Research on the preparation, electrical and mechanical properties of γ-LiAlO₂ ceramics

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Abstract

A combustion synthesis technique, the glycine–urea–nitrate process is described and investigated in this paper. A combination of the aqueous solution of glycine–urea and metal nitrates was employed as a precursor for the process. Pure γ-LiAlO₂ powders with fine crystal structure and high reactivity could be obtained by the combustion technique. γ-LiAlO₂ ceramics with homogeneous microstructure, high lithium conductivity and bending strength was prepared from the powder. Lithium rich ceramics and lithium deficient phases demonstrated improved ionic conductivities, which can be attributed to different mechanisms.
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1. Introduction

γ-LiAlO₂ ceramic is one of the most promising candidates for tritium-breeding materials. The most widely used method to prepare this ceramics is the simple solid-state reaction between various lithium precursors and highly reactive aluminas [1–3]. However, the solid state reaction method requires several heating and grinding steps to ensure homogeneous mixing of various oxides, and therefore, the solid-state reaction method would restrict the improvement of properties of the ceramics. Wet-chemical methods such as sol–gel method starting from metal alkoxide [4], the thermal decomposition of mixed citrate or oxalate complexes [5], hydrothermal methods [6] have been demonstrated effective to improve the overall performances of γ-LiAlO₂ ceramics. However, since wet-chemical methods usually demand high cost starting materials and high cost process equipment, it is important to develop new cost-effective methods to prepare high quality γ-LiAlO₂ powders. A novel combustion synthesis technique appeared promising for γ-LiAlO₂ synthesis because of its success in producing single or multi-phase oxide powders [7–9]. In this paper a combustion synthesis technique, the glycine–urea–nitrate process, is described and investigated. The process makes use of the heat energy liberated by the redox exothermic reaction between metal nitrates (oxidizers) and glycine–urea (fuels). Homogeneous fine crystalline powders can be directly obtained by this method.

Tritium release rate of a ceramic breeder is one of the most important factors controlling the tritium recovery from the breeder, and is greatly dependent on the migration behavior of tritium in the breeder material. It is known that tritium diffusion in breeding blanket materials has a close relationship to lithium diffusion or conduction in the materials [10]. In addition, mechanical strength is also an important property of breeding blanket ceramics, which influence the stability of the materials. In this paper, we will also present morphology, mechanical, and electrical properties of γ-LiAlO₂ ceramics obtained under different conditions.

2. Experimental

2.1. Sample preparation

γ-LiAlO₂ powders were prepared by a combustion method. Reagent-grade lithium nitrate (LiNO₃) and aluminum nitrate (Al(NO₃)₃·9H₂O) were used as

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lithium and aluminum sources. Stock solutions at approximately one mole concentration were prepared by dissolving the lithium nitrate ($LiNO_3$) and aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) in de-ionized water. These stock solutions were analyzed by ethylenediamine tetra-acetic acid (EDTA) titration to determine the cation concentration to a precision of better than 0.5%. Reagent-grade glycine and urea were used as fuels and added in granular form.

The solutions were heated on a hot plate at about 80 °C until excess free water was evaporated and spontaneous ignition occurred at about 250 °C. The solution boiled and underwent dehydration followed by decomposition with the evolution of large amounts of gases (oxides of nitrogen and ammonia). The final products were foamy in character and the whole decomposition process took place in a few seconds. Homogeneous fine crystalline γ-$LiAlO_2$ powder was therefore obtained directly.

The disks of 20 mm diameter were prepared by cold-pressing γ-$LiAlO_2$ powders with appropriate amount of binder in stainless-steel dies and further sintering the disks at 1473 K for 3 h under controlled atmospheres.

2.2. Physical measurements

The XRD analysis was carried out by using an RAX-10 X-ray diffractometer. The particle size of the combustion products was measured by a SICAS-4800 Photo-Size Analyzer based on photo-extinction and sedimentation principles. The particle morphology and size were evaluated using a JEOL TEM-200CX transmission electron microscope (TEM). Microstructures of γ-$LiAlO_2$ ceramics was examined with an EPMA-8705QH$_2$ scanning electron microscope (SEM). The mechanical properties of ceramics were measured by three-point bending of specimens with cross section of 3×4 mm and test span of 24 mm using an Instron-1195 Mechanical Tester. Ionic conductivity of the ceramics was obtained from impedance plots determined with symmetrical platinum electrodes on a Solartron 1260 frequency response analyzer over a frequency range of 1 Hz to 1 MHz and temperature range of 400–800 °C.

