Reduction of Indium(III) Oxide to Indium through Mechanochemical Route

Junya Kano,* Eiko Kobayashi, William Tongamp, and Fumio Saito
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577

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A nonthermal reduction of indium(III) oxide (In_2O_3) to metallic indium (In) was achieved through mechanochemical route in this work. A mixture of In_2O_3 and lithium nitride (Li_3N) under ammonia (NH_3) and/or nitrogen (N_2) gas environments was milled in a planetary ball mill with uni-size ZrO_2 balls to induce mechanochemical reaction between the starting materials. Metallic indium was obtained after milling for 120 min, and the results are confirmed by X-ray diffraction (XRD) analysis. Washing of the milled product with water to remove by-products using the planetary ball mill for a further 10 min resulted in formation of pellets which were analyzed by EPMA, results clearly show that high purity indium metal was obtained.

Indium (In) is a rare element principally obtained as a by-product of the electrolytic refining of zinc. It has many important applications; mainly as thin films of indium–tin oxide (ITO) for liquid-crystal displays. It also finds application as constituent of fusible alloys with precious and base metals to lower their melting points and as electrical components and semiconductors in the form of indium phosphide (InP).[1–3] Demand for indium in Japan reached 335 t in 2000, of which about half of the material was recovered from scrap: a large amount could be recovered from weld metal alloys, scraped ITO, and indium phosphide in LCDs.[1] Recovery of indium by dissolving in chloride media and subsequent extraction and separation is reported by other researchers.[4,5] A reductive decomposition of In_2O_3 to metallic indium by cathodic reduction is also reported in the literature.[6]

Mechanochemical route to material synthesis could be applied, and recently, mechanochemical reaction between Ga_2O_3 and Li_3N to prepare GaN has been applied.[7]

In this work, we performed a nonthermal reductive decomposition of In_2O_3 to In metal by milling to effect mechanochemically induced solid-state reactions with Li_3N as a reactant under NH_3 and/or N_2 gas environments.

Starting materials, indium oxide (In_2O_3) and lithium nitride (Li_3N), were supplied by Wako pure chemical industries, Ltd., Japan. A planetary ball mill (P-7, Fritcsh, Germany), having a pair of ZrO_2 mill pots, charged with 24 × 10 mm diameter ZrO_2 balls each was used for the milling of In_2O_3 and Li_3N, and the milling was conducted under NH_3 and/or N_2 gas environments to induce mechanochemical reaction between the starting materials. The diameter and length of the two mill pots are 40 mm, and inner pot vol is 45 cm^3. In_2O_3 (2.0 g) and Li_3N (0.76 g) (1:3 (mol/mol) ratio) were 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 both NH_3 and N_2 gases were charged at 0.8 MPa. The charged mill pots were set on mill device and rotated at 300 rpm for 120 min. After the milling operation, a portion of the fine powder in the product was removed for characterization, and the milled product was further washed in the same mill with water for 10 min to remove the by-product. The milled samples were characterized by X-ray powder diffraction (XRD) analysis using Rigaku, RINT-2200/PC system with a Cu Kα irradiation source ($\lambda = 1.5405$ Å) at 40 kV and 20 mA in a continuous scan mode between 5 and 60° in 2θ. The solid pellets obtained after washing was analyzed by an Electro-Probe Micro-Analyzer (EPMA).

X-ray diffraction patterns of In_2O_3 milled with Li_3N under NH_3 and N_2 gas environments are shown in Figure 1; (a) In_2O_3 before milling, (b) and (c) patterns of powder fractions obtained after milling of the starting materials. It could be seen from the X-ray diffraction patterns that peaks of In_2O_3 have been completely reduced within 120 min of milling at 300 rpm, and that peaks of In metal appear dominant in the product. Unreacted fractions of the starting materials are reduced to amorphous phase and may be below detection limit, and lithium compounds after reaction remain in amorphous phase owing to the milling effect. Intensity of the patterns obtained with N_2 as gas environment was slightly lower than that obtained with NH_3 gas; however, in both experimental systems In_2O_3 was successfully reduced to indium metal.

Washing the powder products obtained after milling for 120 min at 300 rpm and a further 10 min with water to remove the by-products resulted in formation of larger pellets of size around 10 mm. EPMA patterns of the pellet obtained is shown

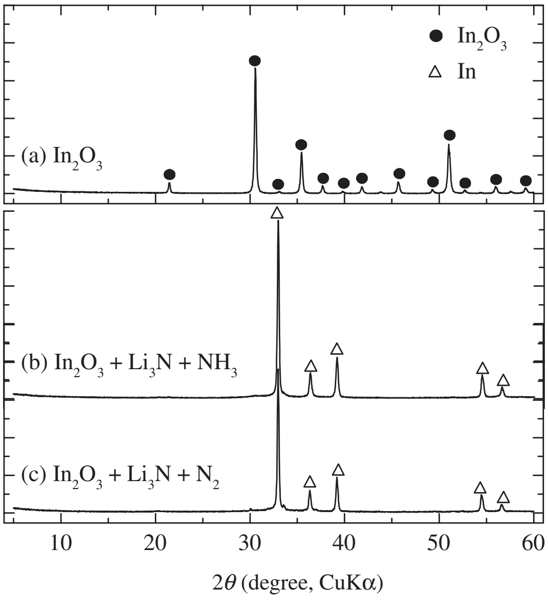

Figure 1. X-ray diffraction patterns of; (a) pure In_2O_3 before milling, (b) In_2O_3/Li_3N mixture milled under NH_3 gas environment; (c) In_2O_3/Li_3N mixture milled under N_2 gas environment. All samples were milled for 120 min at 300 rpm.

