

## Preparation of indium oxide from waste indium tin oxide targets by oxalic acid

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**Abstract**—Indium oxide manufacturing process from waste indium tin oxide (ITO) targets by oxalic acid was experimentally studied. The process was composed of precipitation of intermediate (indium-oxalate salt), re-crystallization and its thermal decomposition. The waste ITO targets were generated from vacuum sputtering process. The effects of operating parameters, such as solid dosage, oxalic acid concentration, reaction temperature and time, on the precipitation and re-crystallization of indium-oxalate salt were examined. Thermal decomposition to indium oxide was also investigated. The optimum reaction conditions to indium-oxalate salt were oxalic acid concentration 1.5 M, solid dosage 50 g/L, reaction temperature 80 °C and reaction time 8 hours. The purity of indium-oxalate salt prepared by precipitation and re-crystallization was 99.99% (4 N), and the salts were thermally decomposed to indium oxide at over 600 °C. The purity of the final product, indium oxide, was dependent on that of the intermediate, indium oxalate salt.

**Keywords:** Indium-oxalate Salt, Waste ITO Targets, Oxalic Acid, Indium Oxide

### INTRODUCTION

ITO targets are a core component of flat panel displays, such as LCDs, PDPs, and OLEDs. The rapid expansion of the IT industry and development of new and renewable energy sources have led to the high demand on ITO targets. The demand is expected to increase continuously in various devices, such as solar cells, TVs, and smart phones [1].

For the fabrication of ITO targets in a conventional process, indium metal is first converted into highly pure indium oxide ( $\text{In}_2\text{O}_3$ , 99.995%) via physical and chemical purification processes. Indium oxide is the mixed with tin oxide, and then molded and sintered. The sintered body can be used for ITO targets [2]. At the final stage, ITO coating should be applied on the surface of a glass substrate to achieve conductivity and transparency toward visible light [3].

Conductive and transparent ITO films on a substrate could be made by sputtering process. In this process, only about 3% of the ITO is deposited on a substrate to make ITO targets, about 27% is deposited on the sputtering equipment and mask, and 70% is discarded as waste.

Because indium is very expensive and has limited availability, it is important to develop recycling technologies of waste ITO targets. The conventional methods for recycling waste ITO targets recover indium metal by electrolysis or chemical precipitation [4-8]. Unfortunately, these methods are known to have various disadvantages. Some of these processes cause environmental pollutions, and/or generate a large amount of waste acids. In addition, the processes are complex and expensive.

Recently, recycling processes, including solvent extraction, absorp-

tion and grinding, have been actively studied [9-12]. However, even though the purity of indium recovered by these processes is fairly high (>99.995%), the problems due to expensive solvent extractants and operating costs need to be solved. Furthermore, these pro-

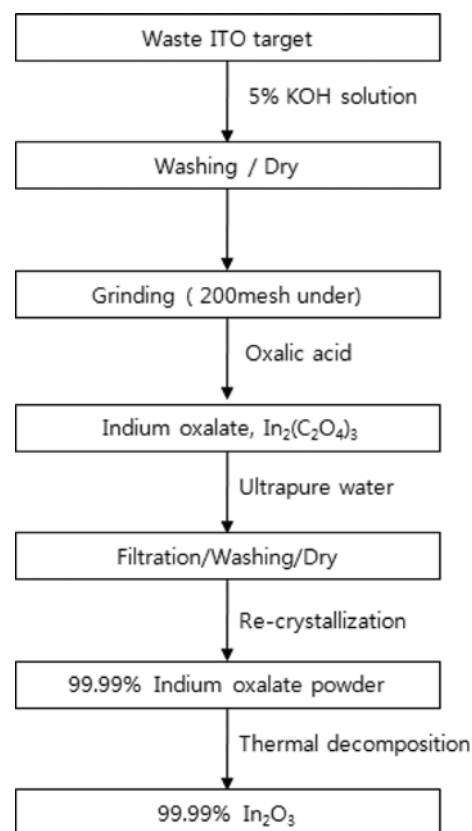


Fig. 1. Flow diagram of waste ITO targets recycling process to indium oxide.

