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Phase transitions of LiAlO₂ at high pressure and high temperature

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ABSTRACT

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1. Introduction

Lithium aluminate, LiAlO₂, has attracted attention mainly in two fields: solid-state chemistry [1,2] and nuclear physics [3–5]. It 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 appears to be promising lithium ceramic suitable as tritium breeding material in fusion reactors [3–5]. 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. The γ -phase is tetragonal with lattice parameters a = 5.169 Å and c = 6.268 Å, space group P4₁2₁2 and a density of 2.615 g/cm³ [7,8]. β -LiAlO₂ was first mentioned by Thery et al. [9] as a lowtemperature form. This form has orthorhombic symmetry with lattice parameter a = 5.280 Å, b = 6.300 Å and c = 4.900 Å, space group *Pna2*₁ and a density of 2.685 g/cm³ [9–11]. Its crystal structure can be described as a three-dimensional network of LiO₄ and AlO₄ tetrahedron [10]. Marezio and Remeika [8,12] and Chang and Margrave [13] have documented the existence of other two LiAlO₂ modifications, which can be synthesized under high pressures. The hexagonal α -phase was obtained for the first time by Lehmann by heating an equimolar mixture of Li₂CO₃ and α -Al₂O₃ at 873 K [14], and then by Marezio, starting with γ -phase, at 3.5 GPa and 1123 K. α -Phase LiAlO₂ is hexagonal with space

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This work presents a comprehensive study on phase transitions in LiAlO₂ system at high pressures and temperatures (0.5–5.0 GPa and 300–1873 K, respectively), as well as the phase stability for polymeric phases of LiAlO₂ in the studied *P*–*T* space by X-ray diffraction (XRD). Besides the previously described polymorphic hexagonal α -phase, orthorhombic β -phase and tetragonal δ -phase, a possible new phase of LiAlO₂ was observed after the tetragonal γ -LiAlO₂ sample was treated at 5.0 GPa and 389 K. The stable regimes of these high-pressure phases were defined through the observation of coexistence points of the polymeric phases. Our results revealed that LiAlO₂ could experience structural phase transitions from γ -LiAlO₂ to its polymorphs at lower pressures and temperatures compared to the reported results. Hexagonal α -LiAlO₂ with highly (003) preferential orientation was prepared at 5.0 GPa and 1873 K.

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group *R*-3*m*, lattice parameters a = 2.799 Å and c = 14.180 Å, and the density of 3.401 g/cm³ [8,12]. Another high-pressure polymorph, confusingly called " β -LiAlO₂", was first synthesized in an opposed-anvil press at 1.8 GPa and 643 K, starting with a mixture of Li₂O₂ and Al₂O₃. This form has been indexed on the basis of a monoclinic structure with cell dimensions a = 8.147 Å, b = 7.941Å, c = 6.303 Å and $\beta = 93.18^{\circ}$ [13]. Recently, a new high-pressure phase of LiAlO₂ has been recovered through a shock compression technique at pressure above 9 GPa. The δ -phase has a tetragonal structure with lattice parameters of a = 3.8866 (8)Å and c = 8.3001 (18)Å and a calculated density of 3.51 g/cm³, about 34% denser than γ -LiAlO₂ [11]. The sixth reported modification, ε-LiAlO₂, is indexed with a cubic symmetry with lattice constant a = 12.650 Å and space group $I4_132$ [15], synthesized by reducing corundum with lithium hydride at about 773 K. The X-ray diffraction (XRD) pattern for this phase is very similar to the one for γ -LiAlO₂ [7]. The molar volume of ε -phase is practically identical with the γ -phase [10]. Table 1 summarizes the structure details, densities and references for the previously reported modifications of LiAlO₂.

