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Pressure-Iduced Phase Transition of $LiAl_5O_8$ *

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Abstract: A phase transition concerning lithium aluminate oxide ($LiAl_5O_8$) was observed. High pressure synchrotron radiation X-ray diffraction was used to explore its structure in a diamond anvil cell up to 47.0 GPa. We found the two phases are coexisted over a very large pressure range in the experiments. According to the analysis on the dynamic change of diffraction peaks with the increasing of pressure and the data reduction using indexed program, a new high-pressure phase of $LiAl_5O_8$ was identified at pressure below 45.0 GPa. This new phase has potentially a orthorhombic structure with $a=0.995\,9$ nm, $b=0.644\,7$ nm, $c=0.333\,4$ nm and the space group of $Pmm2$.

Key words: $LiAl_5O_8$; high pressure; phase transition

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1 Introduction

The spinel $LiAl_5O_8$ has been widely used as a carrier compound for optical studies of d elements in tetrahedral sites[1-5]. Doped with small amounts of Fe^{3+}, V^{3+}, Cr^{3+} and Mn^{4+}, it exhibits interesting fluorescent and magnetic hyperfine properties[1-3]. $LiAl_5O_8$ is also a kind of material which has potential applications. Since the beginning of high p-T experimental explorations of the deep mantle, the spinel to post-spinel structural transitions have long been a central subject in deep Earth studies, many different types of transitions have been discovered[6-10]. Up to now, the properties of $LiAl_5O_8$ under high pressure has not been reported.

In the spinel structure, the cations occupy both tetrahedral and octahedral sites. These are located at the interstices of a close-packed oxygen lattice. In the case of $LiAl_5O_8$, two stable crystalline phases are possible, depending on the formation temperature of the system. Below 1 295 ℃, there exists a 1∶3 ordering of the lithium and trivalent aluminum ions along the [110] direction of the unit cell[11]. Primitive cell is primitive cubic, being characterized by the space group $P4_332$ (O^7) or $P4_132$ (O^6). The lattice parameter is 0.790 7 nm. Above 1 295 ℃, 1∶3 ordering is destroyed and the two types of cations are randomly distributed over the octahedral sites. In this disordered or high-temperature phase, the average structure is one of higher over-all symmetry and the space group corresponds to the standard spinel structure $F4_1/d32m$(O_h^7). The lattice parameter is 0.792 1 nm[11]. In this two types of $LiAl_5O_8$, the exchange of Li^+ and Al^{3+} are carried out by temperature. With increasing of temperature, Li^+ and

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Al^{3+} obtain activation energy and exchanges happen in lattice.

In this study, we investigated $LiAl_5O_8$ at ambient temperature and high pressure using synchrotron radiation X-ray diffraction and diamond anvil cell techniques. We reported the observation of a phase transition from bcc(body centered cubic) to orthorhombic in $LiAl_5O_8$ at room temperature for the first time. The sample displays the characteristics of a second-order phase transition across which the pressure dependences of lattice parameters are continuous, but their slopes are discontinuous. Pressure make lattice of $LiAl_5O_8$ produce distortion and change the interaction of Li, Al and O ion. With increasing of pressure, Li^+ and Al^{3+} move or exchange in lattice. The phase transition happens in $LiAl_5O_8$ under high pressure.

2 Experiment

The starting cubic-phase $LiAl_5O_8$ sample was synthesized using a self-flux method from high-purity α-Al_2O_3 (>99.999%) and Li_2CO_3 (>99.99%) powders with molar ratio of 1∶5. $LiAl_5O_8$ was formed by $Li_2CO_3 + 5Al_2O_3 \longrightarrow 2LiAl_5O_8 + CO_2\uparrow$ [12]. The oxide mixture was treated at 1 300 K for 2 h, and then quenched by cooling to room temperature in air. The starting materials were characterized by powder XRD (Philips X'Pert powder diffratometer) using Cu K_α radiation in a reflection mode, and the scan range of $10° \leqslant 2\theta \leqslant 80°$ in a step increment of 0.02° was utilized (see Fig. 1).

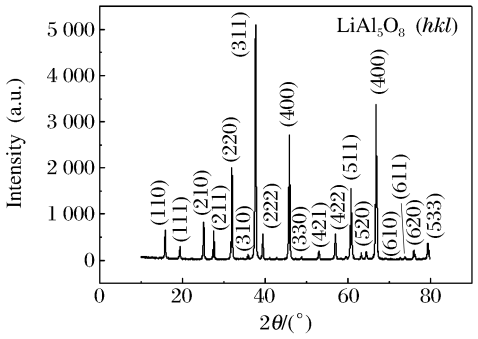


Fig. 1　XRD pattern of sample at room temperature and pressure

A Mao-type symmetric diamond-anvil cell with two beveled diamond anvils (100 μm central flat beveled at 8° angle from the 300 μm culet) was used and preindented the T301 gasket from the original thickness of 250 μm to 25 μm central thickness. A 100 μm diameter hole was drilled at the center of the gasket to form the sample chamber. $LiAl_5O_8$ powder was loaded in the sample chamber. A piece of Ruby chip was placed on top of the sample and served as a pressure standard. Silicone oil was used as pressure medium. High-pressure energy-dispersive X-ray diffraction experiments[13-14] were performed at 16BM-B beamline of the HPCAT Sector, Advanced Photon Source, Argonne National Laboratory, USA. The diffracted intensity was detected by a Ge solid state detector with a fixed Bragg angle at $2\theta = 12.000°$, and the exposure time was typically 300-350 s. Experiments were carried out up to 47.0 GPa and as many as 7 pressure steps were investigated in experiments.