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**Table 1. Composition of waste ITO target analyzed by ICP-OES**

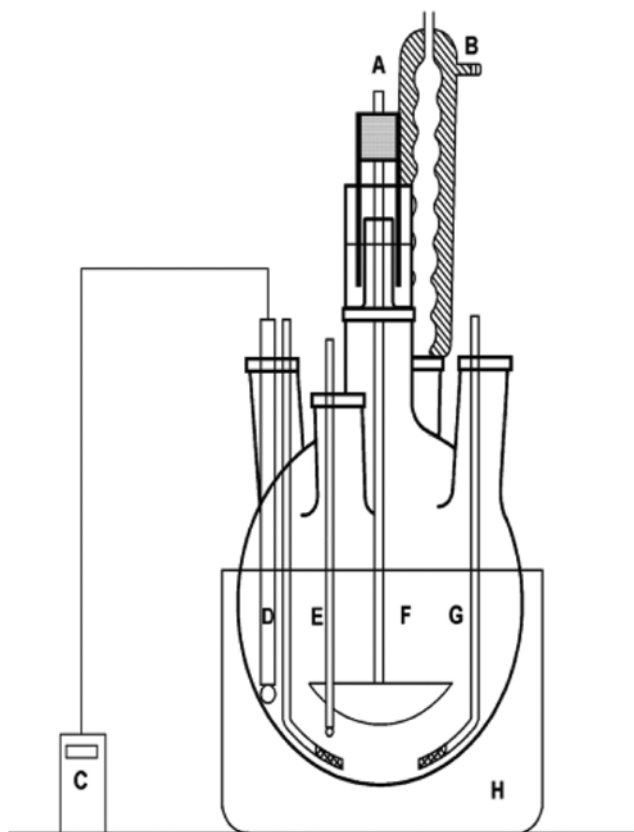
Components	In	Sn	Ni	Cu	Fe	Pb	Al	Mo
Composition [ppm]	767,750	74,800	570	180	2,400	1,400	460	110

cesses also generate environmental pollution problems.

In this study, to recover highly pure indium oxide by an economical and environmentally friendly method, we investigated a process which goes via indium oxalate salt. As shown in Fig. 1, oxalic acid precipitates indium oxalate salt by formation of a metal-complex compound. During the precipitation and re-crystallization, impure metallic ions could be removed to form highly pure indium-oxalate salt. The resultant indium oxalate salt could be thermally decomposed to give indium oxide by calcination.

### EXPERIMENTAL

In this research, waste ITO targets generated from ITO targets manufacturing process were used. The waste ITO targets were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, Optima 5300DV, Perkin Elmer, USA) and the result is listed in Table 1. As shown, waste ITO contains several impure metal ions, such as Fe, Pb, Ni, Al, etc.

**Fig. 2. Schematic diagram of experimental apparatus.**

- |                     |                                      |
|---------------------|--------------------------------------|
| A. Sealing stirrer  | E. Thermometer                       |
| B. Reflux condenser | F. 5-Neck flask (Pyrex glass 500 mL) |
| C. pH meter         | G. Glass baffle                      |
| D. pH electrode     | H. Oil bath                          |

The waste ITO targets were pretreated using 5% KOH solution to eliminate organic contaminants and then roughly ground in a mortar. For more pulverization, a Mill-type grinder (MF-10.2 Impact grinding, IKA, Germany) equipped with a 200-mesh sieve was used.

Finely pulverized waste ITO reacted with oxalic acid solution to precipitate indium-oxalate salt. Ultrapure water was used for preparing all the solutions in these experiments. The salt was then thermally decomposed to indium oxide by calcination at 600 °C.