3. Results and discussion

3.1. Influence of combination of glycine–urea fuel

Phase purity of the powders obtained is an important criterion for the selection of a γ-$LiAlO_2$ synthetic production processes. Table 1 shows the XRD results obtained using the fuels of different combination while the mole ratio of Li/Al for the three solutions was fixed at 1:1.

As can be seen from Table 1, the mixture A was most reactive and underwent an abrupt and continuous reaction, which finished after a few seconds. However mixtures B and C underwent continuous but slow reaction. The color of the products varies from white (mixture A) over grey (mixture B) to black (mixture C). This was caused by different amounts of residual amorphous carbon-containing compounds resulting from incomplete oxidation of the glycine–urea.

3.2. Phase and particle morphology

Fig. 1 shows typical XRD-patterns of products obtained from the reactant mixtures with Li/Al molar ratio of 1:1 containing different combination of glycine–urea fuels. It was found that the reaction product obtained from mixed fuel of type A had well-crystallized γ-$LiAlO_2$ and a very small amount of the $LiAl_5O_8$ phase. The appearance of lithium-deficient compound such as $LiAl_5O_8$ indicates a higher flame temperature for mixture A, which caused significant evaporation of lithium. Comparing Fig. 1(b) with Fig. 1(a), one can see that the XRD patterns are almost the same but the mixture B leads to low crystalline γ-$LiAlO_2$. Fig. 1(c) does not show any sharp peaks of γ-$LiAlO_2$ but some small peaks were possibly attributed to compounds such as $LiAl_2(OH)_7 \cdot xH_2O$ or $LiAlO_2(H_2O)_n$ [11]. It indicated that with increasing ratio of mixed glycine/urea fuel, the flame temperature decreased. Kingsley [12] also reported that it is possible to modify the exothermic combustion reactions by changing the oxidizer:fuel ratio. So for the γ-$LiAlO_2$ powders, the best properties (lowest residual carbon, fine particle sizes, best crystallinity) were obtained at glycine/urea ratio of 1:3, and this glycine–urea ratio has also been adopted for the preparation of the

Table 1
Experimental results for product phase and reaction behavior

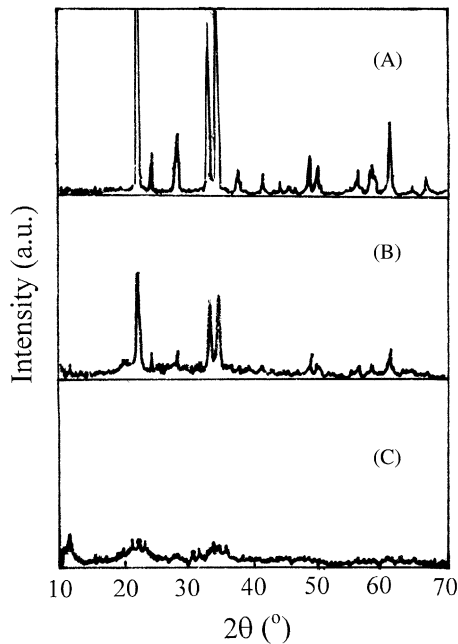| Type of fuel mixture	Ratio of glycine:urea	Reaction product	Reaction behavior
A	1:3	White, foamy, fine crystalline γ-$LiAlO2$, very small amount of $LiAl_5O_8$	Abrupt and continuous reaction
B	1:1	Grey, low crystalline γ-$LiAlO2$	Slow and continuous reaction
C	3:1	Black ashes, amorphous	Slow and continuous reaction

Fig. 1. X-ray diffraction patterns of products obtained from: (a) mixture A; (b) mixture B and (c) mixture C.

powder with Li/Al molar ratio of 1.05:1, i.e., 5 at.% rich in the lithium component.

Fig. 2 shows typical transmission electron microscopy of the powder prepared with mixture A. From the figure we can see that the very fine (50–100 nm diameter) γ-LiAlO$_2$ particles were linked together in chains. Individual crystals joined at grain boundaries and no amorphous phase was found. Similar particle morphology and particle size was obtained with γ-LiAlO$_2$ powders with different Li/Al molar ratios.