As mentioned above, LiAlO₂ crystallizes with three highpressure structures: the hexagonal α -LiAlO₂, tetragonal δ -LiAlO₂ and monoclinic LiAlO₂ [8,11–13]. 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. The phase transition from hexagonal α -phase to tetragonal γ -phase has been extensively studied [16–21] but less known about its reverse transformation. Marezio reported about 40 years ago that the tetragonal γ -phase could transform into the hexagonal α -phase at



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ModificationCrystal structureSpace groupCN. ^a Lattice parametersDensity (g/cm ³)Ref. α Hexagonal $R-3m$ 6 $a = 2.799$ Å, $c = 14.180$ Å 3.401 [12,14] β Orthorhombic $Pna2_1$ 4 $a = 5.280$ Å, $b = 6.300$ Å, $c = 4.900$ Å 2.685 [9] $(\beta)^b$ Monoclinic $P2/m$ 4, 6 $a = 8.147$ Å, $b = 7.941$ Å, $c = 6.303$ Å, $\beta = 93.18^{\circ}$ 0.269 [13,26] γ Tetragonal $P4_{12}_{12}$ 4 $a = 5.169$ Å, $c = 6.268$ Å 2.615 [7,8] δ Tetragonal $14_1/amd$ 6 $a = 3.887$ Å, $c = 8.300$ Å 3.51 [11] ϵ Cubic 14_132 4 $a = 12.650$ Å ~ 2.615 [10,15]							
α Hexagonal $R-3m$ 6 $a = 2.799$ Å, $c = 14.180$ Å3.401 $[12,14]$ β Orthorhombic $Pna2_1$ 4 $a = 5.280$ Å, $b = 6.300$ Å, $c = 4.900$ Å2.685 $[9]$ $(\beta)^b$ Monoclinic $P2/m$ 4, 6 $a = 8.147$ Å, $b = 7.941$ Å, $c = 6.303$ Å, $\beta = 93.18^{\circ}$ 0.269 $[13,26]$ γ Tetragonal $P4_{12}_{12}$ 4 $a = 5.169$ Å, $c = 6.268$ Å2.615 $[7,8]$ δ Tetragonal $I4_1/amd$ 6 $a = 3.887$ Å, $c = 8.300$ Å3.51 $[11]$ ϵ Cubic $I4_132$ 4 $a = 12.650$ Å ~ 2.615 $[10,15]$	Modification	Crystal structure	Space group	CN. ^a	Lattice parameters	Density (g/cm ³)	Ref.
ϵ Cubic $I4_{1}32$ 4 $a = 12.650$ Å ~ 2.615 [10,15]	α β (β) ^b γ δ	Hexagonal Orthorhombic Monoclinic Tetragonal Tetragonal	R-3m Pna2 ₁ P2/m P4 ₁ 2 ₁ 2 I4 ₁ /amd	6 4 4, 6 4 6	$ \begin{array}{l} a = 2.799 \text{\AA}, c = 14.180 \text{\AA} \\ a = 5.280 \text{\AA}, b = 6.300 \text{\AA}, c = 4.900 \text{\AA} \\ a = 8.147 \text{\AA}, b = 7.941 \text{\AA}, c = 6.303 \text{\AA}, \beta = 93.18^{\circ} \\ a = 5.169 \text{\AA}, c = 6.268 \text{\AA} \\ a = 3.887 \text{\AA}, c = 8.300 \text{\AA} \end{array} $	3.401 2.685 0.269 2.615 3.51	[12,14] [9] [13,26] [7,8] [11]
	з	Cubic	I4 ₁ 32	4	a = 12.650 Å	\sim 2.615	[10,15]

Table 1Crystal data for modifications of LiAlO2

^a CN. = coordination number.

^b Confusingly called "β-LiAlO₂".

3.5 GPa and 1123 K [8,9]. To date, however, experiments on LiAlO₂ at static high pressure above 3.5 GPa have not been reported yet. Whether the γ - to α -phase transformation can also take place under other *P*–*T* conditions remains to be confirmed. Recent shock-wave experiments showed that tetragonal δ -phase has been synthesized from shock-compressed γ -LiAlO₂ at about 9 GPa [11]. But it is not clear whether this tetragonal δ -phase can be synthesized by static high-pressure method. It is also interesting to define the phase stable regions for different structure modifications of LiAlO₂. In this work, we investigated the phase transitions of LiAlO₂ at high pressure from 0.5 to 5.0 GPa and temperature from 300 to 1873 K using γ -LiAlO₂ as a starting phase. The behavior of modifications of LiAlO₂ polymeric phases were defined by XRD observations over the experimental *P*–*T* range.

2. 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 h, 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 (hBN), 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. Conditions of high pressure and high temperature (HPHT) were generated with a large-volume cubic-type multi-anvil high-pressure apparatus [22]. 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 [23]. 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 for 30 min. 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 HPHT for a period of 30 min, the quenched samples are recovered from the hBN capsule.