3 Results and Discussion

The XRD patterns of the sample at each pressure from 3.0 GPa to 47.0 GPa are shown in Fig. 2. The XRD lines (533), (440), (511), (422), (421), (400), (222), (311), (220) and (210) of c-$LiAl_5O_8$ were given in the pattern of 3.0 GPa. All these lines shift to higher values of energy and have no unconventionality till 11.9 GPa. At 11.9 GPa, three lines (Labeled as 1, 2 and 3, marked solid circles) attracted our attention, and the emergence of the three lines indicated that another phase appeared. The disappearance of line (421) (Labeled as 4) further proves that a phase transition occurs, and the absence of broadening in other lines provides assurance that the changes in the diffraction lines have no relations with the loss of hydrostatic conditions. The lines 1 and 2 obviously come from another phase.

It is necessary to point out that the line 3 is likely to be mistakenly considered as the line (400). The location of (400) peak appears between line 2 and line 3 at 11.9 GPa. So we could conclude the line 3 belongs to other phase. And at 17.6 GPa, (400) diffraction peaks disappeared. Up to 45.0 GPa, all the peaks of the spinel phase are very weakened. Instead, the all new phase have appeared. Peaks of the new phase are marked by arrows. The new peaks become stronger and stronger with increasing pressure and the diffraction lines of c-$LiAl_5O_8$ exist all along till 45.0 GPa even more high pressure, which indicates that c-$LiAl_5O_8$ and or-$LiAl_5O_8$ coexist over a very wide range of pressure.

Fig. 3 shows the compression curves of $LiAl_5O_8$ from lattice parameters measured at different pressures. The dashed line is drawn by taking account of the visual observation of the transition at 17.6-45.0 GPa. The new phase was indexed as orthorhombic structure having a possible space group *Pmm*2 by FullProf. program [15-17]. The observed and calculated *d* values of the new phase at the 45.0 GPa are compared in Table 1, with lattice parameters of $a=0.9959$ nm, $b=0.6447$ nm, $c=0.3334$ nm and its space group of *Pmm*2.

Table 1 Observed and calculated *d* of the new phase at the pressure of 45.0 GPa

h	*k*	*l*	Observed *d*/(nm)	Calculated *d*/(nm)
3	0	0	0.3321(0)	0.3321(3)
0	1	1	0.2962(4)	0.2962(4)
2	0	1	0.2771(2)	0.2771(2)
0	3	0	0.2149(9)	0.2149(6)
4	0	1	0.1993(1)	0.1995(4)
3	2	1	0.1902(5)	0.1900(6)
6	2	0	0.1476(0)	0.1476(0)
2	3	2	0.1273(9)	0.1273(5)
1	4	2	0.1150(7)	0.1151(0)
7	1	2	0.1067(2)	0.1067(3)

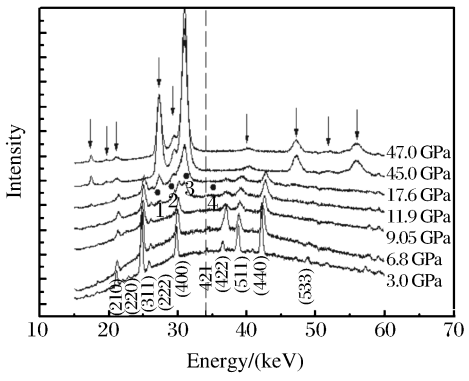


Fig. 2 XRD patterns of sample at high-pressure from 3.0 GPa(bottom pattern) to 47.0 GPa (Peaks for the new phase are marked by arrows)

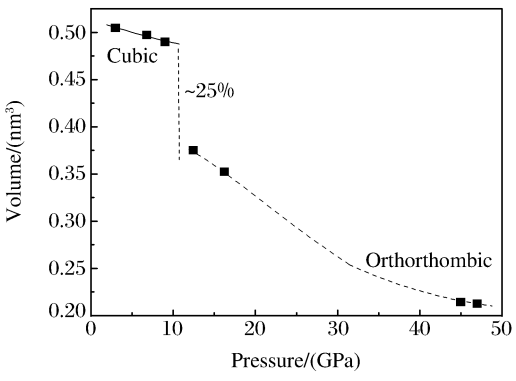


Fig. 3 Change of the cell volume with increasing pressure (The dashed line is drawn by taking account of the visual observation of the transition at 11.9 GPa)

4 Conclusions

In conclusion, the synchrotron radiation X-ray diffraction study has revealed a structural phase transition occurring below pressure 45.0 GPa and room temperature in the spinel-type $LiAl_5O_8$. The high-pressure phase is determined to be the orthorhombic structure with lattice parameters of $a=0.9959$ nm, $b=0.6447$ nm, $c=0.3334$ nm. This study has also duplicated an earlier visual observation of the transition.

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$LiAl_5O_8$ 高压相变研究

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摘要:运用金刚石压砧同步辐射 X 射线衍射,对尖晶石结构的 $LiAl_5O_8$ 进行了高压原位研究。实验发现:在高压下,一组 $LiAl_5O_8$ 的新相衍射峰出现,随着压力的增加,其新相衍射峰逐渐增强,当压力增加到 45.0 GPa 时,$LiAl_5O_8$ 的低压相衍射峰全部消失,而形成了一组高压新相衍射峰。采用指标化程序对衍射数据进行处理和分析,确定这一高压新相为正交晶系结构,其晶胞参数为 $a=0.9959$ nm,$b=0.6447$ nm,$c=0.3334$ nm ,空间群为 $Pmm2$。

关键词:$LiAl_5O_8$;高压;相变

中图分类号:O521.23 **文献标识码**:A