As shown in Fig. 2, a 500 mL 5-neck Pyrex glass flask was used for reaction chamber. For smooth mixing, a stirrer and glass baffles on both sides of the flask were attached. To block any contact with surrounding air, the flask was completely air-tightened. Oil bath and standard thermometer were also used to verify temperature deviation within  $\pm 1$  °C.

For the precipitation of indium-oxalate salt, oxalic acid solution and waste ITO powder were placed in the flask and temperature was controlled in the range 20-100 °C. As the reaction precipitation proceeded, the dark grey color of the waste ITO powder changed to white, the color of the indium oxalate salt. The precipitated indium-oxalate salt was vacuum-filtrated and washed with ultrapure water several times. The salt was dried in a drier at 100 °C for about 8 hours, and recrystallized by oxalic acid solution to increase the purity, and then thermally decomposed to indium oxide by calcination in a furnace.

The purity of the precipitated indium oxalate salt and indium oxide was analyzed by ICP-OES. The crystalline and qualitative analyses of these products were also carried out by X-ray diffraction (XRD, Rigaku D/MAX 2500, Japan). Particle shape was analyzed by scanning electron microscopy (SEM, HITACHI S-2400, Japan).

### RESULTS AND DISCUSSION

#### 1. Effect of Reaction Time

Waste ITO powder used in this research was dark gray initially, and the color gradually turned to white as the reaction to indium oxalate salt proceeded. Therefore, color change of the solid material in oxalic acid solution could be a good parameter for the formation of indium oxalate salt.

Reaction to indium oxalate salt was under the conditions of reaction temperature 80 °C, solid dosage 50 g/L and concentration of oxalic acid solution 1.5 M. And the color change was optically observed. The color of solid material remained the same as that of the waste ITO powder until 7 hours, and it rapidly changed to white.

To exactly verify the transition progress of waste ITO powder to indium oxalate salt, XRD patterns of solid materials in reaction solution at different reaction times were measured and are shown in Fig. 3. XRD peaks of solid materials whose reaction time is less than 6 hours are similar to those of waste ITO powder. The XRD peaks for 8 and 10 hours show clearly different patterns, which is the same as those of indium oxalate salt. Therefore, for the com-

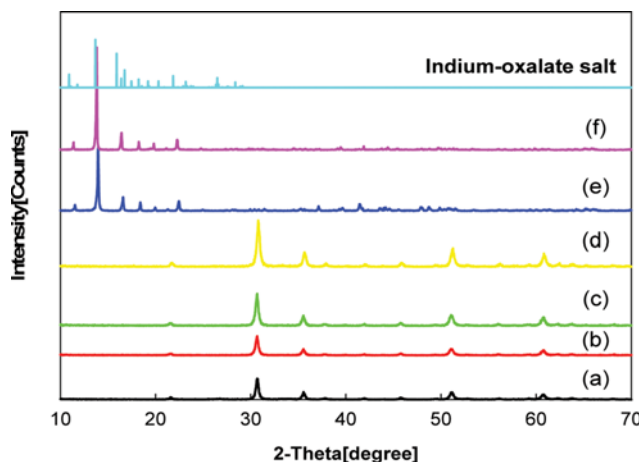


Fig. 3. Variation in XRD patterns of solid materials with reaction time at  $C_{\text{oxalic acid}} = 1.0 \text{ mol}$ ,  $T = 80^\circ\text{C}$ .

(a) Waste ITO, (b) 2 hrs, (c) 4 hrs, (d) 6 hrs, (e) 8 hrs, (f) 10 hrs

plete conversion to indium oxalate salt, it might be recommended that the most appropriate reaction time should be at least 8 hours.

## 2. Effect of Solid Dosage

Some researchers reported that oxalic acid could be used for the precipitation of rare metal oxalate salts to make metal oxides [13, 14]. Renovative researches on the metal leaching using microorganisms also have been carried out, and found *Aspergillus niger* produces organic acids (citric acid and oxalic acid) via metabolism reactions, and the organic acids can be used to leach rare metals [15].