The starting materials as well as the high-pressure-treated samples were characterized by powder XRD (Philips X'Pert powder diffratometer) 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.



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 and (6) thermocouple.

3. Results and discussion

The experimental temperature was measured by a thermocouple that was placed in the bottom center of the sample (see Fig. 1). The thermocouple was used for both the temperature measurement and heating control. The temperature, however, could only be measured at a single point. It is necessary to take account of the thermal gradient resulting from various sample and furnace configurations in the assembly. Owing to the existence of temperature gradient across the sample, the temperature difference between the center and the end of the sample is estimated to be about 20-50 K, and the temperature difference between the bottom center and the furnace wall is estimated to be about 10–20 K. On the other hand, the high-pressure structure of LiAlO₂ has been retained after quenching. Based on above two views, the stability boundaries for high-pressure modifications of LiAlO2 can be determined through the observation of coexistence points of the polymeric phases.

As observed in previous study [8], γ -LiAlO₂ underwent a phase transition to α -LiAlO₂ at 3.5 GPa and 1123 K. We varied experimental conditions, and found that α -LiAlO₂ was stable over a wide *P*–*T* range. Summary of experimental results is illustrated in Fig. 2. It can be seen that even relatively low pressure can induce the γ - to α -phase transition. Pure α -phase LiAlO₂ can be synthesized from γ -phase at 0.5 GPa and 933 K. The phase transition temperature decreased with increasing the pressure. Upon a further increase of pressure up to 5.0 GPa, this phase transformation takes place below the temperature of 700 K. The region I in Fig. 2 is the stable region for the α -phase. The dash line 1, which has a negative slope in lower-pressure region and a nearly vertical slope in higher-pressure region, is a boundary of the stable region for α -phase in the *P*–*T* space. On heating, the α -phase LiAlO₂ will



Fig. 2. Summary of the experimental results in the *P*–*T* space for illustration of the phase diagram of LiAlO₂. Region I is the stable region of α -phase, and region II is the stable region of β -phase. Dash lines 1 and 2 are the boundaries between these stable regions. The Region above dot line 3 is the *P*–*T* space where δ -phase could be observed by XRD in the quenched samples (marked "+ δ " in the diagram). More than 60 experimental points have been collected to construct this diagram. The symbols indicate the conditions for the following key observations: black circles for the pure α -phase, blue circles for the pure β -phase, green circles for the pure γ -phase, red circles for the δ -phase, and two or more color on one circle stand for the single phase in the high-pressure recovered sample by means of RIR.

transform into γ -phase at temperature above 1000 K under ambient pressure [16–21]. Since the volume change is known, hexagonal α -LiAlO₂ (3.401 g/cm³) is about 30% denser than the tetragonal γ -LiAlO₂ (2.615 g/cm³), if we neglect the compressibility for the both phases, an approximate value for ΔG (free energy change) of the γ - to α -phase transition at 3.5 GPa will be 4.56 Kcal/mol. Using the Redlich-Kister equations, Byker et al. [21] calculated the phase diagram for the Li₂O–Al₂O₃ system, and discussed the stability of the α -LiAlO₂ as a function of pressure and temperature. They pointed out that the equilibrium pressure was supposed to be 0.8 GPa at 1123 K [21]. As can be seen from Fig. 2, the equilibrium pressure may be even lower than 0.5 GPa at 1123 K.

We also found that the α -phase was stable at 5.0 GPa and 1873 K. Fig. 3 presents three diffraction patterns of crashed α -LiAlO₂ samples recovered from various P-T conditions. It is obvious that the sample recovered form 5.0 GPa and 1873 K exhibits a highly (003) preferred orientation. As the pressure and temperature were increased, the intensity for the (003) peak of the hexagonal α-LiAlO₂ increased significantly. The polycrystalline sample prepared at HPHT preferentially oriented along (003) plane due to the particular structure of the hexagonal phase and the influence of HPHT annealing. The orientation of crystal with anisotropic elastic properties is strongly related to the stress direction and the strongest axis is preferably oriented along the direction of minimal stress [24]. Texture change of sample under deviatoric stress can be caused by recrystallization, rotation, and/ or sliding of crystalline grains [25]. Under high stress and high temperature, hexagonal α -LiAlO₂ is easy to slide along the direction, which is perpendicular to c-axis. The appearance of strong (003) peak also indicates that the preferred growing direction of α -LiAlO₂ crystals may be perpendicular to the (003) direction during HPHT treatments.

