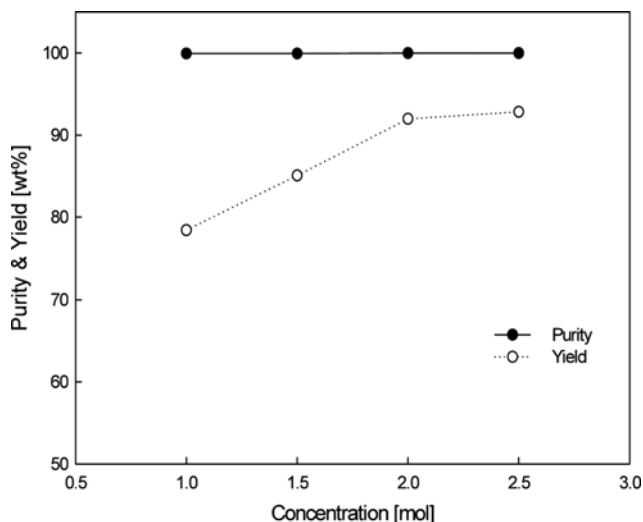


Fig. 3. Variation of purity and yield of indium tin oxalate salt with oxalic acid concentration at T=80 °C.

the increasing tendency significantly decreased above 2.0 M.

Co, Na, and Mn were completely removed regardless of the oxalic acid concentration, whereas Fe was completely removed when the oxalic acid concentration became more than 2.0 M. The removal rates of Cu, Cr, Ni, and Zn were in the range 80-98%, whereas those of Cd and Pb were relatively low (52.7-60.7%).

Purity and yield of indium tin oxalate salt were also examined at the same oxalic acid concentrations, and shown in Fig. 3. Fig. 3 shows that the yield increases with oxalic acid concentration, and gets to similar values above 2.0 M. Regardless of oxalic acid concentration, the purity of indium tin oxalate salt was higher than 99.9%. In detail, the purity slightly increased with oxalic acid concentration from 99.925% to 99.972%.

From these results, it turns out that 2.0 M is the most appropriate oxalic acid concentration for precipitation of indium tin oxalate salt.

The removal rates of trace metallic ions, yield and purity of indium tin oxalate salt were calculated by following equations, respectively:

$$\text{Removal (\%)} = \frac{\text{output wt (g)} \times \text{assay (\%)} - \text{input wt (g)} \times \text{assay (\%)}}{\text{input wt (g)} \times \text{assay (\%)}} \quad (4)$$

$$\text{Yield (\%)} = \frac{\text{output wt (g)} \times \text{Indium assay (\%)}}{\text{input wt (g)} \times \text{Indium assay (\%)}} \times 100 \quad (5)$$

$$\text{Purity (\%)} = 100 - \text{percentage of impurity (\%)} \quad (6)$$

2. Effect of pH

To study the effect of pH of mother solution on the precipitation of indium tin oxalate salt, mother solutions with different pH were prepared using ammonia solution. The mother solutions were mixed with 2.0 M oxalic acid to precipitate indium tin oxalate salt at 80 °C for 6 hours. The results are shown in Figs. 4 and 5.

Fig. 4 shows that the removal rates of trace metallic ions tend to decrease with pH. At pH 3.0, oxalic acid was completely dissolved, and thus no indium-tin oxalate salt was formed. This phenomenon

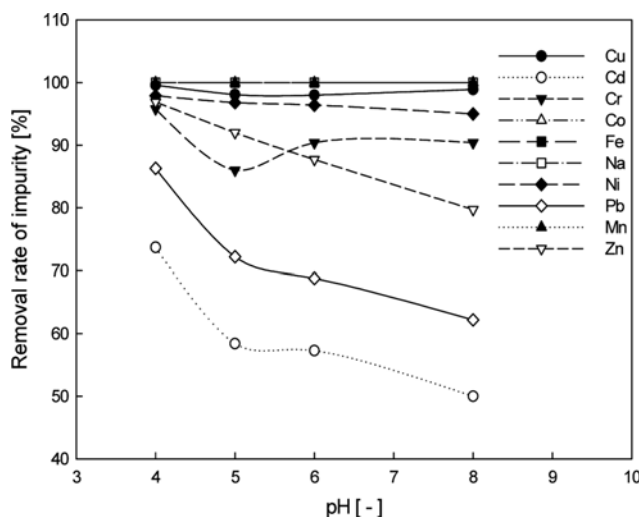


Fig. 4. Variation of removal rates of trace metallic ions with pH of mother solution at 80 °C.

