



## Non-thermal reduction of indium oxide and indium tin oxide by mechanochemical method

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### ABSTRACT

A non-thermal process for reducing indium(III) oxide ( $\text{In}_2\text{O}_3$ ) and/or indium tin oxide (ITO) into indium–metal by milling with lithium nitride ( $\text{Li}_3\text{N}$ ) under ( $\text{NH}_3$ ) or nitrogen ( $\text{N}_2$ ) gas environment is proposed in this paper. Milling operation causes mechanochemical reaction in the systems of  $\text{In}_2\text{O}_3$ /ITO and  $\text{Li}_3\text{N}$ , to form In and LiOH. The latter is soluble in water, so that the milled sample was subjected to washing with water, enabling us to recover indium–metal. According to the characterization of the milled products by X-ray diffraction (XRD), the reduction of  $\text{In}_2\text{O}_3$ /ITO can be achieved in a short period of time. Analytical data by inductively coupled plasma (ICP) from dissolution of the pellets in acidic solution clearly shows that indium–metal concentration is over 95% and the yield of In from the starting oxide sample is more than 97%, depending on the milling condition. The reaction mechanism between  $\text{In}_2\text{O}_3/\text{Li}_3\text{N}$  and  $\text{NH}_3/\text{N}_2$  is also discussed in the paper, and this could be applied to recover indium–metal from electric device wastes containing ITO.

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### 1. Introduction

Indium (In), a rare metal, is generally found in low concentrations in sulphide ores, and most commonly associated with zinc-bearing materials and less in copper and lead from which indium is obtained in by-products such as residues, flue dusts, and slags. It has many important applications; mainly as thin films of indium tin oxide (ITO) for liquid crystal displays (LCDs). It also finds application as constituent of fusible alloys with precious and base metals, lowering their melting points, in electrical components and semiconductors in the form of indium phosphide (InP), among others [1–4]. Demand for indium in Japan reached 888 t in 2006, of which about half of the material was recovered from scrap and a large amount could be recovered from weld metal alloys, scraped ITO and indium phosphide in LCDs [1]. Recovery of indium from sulfate or chloride leach liquors by hydrometallurgical processing routes followed by solvent extraction, cementation etc. is widely reported in literature [5–9]. However, there has still been a strong demand to recover indium (metal) from a waste material containing In. Recently, Zhang et al. have reported on application of mechanochemical phenomena to recover useful materials from wastes [10–13]. Similarly, Kano et al. have reported mechanochemical reaction between gallium (Ga) and/or gallium

oxide ( $\text{Ga}_2\text{O}_3$ ) and  $\text{Li}_3\text{N}$  under  $\text{NH}_3$ , preparing GaN as a main product. This reaction seems to be non-thermal reduction of oxide through mechanochemical reaction with an aid of reducing agents. The reducing agents are  $\text{Li}_3\text{N}$  and  $\text{NH}_3$  in this case, and they play a significant role in the reduction of the oxides. Kano et al. have extended their reduction process to  $\text{In}_2\text{O}_3$  to form In–metal [14–16].

The main purpose of this paper is to provide information on a non-thermal process for recovering In–metal through mechanochemical reduction of  $\text{In}_2\text{O}_3$ /ITO by its milling with  $\text{Li}_3\text{N}$  under non-oxidation state of  $\text{NH}_3$  and/or  $\text{N}_2$  gas environments. The milled sample was subjected to washing with water to recover In–metal as pellets. The purity of the recovered In–metal is over 95%.

### 2. Experimental

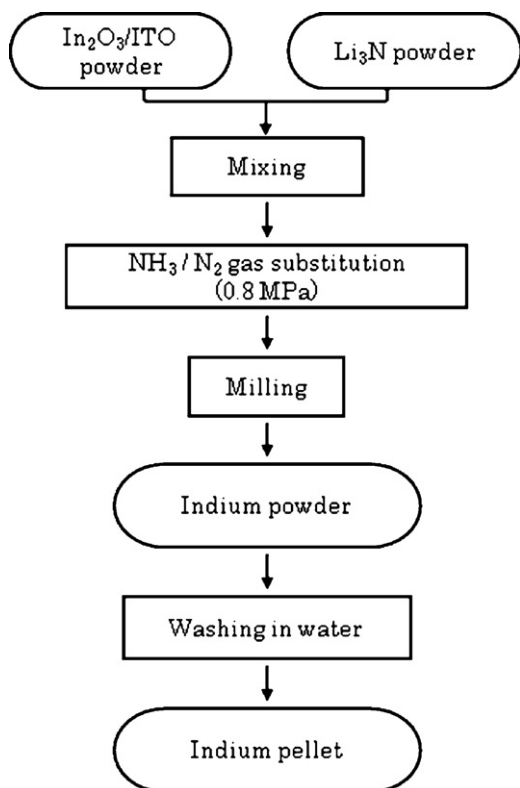
$\text{In}_2\text{O}_3$  and  $\text{Li}_3\text{N}$  used as starting materials were supplied by Wako Pure Chemical Industries, Ltd., Japan and ITO sample was supplied by Aldrich.