The particle size distribution of the γ-LiAlO$_2$ prepared from mixture A was also measured by the photoextinction and sedimentation method. The 50% average
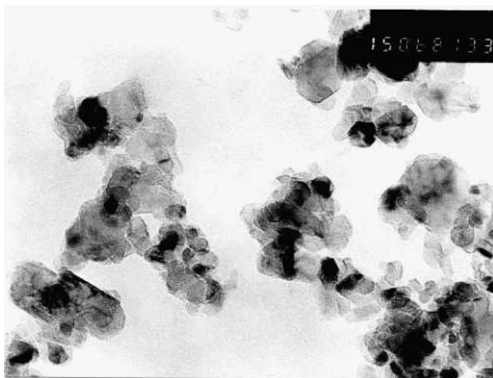
particle size thus obtained was 0.64 μm which is much bigger than that obtained by TEM analysis. Based on this difference it is suggested that weakly bounded agglomerates exist in γ-LiAlO$_2$. It is noteworthy that the particle morphology and average particle size of the powders prepared at Li/Al molar ratio of 1.05/1 are similar to sample A.

3.3. Microstructure of ceramics

Fig. 3(a) and (b) show the SEM fractographs of γ-LiAlO$_2$ ceramics sintered at 1473 K for 3 h with the Li/Al molar ratio of 1:1 and 1.05:1, respectively. As shown in Fig. 3(a), the stoichiometric γ-LiAlO$_2$ sample (Li/Al = 1:1) consists of uniform small grains with small pores. The average particle size was about 1.5 μm and the bigger grains were normally smaller than 2 μm. However the 5 at.% extra lithium sample consists of much bigger particles. As shown in Fig. 3(b), the grain size was in the range of 3–10 μm and the sample contained two types of pores, i.e., intragranular pores and intergranular pores. The intragranular pores could trap some of the tritium components obtained in the neutron irradiation process. Although the average particle sizes of powders with different Li/Al ratios are similar, the large grain size difference between the two ceramics indicated accelerating effects of lithium content on the growth of γ-LiAlO$_2$ grains at higher temperature.

3.4. Ionic conductivity and mechanical strength

Fig. 4 shows Arrhenius plots of the conductivities of several γ-LiAlO$_2$ ceramic samples. It can be seen that the stoichiometric ceramic showed low conductivity within the whole temperature range. The extra lithium content, i.e., 5 at.% rich in lithium, could greatly improve the ionic conductivity of the ceramics, nearly 2 orders of
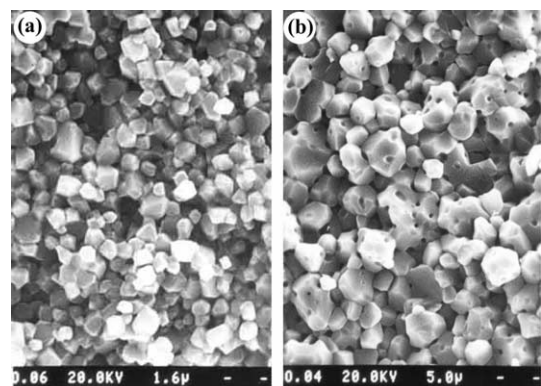

Fig. 2. TEM micrographs of the γ-LiAlO$_2$ powders.

Fig. 3. SEM fractographs of γ-LiAlO$_2$ disks sintered at 1473 K for 3 h: (a) stoichiometric γ-LiAlO$_2$ ceramics and (b) 5 at.% lithium rich ceramics.
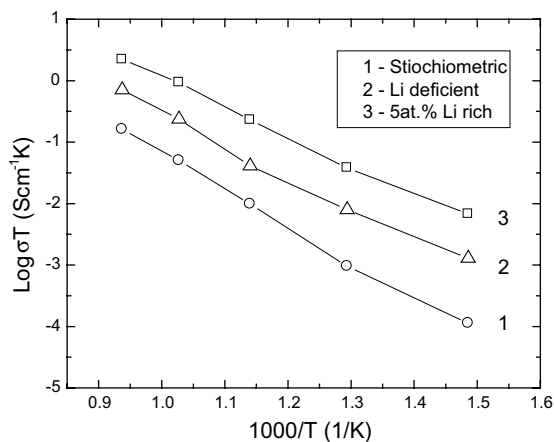
Fig. 4. Conductivity, σT, of γ-LiAlO$_2$ ceramics as a function of reciprocal temperature.