For the preparation of highly pure indium oxide from waste ITO powder, it is necessary to remove the impure metal ions in waste ITO during the precipitation of indium oxalate salt. To establish the optimum conditions for the precipitation of indium oxalate salt, the effect of solid dosage of waste ITO powder on the removal rate of impure metal ions was investigated and shown in Fig. 4.

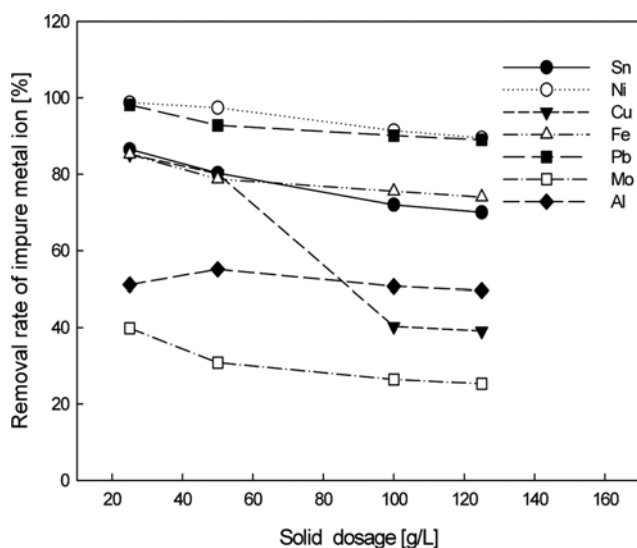


Fig. 4. Variation in removal rate of impure metal ions with solid dosage at  $80^\circ\text{C}$ .

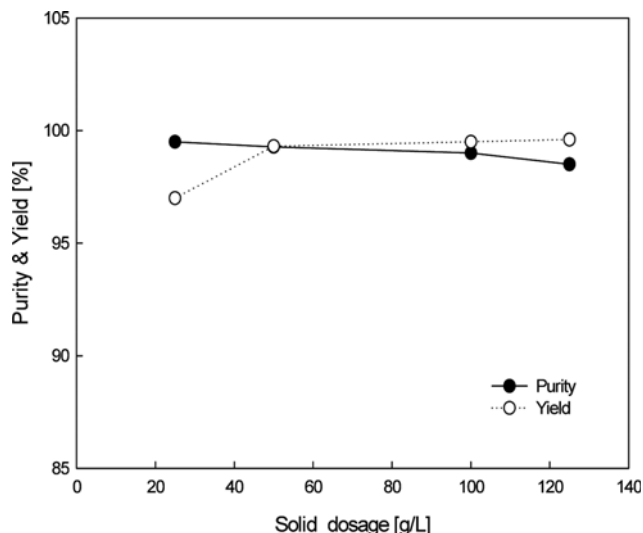


Fig. 5. Variation in purity and yield of indium oxalate salt with solid dosage at  $80^\circ\text{C}$ .

Removal rate was defined as the ratio of amount removed to that in waste ITO. The removal rates mostly decreased with solid dosage. In detail, the removal rates of major impure metal ions (Sn, Ni, Fe, Pb), whose content was more than 500 ppm, were higher than 80% at the solid dosage of 25 g/L.

In case of minor impure metal ions, the removal rate of Cu was 85.2% at 25 g/L, even though the rate rapidly decreased to 40.3% with solid dosage. Al and Mo showed relatively low removal rates of 26.4% and 50.7%, respectively. However, because of their low content in waste ITO, the effect on the purity of indium oxalate salt might be limited.

The decreasing tendency of removal rate with solid dosage might be attributed to the fact that high solid dosage could make more coprecipitates of the impure metal ions over their solubility in oxalic acid solution.

