

Pressure-induced grain size reduction in LiAlO₂

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Abstract: This work presents an experimental study on LiAlO₂ at pressure up to 5.0 GPa at 389 K by using large-volume static high-pressure technology. X-ray diffraction analysis shows that a pressure-induced grain size reduction in LiAlO₂ has been observed. The grain size reduces from ~70 nm to ~20 nm after high-pressure treatment. It has the implications to the high-pressure behaviour of LiAlO₂ and the synthesis of nano-scale materials under high pressure.

Key words: High Pressure; LiAlO₂; Grain Size

0 Introduction

Lithium aluminate (LiAlO₂), a typical ABO₂-type compound, has potential applications in the energy industry as lithium battery cathodes^[1] and electrolyte tiles for molten carbonate fuel cells (MCFC)^[2]. On the other hand, because of its good performance under high neutron and electron radiation, LiAlO₂ is also a promising lithium ceramic suitable as tritium breeding material in fusion reactors^[3, 4, 5]. LiAlO₂ has been known since it was first synthesized by Weyberg in 1906^[6]. Up to now, at least six different modifications have been described^[7-16].

Previous studies show that LiAlO₂ crystallizes with three different high-pressure structures: the hexagonal α -LiAlO₂, orthorhombic β -LiAlO₂ and tetragonal δ -LiAlO₂^[8, 11, 12, 13, 16]. After pressure release, these metastable phases formed at high-pressure were found to be quenchable. Upon heating at ambient pressure, however, the reversal transition into the γ -phase will occur. Generally, high temperature favors the growth of crystal grain, while high pressure induces densification and restrains the grain size growth. Recently, we reported a comprehensive study^[16] on the high-pressure phase transition of LiAlO₂. However the properties of LiAlO₂ at high pressure at low temperature (~100 K higher than room temperature) have not been well studied. It is still interesting to investigate the high-pressure behaviors of LiAlO₂ at high pressure at relative low temperature.

In this work, the high-pressure behaviors of LiAlO₂ have been investigated at high-pressure from 1.2 GPa to 5.0 GPa and the temperature fixed at 389 K. A pressure-induced grain size reduction in LiAlO₂ has been observed. This phenomenon leads us to the further insight into the pressure-induced amorphous and also has the implication to other ABO₂-type compound.

1 Experimental

The starting γ -LiAlO₂ sample was synthesized by standard solid-state reaction method from high purity α -Al₂O₃ and Li₂CO₃ powders with molar ratio of 1:1. The oxide mixture was treated at 1373 K for 12 hours, and then quenched by cooling to room temperature in air. The obtained sample was compacted in advance into a disk shape (7.0 mm in diameter and 4.0 mm in height) and placed in a capsule made of polycrystalline hexagonal BN, and then contained in the pyrophyllite high-pressure cell. The schematic assembly of high-pressure cell in the present study is illustrated in Fig. 1.

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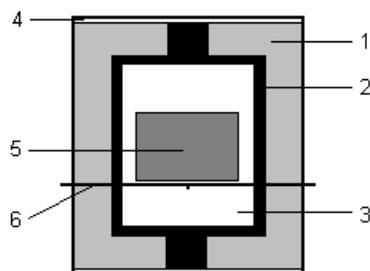


图1 高压实验的样品组装图。(1) 叶腊石;(2) 石墨管;(3) 六方氮化硼;(4) 钼片;(5) 样品;(6) 热电偶
Fig. 1 Schematic diagram of sample assembly for the high-pressure experiments. (1) pyrophyllite; (2) graphite furnace; (3) hexagonal BN; (4) Mo sheet; (5) sample; (6) thermocouple.

The conditions of high-pressure were generated with a large-volume cubic-type static high-pressure apparatus^[16]. Tungsten carbide anvils were used to squeeze the pyrophyllite cell and generate high-pressures up to 5.5 GPa in the sample. The pressure was calibrated at room temperature by means of the known pressure-induced phase transitions of Bi, Tl and Ba^[16]. A graphite furnace installed in the high-pressure cell was used to heat the sample, and the temperature was directly measured by thermocouples. Pressure and temperature uncertainties are estimated to be less than ± 0.1 GPa and ± 10 K, respectively. No correction was applied for the effect of pressure on the thermocouple electromotive force (emf). The sample was first pressurized to a certain pressure, and then heated to a desired temperature (389 K) for 30 minutes. After that, the heating power was cut off and the sample was decompressed to ambient pressure when it was cooled to room temperature. By subjecting high-pressure and high-temperature (HPHT) for a period of 30 minutes, the quenched samples are recovered from the hBN capsule.