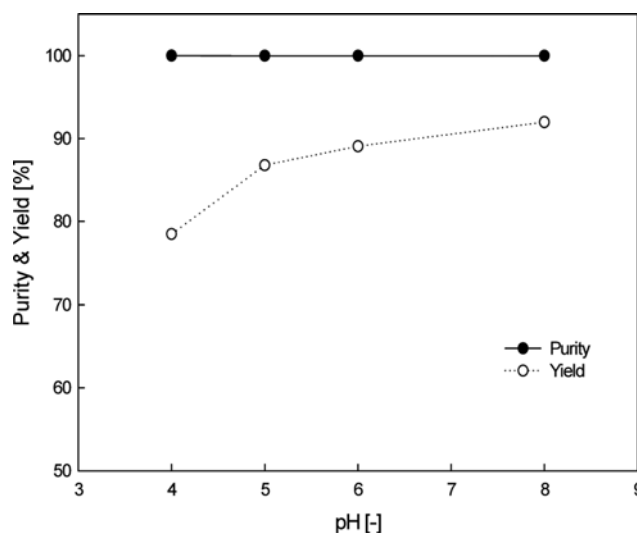


Fig. 5. Variation of purity and yield of indium tin oxalate salt with pH of mother solution at T=80 °C.

might be explained as follows. Indium and tin effectively form hydroxides at the low pH range of 2.0-3.0 [15]. At the higher pH range, the amount of indium and tin hydroxides diminishes and precipitates of other trace metallic ions can be formed. Therefore, trace metallic ions could be involved into precipitates in the high pH range. In case of Na ion, the removal rate remains at 100% regardless of oxalic acid concentration because Na (and Mn) ion does not make any precipitates.

The effect of pH of mother solution on the purity and yield of indium tin oxalate salt was quite different from that on the removal rate. Fig. 5 shows that the yield increases; however, the purity very slightly decreases with pH. These results also seem to be due to the presence of co-precipitation.

High yield of indium tin oxalate salt could be obtained at the cost of slight decrease in purity at pH 8.

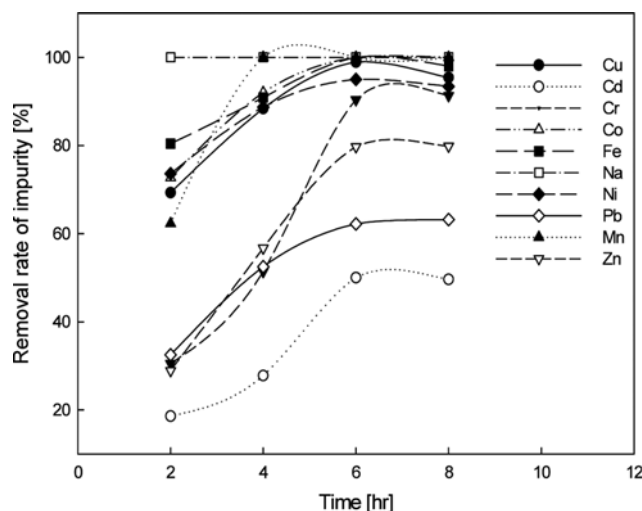


Fig. 6. Variation of removal rate of trace metallic ions with precipitation time at T=80 °C.

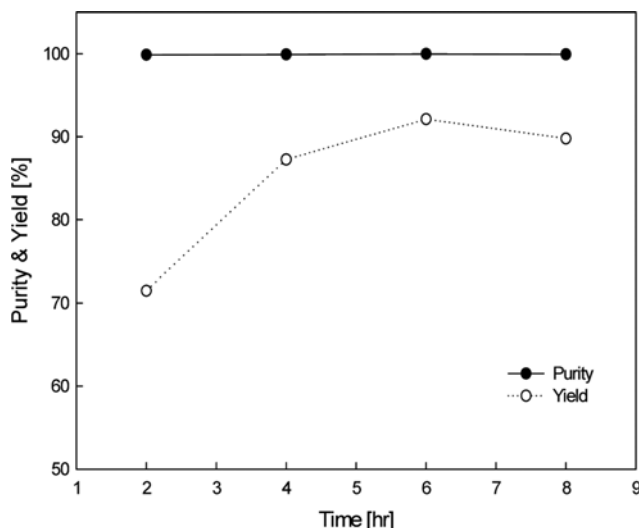


Fig. 7. Variation of purity and yield of indium tin oxalate salt with precipitation time at $T=80^{\circ}\text{C}$.

3. Effect of Precipitation Time and Temperature

To examine the effect of precipitation time on the removal rates of trace metallic ions, indium tin oxalate salt was precipitated at different precipitation times (see Fig. 6). pH of mother solution, concentration of oxalic acid, and precipitation time were 8.0, 2.0 M and 80°C , respectively.

The removal rates generally increased with reaction time up to 6 hours. The purity of indium tin oxalate salt also increased with precipitation time, and the highest purity, 99.974%, was reached at precipitation time of 6 hours (Fig. 7).