Fig. 5 shows the variation in purity and yield of the indium oxalate salt with solid dosage. The yield increases with solid dosage up to 50 g/L and stays almost constant, while the purity slightly decreases in the whole range of solid dosage. Low yield at low solid dosage of 25 g/L might be due to the solubility of indium oxalate salt in oxalic acid solution, and slight decrease in purity with solid dosage is responsible to the decrease in removal rate of impure metal ions.

## 3. Effect of Oxalic Acid Concentration

To examine the effect of oxalic acid concentration on the removal rates of impure metal ions, precipitation reaction was performed at reaction temperature of  $80^\circ\text{C}$ , reaction time of 8 hours and solid dosage of 50 g/L. The oxalic acid concentration was varied from 0.5 to 2.0 M.

Fig. 6 shows that the removal rates of impure metal ions generally increase with oxalic acid concentration up to 1.0 g/L, and remain almost constant with the exception of Cu. Even though the removal rate of Cu decreases with oxalic acid concentration above 1.0 g/L, it may not have a significant effect on the purity of indium oxalate salt because of its low content in waste ITO powder.

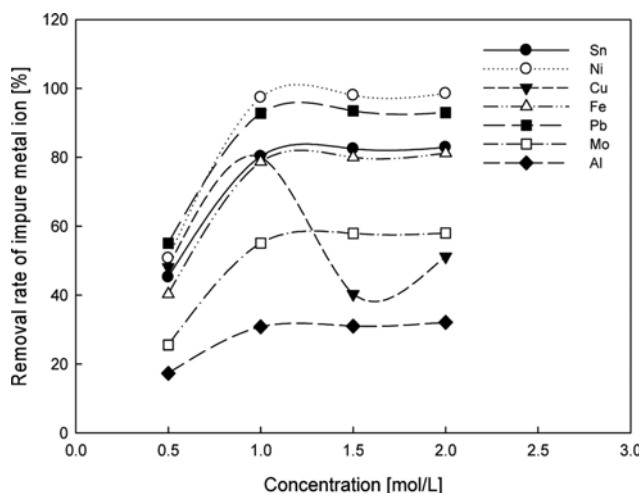


Fig. 6. Variation in removal rate of impure metal ions with oxalic acid concentration at  $T=80\text{ }^{\circ}\text{C}$ .

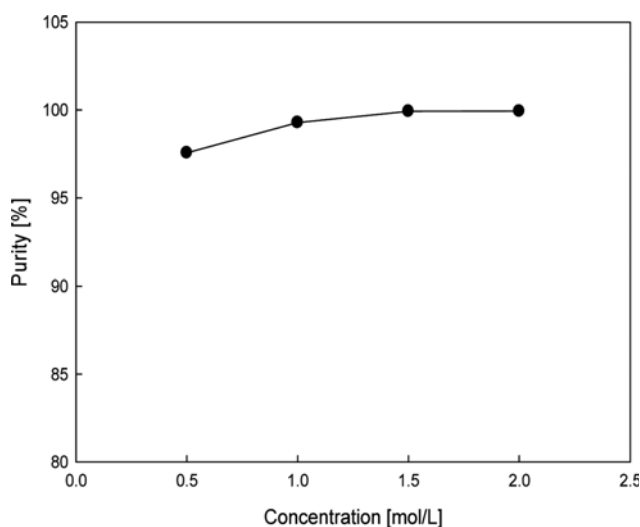


Fig. 7. Variation in purity of indium oxalate salt with oxalic acid concentration at  $T=80\text{ }^{\circ}\text{C}$ .

The effect of oxalic acid concentration on the purity of indium oxalate salt is shown in Fig. 7. The purity slightly increases with the oxalic acid concentration. However, increasing rate decreases with the concentration. As a whole, the purity does not show any meaningful difference with the concentration of oxalic acid solution. Therefore, it could be concluded that appropriate oxalic acid concentration for this precipitation reaction is 1.5 M.