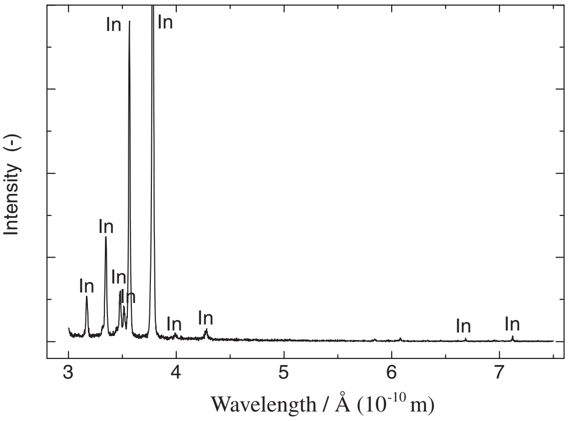

Figure 2. EPMA pattern of In-metal pellet obtained after milling In_2O_3 and Li_3N mixture (molar ratio 1:3) for 120 min under NH_3 gas environment.

Figure 3. Photograph of In-metal pellet obtained after milling In_2O_3 and Li_3N mixture (1:3 = In_2O_3:Li_3N molar ratio) for 120 min under NH_3 gas environment.

in Figure 2, indicating dominant peaks of In metal, and a photograph of In pellet obtained from milling operation is shown in Figure 3.

From the results obtained, the mechanochemically induced solid-state reaction between In_2O_3 and Li_3N under NH_3 and N_2 gases can be represented by the following reaction mechanisms (1) and (2), respectively;

$$In_2O_3 + Li_3N + NH_3 \rightarrow 2In + 3LiOH + N_2 \qquad (1)$$

$$In_2O_3 + 2Li_3N + N_2 \rightarrow 2In + 3Li_2O + 2N_2 \qquad (2)$$

Figure 4 shows In_2O_3 milled under different conditions for 120 min; (a) under NH_3 gas but without Li_3N, (b) with Li_3N but without NH_3 gas, and (c) with Li_3N in NH_3 gas. Milling of In_2O_3 in NH_3 gas but without Li_3N could not lead to formation of indium metal as indicated by Figure 4a. Peaks of indium metal appeared when In_2O_3 was milled with Li_3N without NH_3 gas (Figure 4b); however, peaks of In_2O_3 also remain after 120 min of milling time. Milling of In_2O_3 with Li_3N in the presence of NH_3 gas is shown in Figure 4c. It shows only dominant peaks of indium metal.

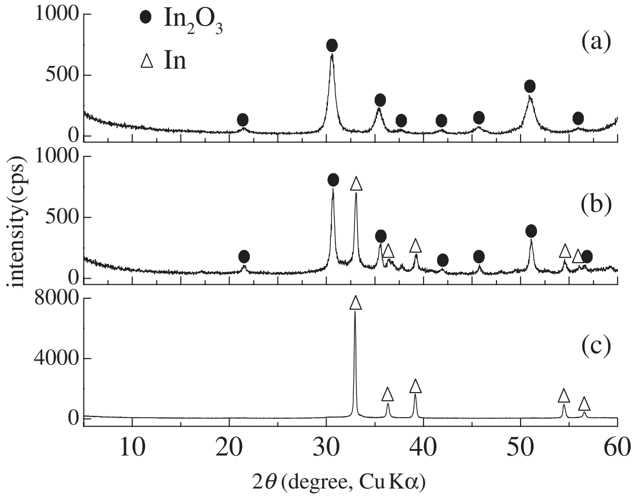

Figure 4. X-ray diffraction patterns of sample mixtures milled for 120 min at 300 rpm; (a) In_2O_3 under NH_3 gas; (b) In_2O_3/Li_3N mixture without NH_3/N_2 gases; (c) In_2O_3/Li_3N mixture under NH_3 gas environment.

Characterization of both powder products obtained after milling and indium pellets obtained after washing of the milled powder products shows that In_2O_3 could be reduced by mechanochemical reaction between In_2O_3 and Li_3N. The rate of reaction is significantly increased when the milling operation is conducted under NH_3 or N_2 gas. High purity In metal can be prepared within 120 min of milling and at a moderate milling speed of 300 rpm. Based on this finding, we propose that a mechanochemical route to recovery of In metal by milling in either NH_3 or N_2 gas environments of In_2O_3 and Li_3N could be developed to treat scrap containing indium such as ITO wastes.

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