When the precipitation time was further increased more than 6 hours, the removal rate and purity did not change significantly. However, the yield was reduced to 89.78%. From these results, it turned out that some of the indium tin oxalate salt was dissolved in the acid.

Fig. 8 shows the effect of reaction temperature on the removal

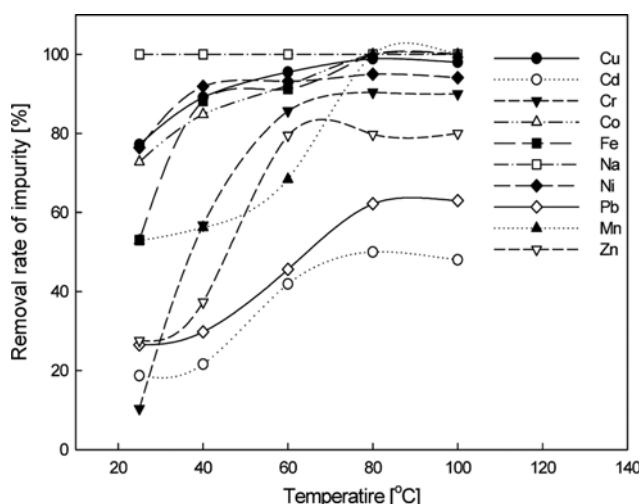


Fig. 8. Variation of removal rate of trace metallic ions with precipitation temperature at oxalic acid concentration of 2.0 M.

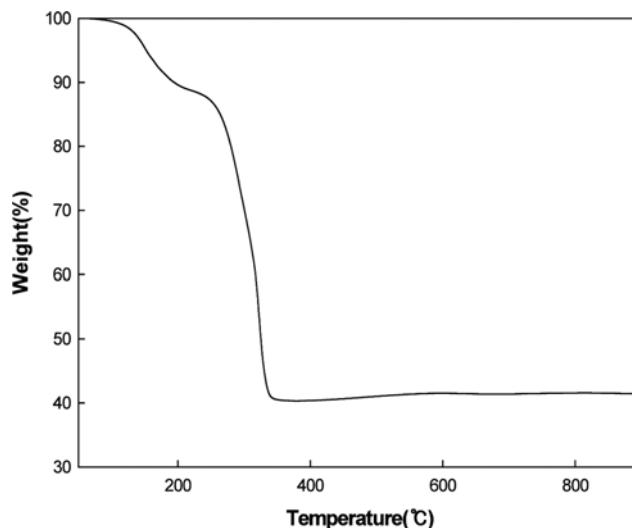


Fig. 9. TGA curve of indium-tin oxalate salt.

rate of trace metallic ions. The precipitation was performed for 6 hours at pH of 8.0 and oxalic acid concentration of 2.0 M. The removal rates increased with precipitation temperature up to 80°C . The purity also increased with precipitation temperature from 99.874% at 25°C to 99.974% at 80°C .

4. Thermal Decomposition

To determine the thermal decomposition temperature of indium-tin oxalate salt to indium/tin oxide, thermogravimetric analysis (TGA) was carried out in the range $50\text{--}900^{\circ}\text{C}$ at a rate of $10^{\circ}\text{C}/\text{min}$ (see Fig. 9). The thermogram shows that the weight of indium-tin oxalate salt began to decrease around 120°C . And the weight rapidly decreased in the temperature range of $260\text{--}340^{\circ}\text{C}$: the weight loss was 60 wt%. This result means the thermal decomposition temperature is 340°C , and our decompositions were at 600°C .

Fig. 10 shows the XRD analysis of indium/tin oxide powder prepared by thermal decomposition of indium tin oxalate salt. The XRD

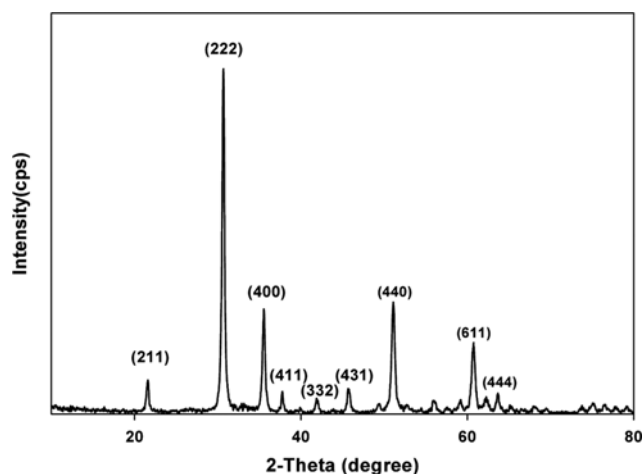


Fig. 10. XRD pattern of indium/tin oxide powder prepared from low grade metallic indium and tin. [Oxalic acid]=2.0 M, pH=8.0, $T=80^{\circ}\text{C}$, $t=6$ hours.