The starting materials as well as the high-pressure treated samples were ground to fine powder and were characterized by powder X-ray diffraction (Philips X'Pert powder diffractometer) using Cu $K\alpha$ -radiation in a reflection mode, and the scan range of $10^\circ \leq 2\theta \leq 80^\circ$ in a step increment of 0.02° was utilized.

2 Results and Discussion

Fig. 2 illustrates five X-ray diffraction spectra for the γ -LiAlO₂ samples treated at different pressure conditions. Upon compression at 389 K, the γ -LiAlO₂ samples experience a significant grain size reduction. The starting material consists of loose powders with average grain size of about 70 nanometers. X-ray diffraction pattern for the starting material was taken at ambient conditions, while other four patterns were obtained for the ground samples treated at different pressure (1.2 GPa, 2.0 GPa, 2.7 GPa and 5.0 GPa) and the temperature of 389 K. The peaks were found to be gradually broadened with the pressure increasing from 1.2 GPa to 5.0 GPa. Some typical peaks, which will be used for the calculation of the grain size, are indexed in the Fig. 2.

X-ray diffraction peak broadening (β) can be caused by small grain size and the presence of micro-strain^[17-19]. The broadening effects of small grain size and micro-strain is superimposed, but contributions of small grain size and micro-strain to peak broadening are able to be separated with the following equation^[17]:

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{L} + \frac{\varepsilon \sin \theta}{\lambda} \quad (1)$$

Where $\beta \cos \theta / \lambda$ represents the physical peak broadening, L is the mean crystalline size and ε is the mean magnitude of micro-strain inside of the grains, θ is the Bragg angle and λ is x-ray wavelength.

According to Eq. (1), different diffraction peaks should give a linear plot of $\beta \cos \theta / \lambda$ vs. $\sin \theta / \lambda$ with slope ε and ordinate intercept $1/L$. Therefore, the average grain size and mean micro-strain can be derived by plotting $\beta \cos \theta / \lambda$ as a function of $\sin \theta / \lambda$ ^[19].

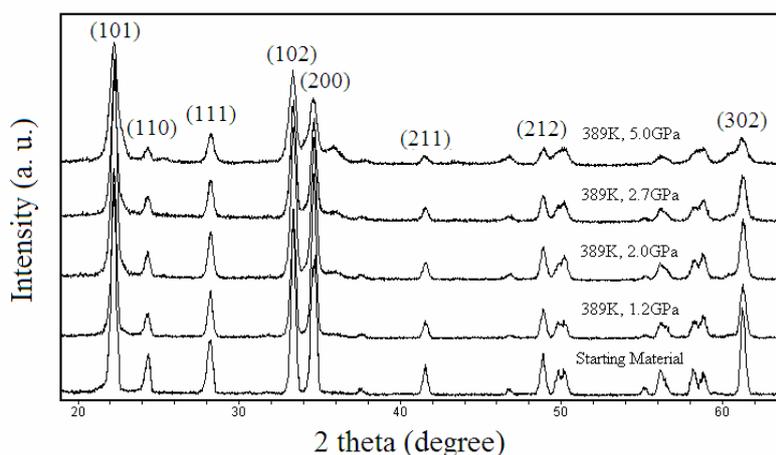


图 2 初始 γ -LiAlO₂粉末样品以及在 389 K 温度条件下高压处理并研磨过样品的 X 射线衍射图谱。该图同时标出了用于计算晶粒尺寸的 X 射线衍射峰的晶面指数。

Fig. 2 X-ray diffraction patterns of starting γ -LiAlO₂ powder and the ground samples recovered from different high pressures at 389K. The peaks for the calculation of grain size are indexed.