#### 4. Effect of Reaction Temperature

Fig. 8 shows the removal rates of impure metal ions at different reaction temperatures. The reaction conditions were reaction time of 8 hours, solid dosage of 50 g/L and oxalic acid concentration of 1.5 M.

The removal rates of all the impure metal ions are very low at  $20\text{ }^{\circ}\text{C}$ , and gradually increase with reaction temperature. However, the rate did not change substantially when the temperature became higher than  $80\text{ }^{\circ}\text{C}$ . The removal rates of major impure metal ions (Sn, Ni, Fe, Pb) at  $80\text{ }^{\circ}\text{C}$  are more than 80%. The increasing ten-

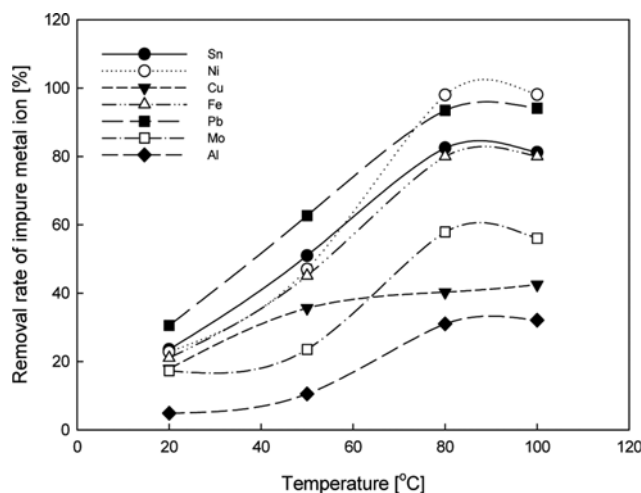


Fig. 8. Variation in removal rate of impure metal ions at different reaction temperatures.  $C_{\text{Oxalic acid}}=1.5\text{ mol}$ , reaction time=8 hrs.

endency of removal rates might be due to the increase in solubility of metal ions with reaction temperature.

The purity of indium oxalate salts formed at 20, 50 and  $80\text{ }^{\circ}\text{C}$  was 97.760%, 99.160%, and 99.921%, respectively. As the temperature was further increased to  $100\text{ }^{\circ}\text{C}$ , the purity increased to 99.931%.

#### 5. Recrystallization

From the results above, it is expected that the indium oxalate salt with highest purity could be prepared at the conditions of reaction time 8 hours, reaction temperature  $80\text{ }^{\circ}\text{C}$ , solid dosage 50 g/L, oxalic acid concentration 1.5 M. The purity of the salt prepared at the conditions was 99.921%. Even though this value is fairly high, it is still unsatisfactory to be used for ITO target.

For the purpose of additional increase in the purity of indium-oxalate salt, recrystallization of the salt by oxalic acid solution was followed at the same precipitation conditions. Indium-oxalate salt in the oxalic acid solution was dissolved and recrystallized during the agitation, and the impure components in the salt were eliminated. After recrystallization, the purity of the salt increased to 99.990%. This purity might be good enough for the use to ITO target; however, the yield to the indium-oxalate salt decreased from 97% to 91%.

#### 6. Thermal Decomposition of Indium Oxalate Salt

Indium oxalate salt was thermally decomposed to prepare indium oxide. To determine the thermal decomposition temperature of precipitated indium-oxalate salt, thermogravimetric analysis (TGA) of the salt was carried out in the temperature range  $50\text{--}900\text{ }^{\circ}\text{C}$  at a rate of  $10\text{ }^{\circ}\text{C}/\text{min}$ . Fig. 9. shows TGA curve of indium oxalate salt. The mass of the salt began to decrease at around  $150\text{ }^{\circ}\text{C}$ , and the mass loss became rapid above  $245\text{ }^{\circ}\text{C}$ , and reached 60 wt% at  $340\text{ }^{\circ}\text{C}$ .

