Effect of Polytetrafluoroethylene additive on low-temperature synthesis of InN crystals via reaction of LiInO₂ and NaNH₂

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We examined the effect of polymer polytetrafluoroethylene (PTFE) additive on the growth of InN crystals by the nitridation of LiInO₂ in NaNH₂ flux at 240°C. LiInO₂ and NaNH₂ powder were heated with/without PTFE pieces in a steel crucible located inside the PTFE-lined autoclave. The additive of PTFE pieces enhanced the decomposition of LiInO₂ with the mass loss of these pieces and progressed the formation of InN and (InOH)₃ byproducts. SEM and TEM images of the products using PTFE additives showed the hexagonal InN crystals of ~1 µm in size, and the optical bandgap of synthesized InN was estimated as ~2.03 eV. We presume that fluorine in PTFE additive subtracts Li from LiInO₂ and enhances the growth of InN crystals.

Organic polymer polytetrafluoroethylene (PTFE, Teflon) has characters of easy handling as a solid form, high chemical stability near room temperature, low toxicity, and shows relatively low decomposition temperature (~400°C) when it compared with inorganic compounds, such as CaF₂. Accordingly, it has attracted a considerable attention as chemical agents containing fluorine for low-temperature reactions.¹ For example, layered-perovskite oxyfluoride, such as RbLaNb₂O₆F, is synthesized by the topotactic reaction of RbLaNb₂O₇ with PTFE at 400°C.² A superconductor, WO₃Fₓ₋x₁₋ is obtained via the reaction between WO₃ and PTFE at 400°C.³ In addition to use of PTFE as a fluoridation agent, it also works as an extraction agent of alkali-metals at relatively low temperature. Synthesis of metastable brookite TiO₂ and rutile-type other oxides is reported from the reactions between lithium oxides and PTFE.⁴,⁵ However, to our knowledge, the reaction using PTFE for the synthesis of nitrides has not been reported.

Indium nitride, InN, is an attractive optoelectronic material for infrared region.⁶ Synthesis processes often require a continuous ammonia flow,⁷⁻¹⁰ which works as a reactive nitrogen source and purges byproducts to satisfy its thermodynamic requirement. Recently, we reported that the synthesis of InN crystals by the reaction of LiInO₂ with NaNH₂ flux in a PTFE-lined autoclave at 240°C.¹¹ Characteristic feature of this method is the low-temperature nitridation of an oxide using NaNH₂ flux in a closed system. However, the possibility of the reaction with PTFE inner layer of autoclave, and pieces of PTFE are added on purpose to investigate the effect of PTFE additives on the synthesis of InN. We found that the additive of PTFE enhances the formation of InN crystals. The increased kinetics of the low-temperature reactions can be explained by the extraction of Li from LiInO₂.

LiInO₂ powder was synthesized by conventional solid-state reaction between Li₂CO₃ and In₂O₃ at 850°C. Inside a nitrogen-filled glove box, LiInO₂ (0.15 g) and NaNH₂ (1.0 g) powders were put in a steel crucible. Then, a piece or three pieces of PTFE (approximately 4 mm × 4 mm × 1.5 mm) were put in the crucible, which was placed in a PTFE-lined steel autoclave. The autoclave was tightly closed and brought out of the glove box, and then kept in an oven at 240°C for 36 or 288 h. After cooled down, it was opened and ethanol was added to the crucible, and the solution was stirred by a magnetic stirrer until the excess NaNH₂ and byproducts were dissolved. The products were collected by filtration, washed with water, and then dried overnight at room temperature. The pieces of PTFE were separately collected during filtration. Crystal structure was examined by powder XRD patterns using an RINT-2000 (Rigaku) system. The scan was performed over the range of 20–60° with a step of 0.02°. Morphologies were investigated by scanning electron microscopy (FE-SEM; JEOL; JSM-6500) and transition electron microscopy (TEM; FEI; Tecnai Osiris). The samples for SEM observation were put on the carbon tape, and ones for TEM observation were prepared by dropping ultrasonically dispersed ethanol suspension on a commercial grid. Optical reflectance was measured by MSV-5200 (Jasco).

The reactions between white LiInO₂ powder and light gray NaNH₂ powder with/without PTFE pieces were performed in a steel crucible at 240°C. After the reaction and subsequent ethanol-water wash, red powders were obtained. The reactions changed smooth surface of PTFE pieces into rough ones. Table 1 summarized the reaction condition and weight change of PTFE pieces. There are weight losses after the nitridation, indicating the difference of mass.

| Pieces of PTFE | Mass/g | Mass loss/g |
|---------------|--------|-------------|
| 0             | —      | —           |
| 1             | 0.178  | 0.037       |
| 3             | 0.555  | 0.175       |

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composition of PTFE.

Figure 1 shows XRD patterns of the products after the reaction between LiInO₂ and NaNH₂ with/without PTFE pieces. All the products show the peaks assigned as wurtzite-type InN though their intensity and impurity phases are different. The product synthesized with no PTFE shows the peaks of InN, LiInO₂, and In(OH)₃ for 36 h, and the peaks of InN and In(OH)₃ for 288 h. Relatively strong peaks of LiInO₂ and weak peaks of InN for 36 h suggest that the reaction does not complete in 36 h. The additive of one piece of PTFE weakens the peaks of LiInO₂ and enhances peaks from both InN and In(OH)₃ for 36 h. The reaction with three pieces of PTFE for 36 h gives strong InN peaks with those of In(OH)₃ subproduct, but no LiInO₂ residual. Thus, more PTFE formed more InN and In(OH)₃ with less LiInO₂ in less reaction time.

Figures 2(a)–2(c) shows SEM images of the products by the reaction for 36 h. All the products show aggregates of nano-sized particles. Hexagonal-like crystals can be also found in the product synthesized using PTFE pieces (indicated by arrows), and they also are covered with small particles. Figure 2(d) shows TEM image of ultrasonically dispersed sample. There is a hexagonal crystal of approximately 1 μm in size and it shows hexagonal electron diffraction spots, indicating the hexagonal InN structure with single-crystalline feature.

Figure 3 shows reflectance spectrum of the product synthesized with three pieces of PTFE for 36 h. The bandgap is estimated as ca. 610 nm (2.03 eV). The bandgap of intrinsic InN is reported as ~0.7 eV, which is known to expand to 1.9–2.3 eV when a substantial number of carrier or oxygen are incorporated. Thus, oxygen incorporation in the products is the likely reason for this wide bandgap. The bandgap of In(OH)₃, which is detected as an impurity of InN phase, is reported as ~5.15 eV. This is far wide when compared with reported bandgap of InN, thus unlikely affect this estimation of InN bandgap.

The additive of PTFE enhances the formation of InN crystals with the mass loss of PTFE. The decrease of LiInO₂ residuals with increasing the amount of PTFE additive in 36 h suggests that the reaction of LiInO₂ with PTFE enhances the formation of InN. Highly electronegative fluorine in PTFE presumably works as an extraction agent of electronegative Li in LiInO₂ similar to reports about the synthesis of oxides, and may form reactive species to enhance the kinetics for the formation of InN phase. The exploration of the detailed reaction route with identification of possible reacting species remains as further challenges.

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