From Fig. 3, some additional weak diffraction peaks can be found in the pattern for $LiAlO_2$ sample quenched from 5.0 GPa and 1873 K. These peaks correspond to the diffractions from a spinel



Fig. 3. Three XRD patterns of α -LiAlO₂ recovered from different pressure and temperature conditions. The hexagonal polycrystalline sample recovered form 5.0 GPa and 1873 K exhibits a highly (003) preferred orientation. Spinel LiAl₅O₈ is a byproduct from high temperature decomposition of LiAlO₂. The inset shows the detail of the XRD pattern for the sample recovered from 5.0 GPa and 1873 K, in which peaks for the spinel LiAl₅O₈ are clearly visible.

 ${\rm LiAl_5O_8}.$ This phenomenon could be attributed to the following reaction:

$5\text{LiAlO}_2 = \text{LiAl}_5\text{O}_8 + 2\text{Li}_2\text{O}$

LiAlO₂ was partially decomposed to LiAl₅O₈ and Li₂O at 5.0 GPa and 1873 K. As Li₂O cannot be detected by XRD, it might exist as an amorphous state. Spinel LiAl₅O₈ is a byproduct from high temperature decomposition of LiAlO₂. At high temperature, the lithium-poor LiAl₅O₈ always appears because of the excessive evaporation of Li from LiAlO₂ [26,27]. At HPHT, however, it is still impossible to completely prevent the decomposition, and it is not determined that which one is the parent phase of the spinel LiAl₅O₈, tetragonal γ -phase or hexagonal α -phase.

Using Li₂O₂ and Al₂O₃ as starting materials, Chang and Margrave [13] first obtained the monoclinic phase of LiAlO₂ (JCPDS 22-0407) at a high pressure and moderate temperature of 1.8 GPa and 643 K. Fischer [28] subsequently synthesized it at ambient pressure and temperature of 773 K. As described by Chang, the monoclinic phase contains both tetrahedral and octahedral coordination of the aluminum ions [13]. It seems unusual that α -, γ - and δ - phase are 12.64, 9.72 and 13.05 times as dense as the monoclinic phase (0.269 g/cm³). Our experiments indicate that this monoclinic phase of LiAlO2 could not be obtained directly from γ -LiAlO₂, while it was the orthorhombic β -phase of LiAlO₂ [9] that could be synthesized from γ -LiAlO₂ at high pressure. This is the first time that the orthorhombic phase of LiAlO₂ has been obtained by HPHT method. The P-T conditions for the γ - to β -phase transition are lower than the conditions under which α -phase could be formed. The region II in Fig. 2 is the stable region of β -phase in the *P*-*T* space. The dash line 2 is a *P*-*T* boundary between the stable regions of γ - and β -phases. Since the stable region of this phase is somewhat narrow, the β -phase is easy to coexist with other modifications in the recovered samples. A pure β -phase sample (marked as "a" in Fig. 2) was obtained at 0.8 GPa and 623 K. The XRD pattern for the pure orthorhombic β -phase LiAlO₂ is shown in Fig. 4, where all diffraction peaks could



Fig. 4. XRD for pure β -phase sample (marked as "a" in Fig. 2) treated at 0.8 GPa and 623 K. The two JCPDS reference patterns 33-0785 and 22-0407 are quite similar. The orthorhombic phase pattern (JCPDS 33-0785) is in better agreement with our experimental data.

be indexed to the single phase of orthorhombic LiAlO₂ and matched with the standard pattern (JCPDS 33-0785). It is interesting that the JCPDS reference pattern 33-0785 and 22-0407 are quite similar except for several additional minor peaks. According to our experimental results, they should be the same phase of β -LiAlO₂, although the previously reported structural information for these two separately synthesized samples is different [9,13]. We also speculate that the density of the so-called "monoclinic" LiAlO₂ phase is ~2.69 g/cm³ instead of ~0.269 g/cm³ in Table 1.

