

## Synthesis of Li-rich LiAlO<sub>2</sub> for application of ceramic growth materials for nuclear fusion

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### 1. Introduction

Nuclear fusion produces six times more energy than nuclear power. It is attracting attention for future energy development. Research on the above is being actively conducted in 7 countries including the US, UK, Japan and Korea. Nuclear fusion reactors currently under development can react even at relatively low energy thus light nuclides such as Deuterium and Tritium are used. Plasma is generated after heating at a high temperature of more than 100 million degrees Celsius. After deuterium and tritium collide with high energy, stable helium molecules are generated, neutrons and thermal energy are generated. Tritium is rare in the air in nature. Supply ceramics contain Li due to difficulty in supply and demand. Research and development of propagation material to supply tritium inside the fusion reactor are required. Among the tritium breeder candidates, LiAlO<sub>2</sub> is one of various solid breeder materials as has the following advantages. Excellent thermal stress relief, mechanical strength and blanket material compatibility [1-2]. In the case of a growth material, the amount of tritium generated is limited according to the amount of Li contained. Therefore, in order to obtain a certain amount of Li, saturated Li is injected [3]. LiAlO<sub>2</sub> will become the first solid breeder candidate if the tritium release characteristics are improved [4]. In this study, a Li-rich LiAlO<sub>2</sub> breeder pebble is synthesized to improve the tritium emission characteristics and to use LiAlO<sub>2</sub> as a fusion pebble as an appropriate solid breeder.

### 2. Methods and Results

The requirements for ceramic growth materials are first, the high content of Li directly affects tritium production. Second, high thermal conductivity, low thermal expansion coefficient, thus wide range of temperature applicability. Finally, the release of tritium becomes easier.

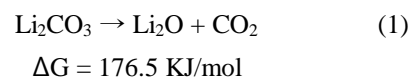
#### 2.1 Synthesis of LiAlO<sub>2</sub> Solid breeder for Tritium propagation

Lithium aluminate has excellent thermal stability in particular, the gamma (γ) phase has better thermal stability than the alpha and beta phases. In the synthesis of Li-rich LiAlO<sub>2</sub>, the Li/Al molar ratio of the precursor is adjusted. It was confirmed that the Li-rich state was maintained. Optimal material was selected by thermodynamic approach. Li/Al molar ratio was

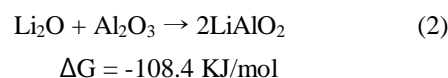
adjusted to 0.8, 1.0 and 1.2 to synthesize LiAlO<sub>2</sub>. As a precursor, a method using Li<sub>2</sub>O + Al<sub>2</sub>O<sub>3</sub> (SIGMA-ALDRICH), which causes the spontaneous reaction thermodynamically, is used. Another method is to use Li<sub>2</sub>O + Al(OH)<sub>3</sub>·xH<sub>2</sub>O synthesized with Li<sub>2</sub>O using Al(OH)<sub>3</sub>·xH<sub>2</sub>O (SIGMA-ALDRICH), which is easily converted into an aqueous solution.

#### 2.2 Optimized Solid State Synthesis Method

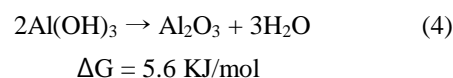
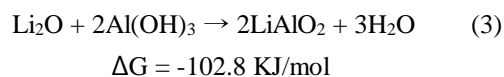
As precursors, Li<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub> and Al(OH)<sub>3</sub>·xH<sub>2</sub>O were selected in the initial stage, however, Li<sub>2</sub>CO<sub>3</sub> was used instead of Li<sub>2</sub>O. Al<sub>2</sub>O<sub>3</sub> is participated in the reaction with Li<sub>2</sub>O through heat treatment at about 500 to 600°C. The CO<sub>2</sub> is blown away in a gaseous state.



The reaction formula of Li<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> is as follows.



The reaction formula of Li<sub>2</sub>O and Al(OH)<sub>3</sub>·xH<sub>2</sub>O is as follows.



During the synthesis of Li-rich LiAlO<sub>2</sub> (Li:Al molar ratio = 1.2:1.0), the molar ratio of Li/Al in the precursor was added at 0.8, 1.0 and 1.2, respectively. High-speed rotation Planetary Ball Milling machine is used. Precursors and zirconia balls were put in the grinding pot before high energy ball milling was performed for 30 minutes at rotation speed of 300 rpm. The atmosphere in the grinding pot does not add anything other than air. Divided into dry and slurry with alcohol added as solvent. The type of alcohol solvent are isopropyl alcohol (IPA), acetone and a solution in which IPA and acetone are mixed in a 1:1 volume ratio. Samples obtained through ball milling were dried in an oven at 70°C for 24 hours after completion, pulverized and stored as powder.

### 2.3 Optimized Liquid State Synthesis Method

The precursors  $\text{Li}(\text{OH})\cdot\text{H}_2\text{O}$  and  $\text{Al}(\text{OH})_3\cdot x\text{H}_2\text{O}$  were used. These reagents have  $\text{H}_2\text{O}$  groups attached to them, so they are easily soluble in aqueous solution. The reaction formula of the above precursor is as follows.