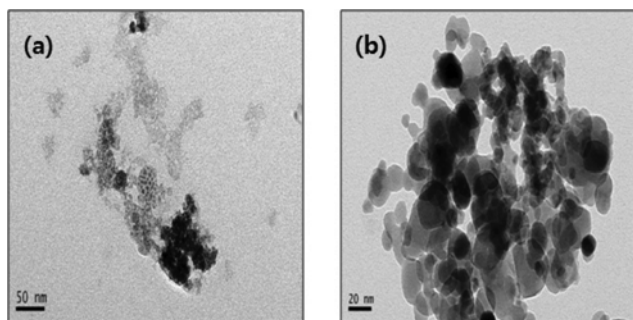


Fig. 11. TEM images of indium/tin oxide powder prepared from low grade metallic indium and tin. [Oxalic acid]=2.0 M, pH=8.0, T=80 °C, t=6 hours.

(a) Before thermal decomposition (Indium Tin Oxalate)
(b) After thermal decomposition (Indium Tin Oxide)

pattern does not show any diffraction peaks except for indium/tin oxide, which represents that indium/tin oxide was successfully prepared by thermal decomposition of indium tin oxalate salt.

Before and after thermal decomposition of indium tin oxalate salt, the shape and size of the powders were observed by TEM (see Fig. 10). Fig. 10 shows that amorphous shaped powders were changed to almost spherical with particle size of 20-50 nm.

Indium tin oxalate salt prepared at the optimum conditions was collected and dissolved again in 1M oxalate solution to increase its purity by recrystallization. The recrystallization process could increase the purity from 99.974% to 99.990%, at the cost of recovery rate decrease by about 7% from 91.97% to 85.50%.

CONCLUSIONS

Indium tin oxalate salt was successfully prepared from low grade metallic indium and tin by oxalic acid. The oxalate salt was then thermally decomposed at 600 °C to obtain indium tin oxide powder. The removal rate of trace metallic ions, purity and yield of the indium tin oxalate salt increased with oxalic acid concentration. These are also affected by the pH of the mother solution, precipitation temperature and time. The purity of indium-tin oxalate salt could be increased by re-crystallization process in 1 M oxalic acid solution. 99.99% indium tin oxide powder with particle size of 20-

50 nm could be obtained by precipitation by oxalic acid solution, re-crystallization and thermal decomposition of indium-tin oxalate salt.

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REFERENCES

1. S. S. Lee, N. L. Lee, K. L. Kim and T. W. Hong, *CLEAN, TECH.*, **18**, 69 (2012).
2. S. K. Park, Y. M. Roh, S. G. Lee, J. Y. Kim, C. H. Shin and J. W. Ahn, *Thin Solid Films*, **516**, 5822 (2008).
3. S. K. Park, Y. M. Roh, S. G. Lee, Y. Kim, C. H. Shin and J. W. Ahn, *RIST*, **21**, 352 (2007).
4. K. S. Park, M. H. Cho, S. J. Jin, C. H. Song and K. S. Nahm, *Korean J. Chem. Eng.*, **22**, 46 (2005).
5. P. Kamonchanok, M. Okorn, P. Joongjar and P. Piyasan, *Korean J. Chem. Eng.*, **24**, 397 (2007).
6. W. S. Nam and G. Y. Han, *Korean J. Chem. Eng.*, **20**, 1149 (2003).
7. F. Tsuyoshji, T. Junichi and K. K. Kohei, *J. Ceram. Soc. Japan*, **102**, 200 (1994).
8. B. H. T. Radhouane, B. Takatuki, O. Yutaka and T. Yasutaka, *J. Appl. Phys.*, **82**, 865 (1997).
9. B. H. T. Radhouane, B. Takatuki, O. Yutaka and T. Yasutaka, *J. Appl. Phys.*, **83**, 2631 (1997).
10. C. P. David, T. Whitson, D. Janiac, R. Beresford and O. Y. Cleva, *J. Appl. Phys.*, **85**, 8445 (1999).
11. M. H. Sung, W. S. Kim and J. S. Kim, *J. Kor. Inst. Chem. Eng.*, **36**, 510 (1998).
12. E. Coronad, C. Marti-Gastaldo, Galan-Mascaros Jr. and M. Cavallin, *J. American Chem. Soc.*, **132**, 5456 (2010).
13. P. A. Prasad, S. Neeraj, S. Natarajan and C. N. R. Rao, *Chem. Commun.*, 1251 (2000).
14. Y. Sihai, L. Guobao, T. Shujian, L. Fuhui and L. Jianhua, *J. Solid State Chem.*, 3703 (2005).
15. N. H. Kenneth, *J. Kor. Inst. Reso. Recy.*, **10**, 3 (2001).
16. Y. I. Lee and Y. H. Choa, *Kor. J. Mater. Res.*, **22**, 174 (2012).