The thermal decomposition of precipitated indium oxalate salt was performed at  $600\text{ }^{\circ}\text{C}$  for 4 hours. The XRD analysis of thermally decomposed indium oxalate salt was performed (see Fig. 10). For the comparison, XRD patterns of reference indium oxide and precipitated indium oxalate salts are also shown in Fig. 10. The XRD pattern of decomposed salt shows the same diffraction peaks as that of reference indium oxide, which is quite different from that

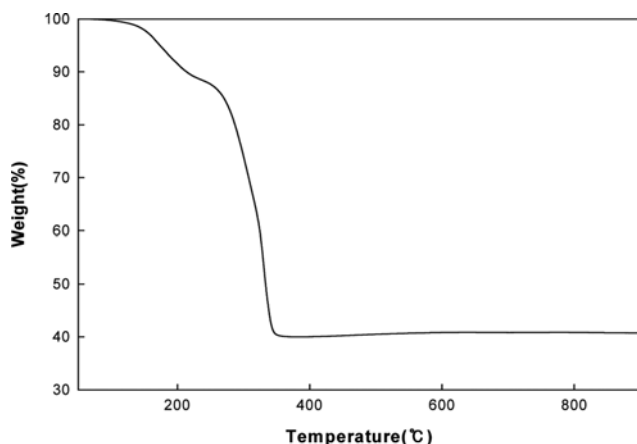


Fig. 9. TGA curve of indium-oxalate salt.

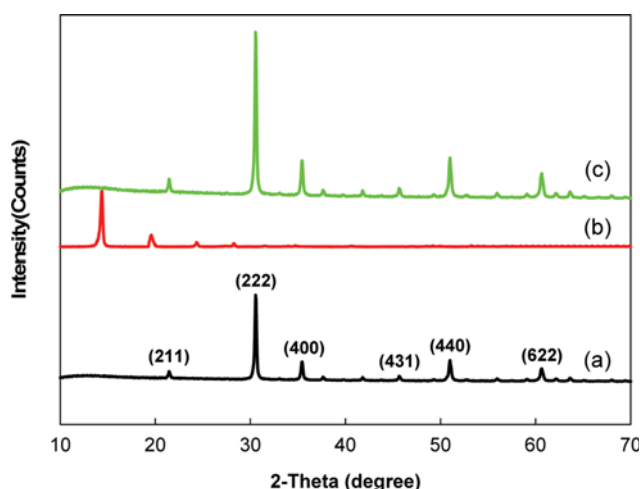


Fig. 10. X-ray diffraction patterns of prepared indium oxide powder from waste ITO target.

(a) Reference indium oxide, (b) before thermal decomposition, (c) after thermal decomposition

of indium oxalate salt. From this result, it could be concluded that a phase change to indium oxide has occurred during thermal decomposition. After the phase change, there was no significant purity difference between indium oxide and indium oxalate salt.

SEM images of prepared indium oxide are examined and shown in Fig. 11. The prepared indium oxide powder has octahedron shapes and the particle size is in the range 20-50 nm.

## CONCLUSIONS

Indium oxide was prepared from waste ITO target and oxalic acid by reaction precipitation. The process was composed of precipitation of intermediate (indium-oxalate salt), re-crystallization and its thermal decomposition. The purity of the indium oxide was dominated by that of indium oxalate salt, which mainly depends on the removal rate of impure metal ions in waste ITO target. The removal rate increases with reaction temperature and concentration of oxalate solution. However, the removal rate of major impure metal ions decreased with solid dosage. Formation of indium oxalate salt took about 8 hours, and the purity of the salt was higher than 99%. The purity of the salt could be increased by recrystallization at the cost of yield. The indium oxalate salt thermally decomposed to indium oxide at 600 °C for 4 hours. The prepared indium oxide has octahedron shapes and the particle size is in the range 20-50 nm.