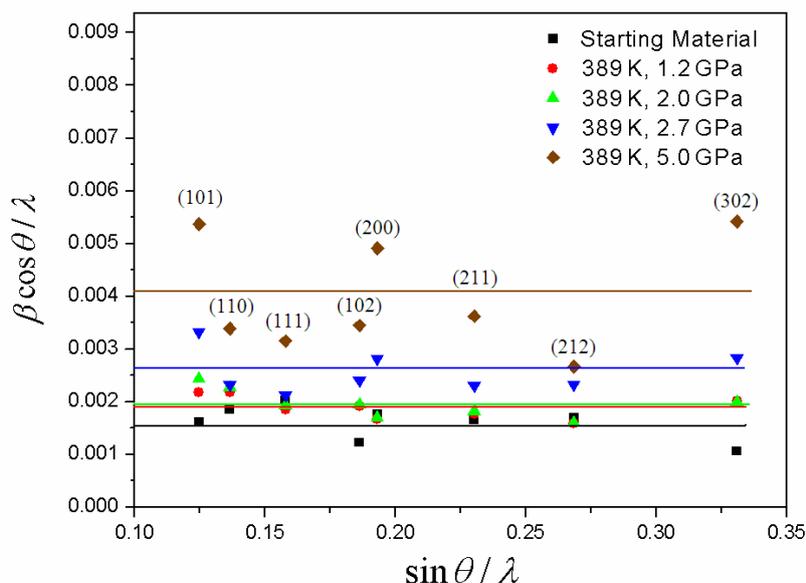


图 3 函数值 $\beta \cos \theta / \lambda$ 随自变量 $\sin \theta / \lambda$ 变化关系。实线为实验数据的线性拟合。通过拟合直线的斜率和截距可以计算出应力和晶粒尺寸对 X 射线峰宽化的贡献。

Fig. 3 Separation of the grain size and strain contributions in the plot of $\beta \cos \theta / \lambda$ against $\sin \theta / \lambda$. The solid lines are linear fits to the experimental data.

Fig. 3 illustrates the separation of grain size and strain contributions in the plot of $\beta \cos \theta / \lambda$ against $\sin \theta / \lambda$. The slope of the straight line reflects the microscopic strain distribution (ϵ) of γ -LiAlO₂ due to the grain-to-grain contact after compression, and the intercept reflects the grain size ($1/L$). The grain size decreases significantly as the pressure increased while the mean micro-strain remains constant at about zero. That is to say, the broadening of the peak is merely the result of reduction of grain size and the contribution of micro-strain in grains can be neglected.

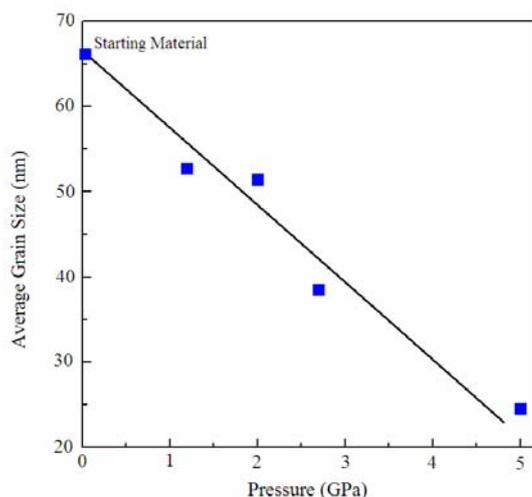


图 4 γ -LiAlO₂样品的平均晶粒尺寸随压力变化关系。实线为实验数据的线性拟合。

Fig. 4 The average grain size of the γ -LiAlO₂ samples as a function of the pressure. The solid line is linear fit to the experimental data.

Fig. 4 shows that the average gain size of the γ -LiAlO₂ samples as a function of pressure. The solid lines are linear fits to the experimental data. It can be seen that the grain size decreases significantly after high-pressure treatment. As the porous powder sample is compacted and densified through the cataclasis and deformation, all the initial void spaces between the grains close up, the grain size of sample treated at high pressure are smaller than the initial one, while the stress in the treated sample released with during the decompression. The phenomenon of pressure-induced reduction of grain size has been attracted increasing interest in high-pressure research [20,21]. A previous study on olivine manifested that the compression at room temperature can induce grain size of olivine from 1 μ m to a few tens of nm [20]. In the present study, we have also observed a process of pressure-induced nanoparticle size reduction in γ -LiAlO₂ from X-ray diffraction observation. This pressure-induced grain size reduction is the threshold of the pressure-induced fully amorphous. It has the implication to the synthesis of amorphous or nano-scale materials under high pressure.

3 Conclusion

In this paper, we report an interesting high-pressure experimental study on LiAlO₂. Using large-volume static high-pressure technology and X-ray diffraction analysis, we have observed a process of pressure-induced nanoparticle size reduction in γ -LiAlO₂. The grain size reduces from ~70 nm to ~20 nm after high-pressure treatment. High-pressure is the powerful method to synthesis of nano-scale materials.

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LiAlO₂的压致晶粒细化

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摘要: 本工作采用大腔体静高压技术和X射线分析手段, 研究高压下LiAlO₂材料的压致晶粒细化特性。在 389 K温度条件下, LiAlO₂材料的晶粒尺寸随着合成压力的升高而降低, 晶粒尺寸从约 70 nm (初始材料) 减小到约 20 nm (5.0 GPa)。该发现对LiAlO₂材料的高压物性研究以及高压纳米材料的合成有意义。

关键词: 高压; LiAlO₂; 晶粒尺寸

中图分类号: O52