A planetary ball mill (P-7, Fritsch, Germany), having a pair of  $\text{ZrO}_2$  mill pots, charged with  $24 \times 10$  mm diameter  $\text{ZrO}_2$  balls each was used for the milling of  $\text{In}_2\text{O}_3$  and  $\text{Li}_3\text{N}$ , and was conducted under either  $\text{NH}_3$  or  $\text{N}_2$  gas atmospheres, respectively to induce mechanochemical reaction between the starting materials. The diameter and length of the mill pots are the same values as 40 mm and inner pot volume of ca.  $45 \text{ cm}^3$ . 2.76 g sample mixture of  $\text{In}_2\text{O}_3$  (2.0 g) and  $\text{Li}_3\text{N}$  (0.76 g) (1:3 (mol/mol) ratio) was carefully mixed inside a glove box under argon gas environment, and charged into the mill pot and the pot was set in a container made of stainless steel (overpot). The inner air in the mill pot was degassed with a vacuum pump, and  $\text{NH}_3$  and/or  $\text{N}_2$  gases were charged at 0.8 MPa, respectively. Both charged mill pots were set on mill device and rotated at 300 rpm for different times ranging from 30 to 180 min.

After the milling operation, a small amount of the product was removed for characterization and the milled product was further washed in the same mill with

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**Fig. 1.** Schematic illustration of the experimental procedure used to effect mechanochemical reduction of  $\text{In}_2\text{O}_3/\text{ITO}$ .

water for 10 min to remove the by-product. A schematic flow of the operation to form In from the oxides is given in Fig. 1.

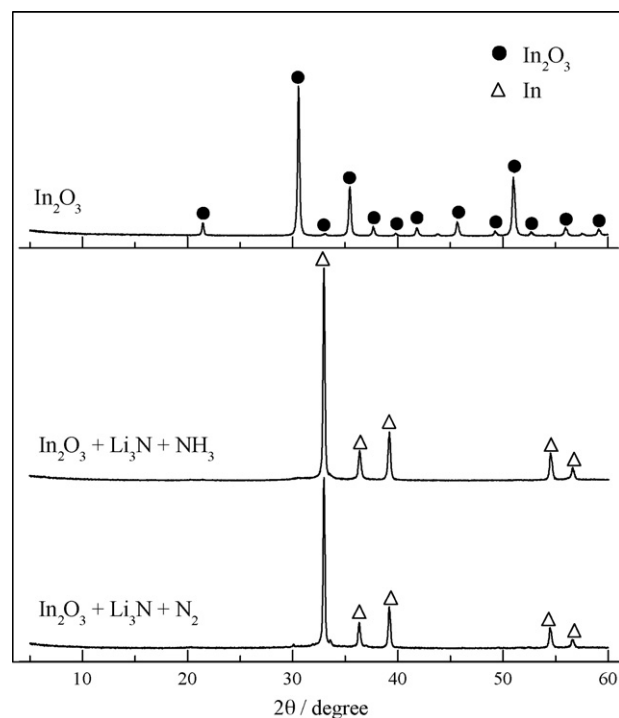
The milled samples were characterized by XRD analysis using Rigaku, RINT-2200/PC system with a  $\text{CuK}\alpha$  irradiation source ( $\lambda = 1.5405 \text{ \AA}$ ) at 40 kV and 20 mA in a continuous scan mode between  $10^\circ$  and  $60^\circ$  in  $2\theta$ . 0.1 g of the solid pellets obtained after washing was dissolved in nitric acid for analysis by ICP (Optima 3300, PerkinElmer) to evaluate purity and recovery of indium.