## ACKNOWLEDGEMENT

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## REFERENCES

1. T. Minami, *Thin Solid Films*, **516**, 5822 (2008).
2. Y. M. Kang, Y. J. Lee, S. B. Heo, H. M. Lee, M. S. Lee, Y. S. Kim and D. I. Kim, *Korean J. Mater. Res.*, **22**, 24 (2011).

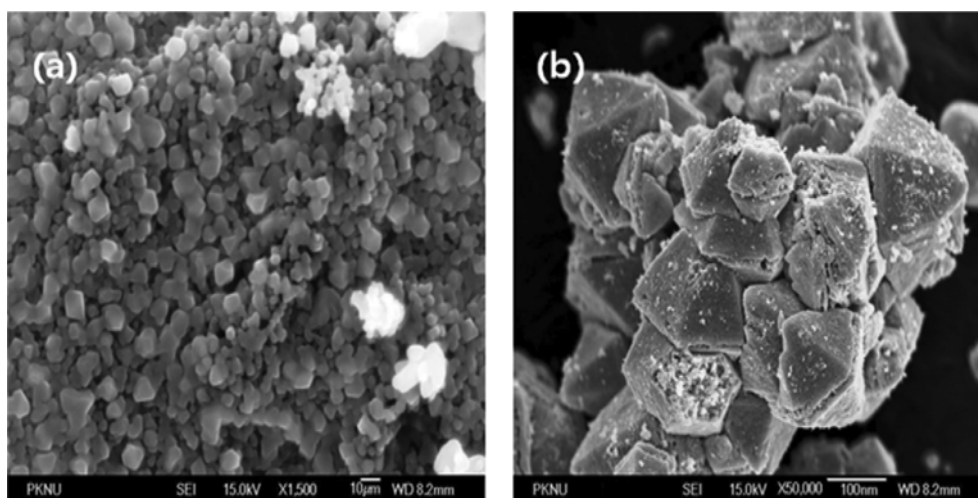


Fig. 11. SEM images of prepared indium oxide powder from waste ITO target.

(a)  $\times 1500$ , (b)  $\times 50000$

3. S. Gardonio, L. Gregoratti, D. Scaini, C. Castellarin-Cudia, P. Dudin, P. Melpignano, V. Biondo, R. Zamboni, S. Caria and M. Kiskinnova, *Organic Electronics*, **9**, 253 (2008).
4. S. J. Hong, *Electro. Parts Comp.*, **12**, 70 (2008).
5. N. H. Kenneth, *J. Korean Inst. Res. Recy.*, **10**, 5 (2001).
6. N. H. Kenneth, S. Kondoju, K. W. Park and H. M. Kang, *Geosystem Eng.*, **5**, 93 (2002).
7. M. K. Barakat, *Hydrometallurgy*, **49**, 63 (1998).
8. H. Y. Lee, S. G. Kim and J. K. Oh, *J. Korean Inst. Res. Recy.*, **2**, 2 (1993).
9. A. P. Paiva, *Sep. Sci. Technol.*, **36**, 1395 (2001).
10. T. N. Kwon and C. Jeon, *Korean J. Chem. Eng.*, **29**, 1730 (2012).
11. Y. I. Lee and Y. H. Choa, *Korean Mater. Res. Eng.*, **22**, 4 (2012).
12. S. J. Koo and C. S. Ju, *Korean J. Chem. Eng.*, **33**, 3511 (2016).
13. B. G. Lee and J. S. Choi, *Appl. Chem. Eng. Res.*, **45**, 2 (2007).
14. M. H. Sung, W. S. Kim and J. S. Kim, *Korean Chem. Eng. Res.*, **36**, 4 (1998).
15. J. C. Lee, D. Y. Shin, B. D. Pandey and K. K. Yoo, *Korean Soc. Miner. Eng. Res. Eng.*, **48**, 3 (2011).