magnitude higher than that of the stoichiometric ceramic at 400 °C. At higher temperatures, the difference between the two ceramics becomes smaller. Furthermore, the activation energy for conductivity of the lithium rich sample is slightly lower than for the stoichiometric one. The influence of Li/Al ratio on the ionic conductivity of γ-LiAlO$_2$ ceramics has also been reported in other references [13–16], it was also deduced that Li$^+$ ion diffusivity was increased when Li/Al atomic ratio of the ceramics was increased, which would be attributed mainly to the formation of the highly conductive Li$_5$AlO$_4$ phase. It is remarkable that the lithium deficient sample, i.e., the sample prepared in an open container and annealed for longer time also showed improved ionic conductivity in comparison with the stoichiometric specimen, about 1 order of magnitude higher at 400 °C. It should be pointed out that the lithium ion conductivity of the low Li/Al ratio phase LiAl$_5$O$_8$ is several orders of magnitude lower than the stoichiometric γ-LiAlO$_2$ phase [16]. The high conductivity of lithium deficient γ-LiAlO$_2$ phase in this work might be ascribed to some defects probably formed in γ-LiAlO$_2$ phase which are favorable to lithium ion conduction.

Bending strength has been tested for γ-LiAlO$_2$ ceramics prepared in this work, they are 135, 102 and 128 MPa for stoichiometric, 5 at.% extra Lithium containing ceramic, and lithium deficient ceramic respectively. It is known that the larger the grain size of a ceramic, the lower will be its bending strength. The low bending strength of the lithium rich sample is attributed to its greatly enlarged grain size as shown in Fig. 3.

4. Conclusions

A combustion synthesis technique, the glycine–urea–nitrate process, can directly prepare homogeneous and fine particle γ-LiAlO$_2$ powders. The best combination of the mixed fuel was glycine:urea $= 1$:3. γ-LiAlO$_2$ ceramics with homogeneous microstructure, high lithium conductivity and bending strength was prepared from the powder produced by this method. Lithium rich ceramics and lithium deficient phase demonstrated improved ionic conductivities, which could be attributed to different mechanisms.

References

[1] M.A. Valenzuela, J. Jimenez-Becerril, et al., J. Am. Ceram. Soc. 79 (1996) 455.
[2] C. Teresita, T. Frianeza-Kullberg, et al., Ceram. Powder Sci. P147 (1996).
[3] T. Frianeza-Kullberg, D. Mcdonald, K. Davis, Ceram. Trans. 12 (1990) 147.
[4] C. Alvanic, S. Casadio, EP235099, 1987.
[5] K.W. Sang, S. Binpark, et al., J. Nucl. Mater. 257 (1998) 172.
[6] L.M. Carrera, J. Jimenez-Becerril, et al., J. Am. Ceram. Soc. 78 (1995) 933.
[7] P. Ravindranathan, S. Komarneni, R. Roy, J. Mater. Sci. Lett. 12 (1993) 369.
[8] L.E. Shea, J. Mckittrick, O.A. Lopez, J. Am. Ceram. Soc. 79 (1996) 3257.
[9] D. Kim, K. Cho, et al., Key Eng. Mater. 161–163 (1999) 87.
[10] H. Ohno, S. Konishi, T. Nagasaki, T. Kurasawa, H. Katsuta, H. Watanabe, J. Nucl. Mater. 155–157 (1985) 181.
[11] Z.Y. Wen, Z.X. Lin, K.G. Chen, J. Mater. Sci. Lett. 15 (1996) 105.
[12] J.J. Kingsley, L.R. Pedrson, Mater. Res. Soc. Symp. Proc. 296 (1993) 361.
[13] S. Konishi, H. Ohno, T. Hayashi, K. Okuno, T. Matsuo, in: G.W. Hollenberg, I.J. Hastings (Eds.), Fabrication and Properties of Lithium Ceramics, Advances in Ceramics, vol. 27, The American Ceramic Society, Westerville, OH, 1990, p. 173.
[14] S. Konishi, H. Ohno, J. Am. Ceram. Soc. 67 (1984) 418.
[15] F. Alessandrini, C. Alvani, S. Casadio, F. Croce, High Temp. High Press. 20 (1988) 113.
[16] F. Alessandrini, C. Alvani, S. Casadio, M.R. Mancini, C.A. Nannetti, J. Nucl. Mater. 224 (1995) 236.