### 3. Results and discussion

#### 3.1. Milling under $\text{NH}_3$ and $\text{N}_2$ gas environments

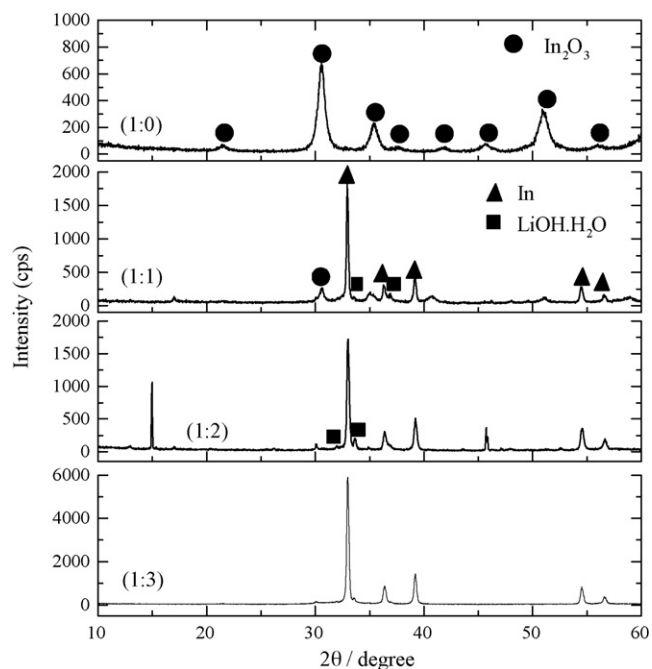
Fig. 2 shows XRD patterns of the samples of  $\text{In}_2\text{O}_3$ , and the mixture of  $\text{In}_2\text{O}_3$  and  $\text{Li}_3\text{N}$  at (1:3) molar ratio each milled for 120 min under  $\text{NH}_3$  and  $\text{N}_2$  gas environments. The XRD patterns of the milled mixtures indicate that complete reduction of  $\text{In}_2\text{O}_3$  to In-metal has been achieved under both gas environments, with no significant effect, except for the peak height. The height of the main peak for  $\text{NH}_3$  is slightly higher than that for  $\text{N}_2$ , suggesting that  $\text{NH}_3$  is rather effective reductant than  $\text{N}_2$ . All the same, peaks of the starting materials in both products are not seen in the patterns, indicating complete reduction of oxide is achieved within 120 min of milling under this condition.

Fig. 3 shows XRD patterns of  $\text{In}_2\text{O}_3$  sample and other three kinds of mixture of  $\text{In}_2\text{O}_3$  and  $\text{Li}_3\text{N}$  at different molar ratios of (1:1) to (1:3), each milled for 120 min under  $\text{NH}_3$  gas atmosphere. It is seen that the sample of  $\text{In}_2\text{O}_3$  without  $\text{Li}_3\text{N}$  (1:0) shows no peaks of In-metal in the pattern. As for the milled mixtures, significant peaks of In are seen in the patterns, and the peaks of In for the (1:3) mixture is more sharp than those for the (1:2) mixture. This means that the amount of  $\text{Li}_3\text{N}$  added to  $\text{In}_2\text{O}_3$  is important and more amount of  $\text{Li}_3\text{N}$  is better for the reduction of  $\text{In}_2\text{O}_3$ . In other words, excess  $\text{Li}_3\text{N}$  is appropriate to cause the reduction of  $\text{In}_2\text{O}_3$  into In in the milling condition.



**Fig. 2.** X-ray diffraction patterns showing effects of  $\text{NH}_3$  and  $\text{N}_2$  gases during MC reduction of  $\text{In}_2\text{O}_3$  by milling in the presence of  $\text{Li}_3\text{N}$ . Mixing ratio of  $\text{In}_2\text{O}_3/\text{Li}_3\text{N}$  was fixed at (1:3) moles and milling conducted for 120 min at 300 rpm.

Fig. 4 shows XRD patterns of a mixture of  $\text{In}_2\text{O}_3$  and  $\text{Li}_3\text{N}$  at (1:3) molar ratio milled for different periods of time under  $\text{NH}_3$  gas atmosphere. Peaks of In-metal clearly appear for the sample mixtures milled for 30 min and as milling is progressed, the  $\text{In}_2\text{O}_3$  peaks completely disappear from the patterns. It is seen that intensity of In-metal peaks significantly increase in the patterns of the mixtures as milling progresses. However, further milling for more



**Fig. 3.** X-ray diffraction patterns showing effect of  $\text{Li}_3\text{N}$  addition from 0 to 3 mols ( $\text{In}_2\text{O}_3/\text{Li}_3\text{N} = 1:0, 1:1, 1:2, 1:3$ ) on MC reduction of  $\text{In}_2\text{O}_3$  by milling in  $\text{NH}_3$  gas for 120 min at 300 rpm.

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