RIR is the reference intensity ratio for each phase relative to the intensity for corundum. It can be applied for constructing phase diagram from the XRD data. We can perform quantitative analysis on multi-phase XRD patterns with the RIR values known for each phase. Based on the definition of RIR, we have calculated the RIR for β -LiAlO₂. The ratio of the peak height of the strongest line (120) of β -LiAlO₂ to the strongest line of corundum-hexagonal reflection (113) for a 1:1 mixture by weight of the two phases has a value of 0.63. Combined with the known RIR values for γ - and α -LiAlO₂, we can determine the content of each form in a multiphase sample. The relative content of the each phase (shown in Fig. 2 for colorized area in the pie) and the boundaries between the stable regions of different modifications were defined in terms of the RIR values for LiAlO₂.

According to previous experimental results, the new δ -phase discovered at above 9 GPa is a high-pressure stable phase compared to α -LiAlO₂ [11]. In the present study, this tetragonal δ -phase can only be synthesized at the static pressure above 2.0 GPa. The dot curve 3 in Fig. 2 is a boundary, above which the δ -phase can be detected by XRD in the quenched samples. δ -LiAlO₂ is only stable at low temperature [11]. The forming temperatures of the six-fold coordinated δ -LiAlO₂ are expected to be relatively modest at high pressure and further transition to β - and/or α -phase would occur once the treating temperature was

increased. As shown in Fig. 2, the content of δ -phase in high *P*-*T*-treated samples increased with increasing the pressure. Under our experimental conditions, however, the δ -LiAlO₂ has not been prepared as a single phase. The formation of δ -LiAlO₂ under relatively modest *P*-*T* conditions might be due to the following three possible reasons: first, some local grain-to-grain contacts under compression yield higher stress than the average stress of the whole polycrystalline sample, the part near the contacts could obtain enough driving force for a phase transformation to another denser form (δ -phase); second, during the quenching process, δ -LiAlO₂ might be formed from other modifications (β - or α -phase); and third, the minimum pressure required for the γ - to δ -phase transition might be about 2 GPa under static compression.

Fig. 5 presents the diffraction pattern for the sample (*P*–*T* condition marked as "b" in Fig. 2) recovered from 5.0 GPa and 593 K, in which α , β and δ phases are coexisting. Peaks for the δ -LiAlO₂ phase in the pattern are clearly visible. The XRD reference pattern of δ -LiAlO₂ is taken from Ref. [11]. As shown in Fig. 6, another sample recovered form 5.0 GPa and 525 K ("c" in Fig. 2) is found to be a coexistence of α , β , γ and δ -phases. The existence of samples with multi-phases are likely due to the narrow stable regions of these phases as well as the temperature and stress gradient across the samples during the HPHT treatments.

In order to make certain whether the HPHT treatment time, which is not always a period of 30 min, would have any effect on the product of phase transitions. Additional experiments were carried out. We selected a typical phase coexistence point ("d" in Fig. 2) in the foregoing phase transition diagram. Samples were treated at the same pressure and temperature (1.2 GPa, 593 K) for the periods of 15, 30 and 60 min, respectively. Fig. 7 presents the XRD patterns for these three samples. The results show that samples treated for different time have no remarkable change in



Fig. 5. Selected XRD pattern for LiAlO₂ sample recovered from 5.0 GPa and 593 K. α , β and δ phases are coexisting in a sample. Peaks for the previously described δ -LiAlO₂ are observed clearly.



Fig. 6. Selected XRD pattern for LiAlO₂ sample recovered from 5.0 GPa and 523 K. α , β , γ and δ phases are coexisting in the sample. Peaks for these four phases are identified.



Fig. 7. XRD patterns of the samples treated at the same pressure and temperature (1.2 GPa, 593 K) for the periods of 15, 30 and 60 min, respectively. The samples treated for different time have no remarkable change in phase composition.

phase composition. Therefore, 30 min experimental P-T time for each specimen is considered to be adequate for the purpose of the present study.