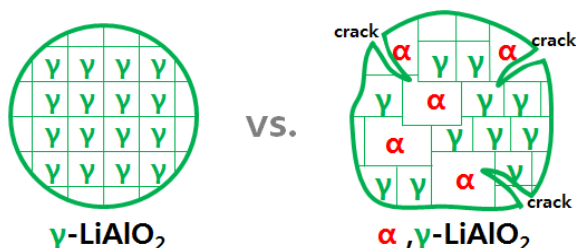
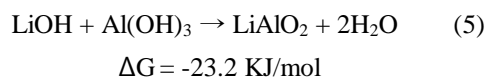


Fig. 1. Schematic diagram of phase transition after pebble heat treatment of single phase and multiphase  $\text{LiAlO}_2$  powder

During the synthesis of Li-rich  $\text{LiAlO}_2$  (Li:Al molar ratio = 1.2:1.0), the molar ratio of Li/Al in the precursor was added to 0.8, 1.0 and 1.2 respectively, to change the Li content. After adding 120 ml of distilled water to the above reagent, the mixture was stirred for 1 hour 400 rpm and  $80^\circ\text{C}$  in a heated plate magnetic stirrer. After an hour, the pH of the aqueous ammonia solution (28~30%) is adjusted to 11.5~12.0. The above process is the process up to the entry stage of each liquid phase process. First, co-precipitation method, the prepared solution is stirred in a heated plate magnetic stirrer at 400 rpm and  $80^\circ\text{C}$  for 3 hours. When the temperature of the solution returns to room temperature, centrifuge 5 times with distilled water and then dry in an oven at  $70^\circ\text{C}$  for 24 hours. In the second microwave method, the prepared solution is placed in a microwave-only vessel capable of magnetic stirring, the temperature of the solution is returned to room temperature by raising the temperature to  $150^\circ\text{C}$  at a ramping rate of  $5^\circ\text{C}/\text{min}$  and maintaining it for 30 minutes in a microwave capable of controlling temperature and pressure. When it comes, it is centrifuged 5 times with distilled water and dried in an oven at  $70^\circ\text{C}$  for 24 hours. Lastly, in the hydrothermal synthesis method (Hydrothermal), the prepared solution is placed in a vessel dedicated to Hydrothermal that can withstand high temperature, high pressure. The ramping rate is raised to  $150^\circ\text{C}$  at  $5^\circ\text{C}/\text{min}$  and maintained for 12 hours. When the temperature of the solution returns to room temperature, distilled water is used. After centrifugation twice, dry in an oven at  $70^\circ\text{C}$  for 24 hours.

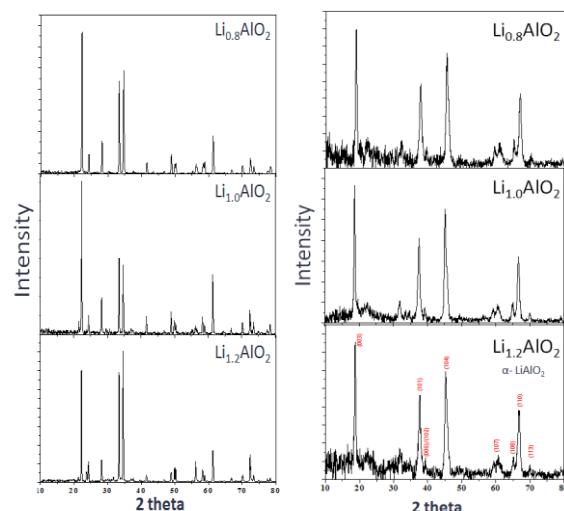


Fig. 2. (Left) XRD of  $\text{Li}_x\text{AlO}_2$  by solid phase synthesis (right) Synthesis in liquid phase

### 3. Conclusions

In the solid phase method, a precursor with an  $\text{H}_2\text{O}$  group that can be easily soluble in a solvent using  $\text{Li}_2\text{O}$  and  $\text{Al}(\text{OH})_3\cdot x\text{H}_2\text{O}$  as precursors was used. However, when analyzing the spontaneity of the reaction thermodynamically, it is more involuntary than the  $\text{Li}_2\text{O} + \text{Al}_2\text{O}_3$  reaction. As a result of confirming the structure through XRD graph analysis of the sample subjected to heat treatment after high-speed ball milling in the form of a slurry using IPA/Acetone as a solvent, it was found to be tetragonal  $\gamma\text{-LiAlO}_2$  under all conditions as in the above case using  $\text{Al}_2\text{O}_3$ . When  $\text{Li}_2\text{O}$  and  $\text{Al}(\text{OH})_3\cdot x\text{H}_2\text{O}$  were used as precursors, the peak split on the XRD graph did not occur in some samples. Both the addition of the solvent and the non-addition of the solvent showed a non-uniform peak pattern in the XRD graph. In conclusion, the structural analysis of Li-rich  $\text{LiAlO}_2$  according to the synthesis method and Li content then heat treatment temperature, almost single-phase tetragonal  $\gamma\text{-LiAlO}_2$  appears when synthesized by the solid phase method and heat treated. Hexagonal  $\alpha\text{-LiAlO}_2$  contains many impurities when applied to nuclear fusion operation, it is more effective to synthesize through solid-phase method than liquid-phase method because structurally stable and single-phase  $\text{LiAlO}_2$  are advantageous for stably releasing tritium. Currently, research on proliferative materials is actively underway. However, research on proliferation materials applicable to actual fusion reactors are inadequate. To solve this problem, various synthetic methods such as vacuum cold-spray, sol-gel synthesis, mask coating, microwave and hydrothermal synthesis are introduced. Neutron simulation test, thermal property evaluation and property change due to phase shift were confirmed. It

was confirmed by securing phase stability according to the synthesis method for each condition above. The fundamental-base solid breeder characteristic standard is presented rather than the zero-base characteristic deduction. Consequently, the ceramic manufacturing technology and characteristic analysis method of this study are conducted in improving the performance of materials as well as in fusion power generation research. Growing materials produced under optimal conditions can advance the ceramic technology itself.

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