The major peaks for δ -LiAlO₂ were observed in the XRD pattern, which was taken from a sample recovered form 5.0 GPa and 389 K. The (101), (004) and (200) peaks of the δ -phase are



Fig. 8. Selected XRD patterns of starting γ -LiAlO₂ powder and samples recovered from different high pressures at 389 K. The δ -phase can be detected in the sample recovered from 5.0 GPa and 389 K. The (101), (004) and (200) peaks for δ -LiAlO₂ are marked by arrows. The intensities of two new diffraction peaks (marked by triangles) increased with increasing pressure. The two new peaks might be come from a new high-pressure phase of LiAlO₂, which has not been identified with the current data.

marked by arrows in Fig. 8. Since the δ -phase (200) peak overlapped with the γ -phase (103) peak (marked by circle), the relative intensity of the XRD peak, located at 2θ of 46.86°, increases with pressure might be due to the contribution of the δ -phase formation. As also can be seen in Fig. 8, it appears that the intensities of two new diffraction peaks (marked by triangle) increase with increasing pressure. However, these two peaks have not been identified because some of the other peaks for the possible new phase might be overlapped by the peaks of γ and/or δ phases as well as the number of peaks for the possible new phase is not enough for structure refinement. The observed dspacing of the two new peaks are 2.5008 and 1.5829 Å, respectively. As shown in Fig. 8, the intensities of two new diffraction peaks increase with increasing pressure. So the formation of this possible new phase is related to the effect of pressure. Since pure γ -LiAlO₂ was used as the starting material, these two new peaks might be come from a new phase of LiAlO₂ or a new daughter phase of LiAlO₂. Under the moderate temperature of 389 K, the effect of increasing pressure is unlikely to have LiAlO₂ decomposed. Therefore, the two new peaks are likely from a new phase of LiAlO₂.

Both the Li and Al atoms are four-fold coordinated in the starting tetragonal *y*-LiAlO₂ structure, but the coordination number for Li and Al change from four-fold in the γ -LiAlO₂ to six-fold in other two polymorphs (hexagonal *α*-LiAlO₂ and tetragonal δ -LiAlO₂) after high-pressure treatments. From the crystal-chemical point of view, the driving force for breakdown of the γ -LiAlO₂ structure framework at high pressure may be associated with the stability of the tetrahedral coordination around the Li and Al atoms. It can be extrapolated that the average coordination number for the cations would increase on going from the phase stable at low pressure to the one stable at high pressure. Since this possible new phase can be obtained from γ -phase under pressure, the coordination numbers for Li and/or Al of this possible new high-pressure polymorph might be larger than that of γ -phase (>4), and the density of this possible new phase could be denser than γ -phase. According to solid-state chemistry, it is worthy to address the structural similarity between LiAlO₂ and LiFeO₂ [11]. LiFeO₂ has three polymorphisms:

rhombohedral, cubic and tetragonal structures. The radius of Al^{3+} ion in LiAlO₂ is close to that of Fe³⁺ in LiFeO₂. α -LiAlO₂ and δ -LiAlO₂ are isostructural to the rhombohedral and tetragonal LiFeO₂, respectively. The structural similarity between LiAlO₂ and LiFeO₂ can shed some light on the possible new high-pressure structure of LiAlO₂. The possible new phase found in our experiment might have a cubic symmetry, corresponding to the cubic LiFeO₂. Since the pressure above 5.0 GPa is currently out of our experiment capability, we cannot get further information on the possible new phase. It may be interesting to compress the LiAlO₂ above 5.0 GPa to investigate more in details on its phase transition in the future.

4. Conclusions

A detailed study of the phase stability of LiAlO₂ over a wide range of pressures and temperatures (0.5–5.0 GPa and 300–1873 K) is presented in this work. Modifications (α , β and δ) of γ -LiAlO₂ can be obtained under relatively modest *P*–*T* conditions compared to the previous description. We found that the α -LiAlO₂ sample recovered form HPHT exhibited a highly (003) preferred orientation, and the high pressure could not completely prevent the high-temperature decomposition behavior. We searched for the most appropriate *P*–*T* conditions for γ - to β -phase transformation, and have obtained a pure β -LiAlO₂ sample at 0.8 GPa and 623 K. In order to perform quantitative analysis on the samples with multi-phase, we have calculated the RIR for β -LiAlO₂. When high pressure is applied to γ -LiAlO₂ at 389 K, two new peaks from an unknown high-pressure phase were appeared. The two new peaks might be come from a denser form compared to γ -LiAlO₂.

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