A New Polymorph of FeAlO₃ at High Pressure

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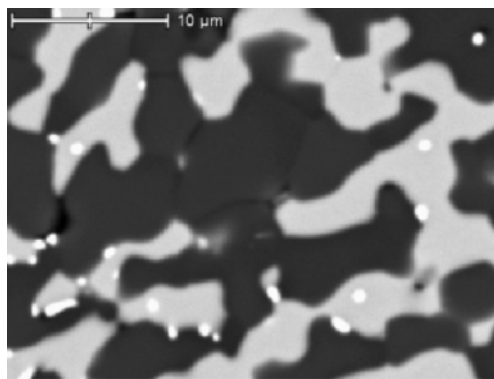*Received: August 8, 2005; In Final Form: August 29, 2005*

Synchrotron X-ray diffraction measurements confirmed that a new polymorph of FeAlO₃ could be synthesized at about 1800 K and 72 GPa. This phase can be indexed on an orthorhombic cell and transforms into the trigonal form on release of pressure. The c/a ratio of about 2.71 of the trigonal phase suggests corundum structure of FeAlO₃ rather than LiNbO₃ or ilmenite structure. This conclusion also suggests that the high-pressure orthorhombic phase could be the Rh₂O₃(II) structure rather than the GdFeO₃-type perovskite structure.

1. Introduction

The Al_2O_3−Fe_2O_3 system is important not only in nature but also in industry. It is well-known that the solid solution of $(Al,Fe)_2O_3$ is limited at ambient pressure, although α-Al_2O_3 (corundum) and α-Fe_2O_3 (hematite) are isostructural, and the ionic radii of Al^{3+} and Fe^{3+} are quite similar in an octahedral site. FeAlO₃, an intermediate composition of $Al_2O_3/Fe_2O_3 =$ 1:1, appears to be isomorphous with the FeGaO₃ form at high temperature.[1]

Preliminary reports have said that FeAlO₃ with the FeGaO₃ form transforms to the tetragonal garnet form and then the GdFeO₃-type perovskite form at high pressures.[2,3] However, further details have been unclear so far, and our preliminary experiments using a Kawai-type multianvil apparatus showed that the FeGaO₃-type of FeAlO₃ decomposes into Fe-bearing corundum and Al-bearing hematite up to 25 GPa at about 1300−1500 K (See Figure 1).

Recently, the solubility of Al^{3+} into MgSiO₃ perovskite has been focused on. The bulk modulus of Al-bearing MgSiO₃ perovskite is significantly smaller than that for Al-free MgSiO₃ perovskite at lower mantle conditions.[4,5] It was also pointed out that the electrical conductivity of Al-bearing silicate perovskite is much greater than that of Al-free silicate perovskite.[6] The substitution mechanism of Al^{3+} into Fe-free MgSiO₃ perovskite could be understood in the $MgSiO_3$−$MgAlO_{2.5}$ system.[7] On the other hand, some studies pointed out that the $MgSiO_3$−$FeAlO_3$ system could be important in understanding the substitution mechanism of Al^{3+} into (Mg, Fe)SiO₃ perovskite with higher Al content.[8−10] Thus, clarification of the existence of FeAlO₃ perovskite at high pressure and high temperature should give important information to understand the correlation of Al^{3+} and Fe^{3+} solubility in silicate perovskite.

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Figure 1. A backscattered image of a recovered sample from 25 GPa at about 1300−1500 K. Bright gray colored grains are Al-bearing hematite and dark gray colored grains are Fe-bearing corundum.

FeAlO₃ is reported to be ferromagnetic, magnetoelectric, and piezoelectric. Existence of corundum and hematite in the orthorhombic FeAlO₃ phase makes it difficult to synthesize FeAlO₃ in the pure form by conventional methods. Devaux et al.[11] reported the synthesis of impurity-free FeAlO₃ by oxalate precipitation. We have carried out high-pressure and high-temperature experiments with the pure FeGaO₃ type of FeAlO₃ powder prepared by a citrate−nitrate gel combustion process using a double-sided laser-heated diamond anvil cell technique.[12] We report here a new high-pressure polymorph of FeAlO₃ that has been identified by synchrotron X-ray diffraction measurements and a structural transition exhibited by the same during decompression.

2. Experimental Section

The FeGaO₃ type of FeAlO₃ powder was used as a starting material and was synthesized as follows. An amorphous citrate−nitrate gel combustion process was followed to prepare FeAlO₃ precursor powder. For a typical batch preparation, 0.5 M solutions each of $Al(NO_3)_3 \cdot 8H_2O$ and $Fe(NO_3)_3 \cdot 8H_2O$ were

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Figure 2. Synchrotron X-ray diffraction patterns (a) measured at 72 GPa and 300 K after heating and (b) measured at ambient conditions after decompression. Asterisks in (a) represent peaks from the B2 phase of NaCl, and asterisks in (b) represent peaks from the B1 phase of NaCl.

mixed in such a way so that the molar ratio of Fe/Al = 1:1 was maintained. The mixed solution was continuously stirred while heated on a hot plate. An accurately weighed amount of citric acid (with citrate/nitrate mole ratio of 0.75) dissolved in water was added to the above mixture during stirring. The dark brown colored solution thus obtained was allowed to evaporate on a hot plate at 85−90 °C (solution temperature). The homogeneously mixed solution became viscous and turned into a gel during heating. The gel slowly foamed, swelled, and finally burnt on its own with glowing flints, and once ignited, it slowly propagated to the entire volume of the gel container. The brown-black ash powder thus obtained was calcined at 1673 K. After holding for an hour at 1673 K, the sample was quenched in water. The red powder thus obtained was confirmed as a single-phase orthorhombic $FeGaO_3$-type $FeAlO_3$ phase by X-ray powder diffraction.

High pressures were generated by a diamond anvil cell (DAC) with a 300 μm culet of diamonds. The $FeGaO_3$ type of $FeAlO_3$ powder sandwiched by NaCl powder was loaded into a 120-μm-diameter sample chamber, which was drilled into a pre-indented rhenium gasket. NaCl powder works as a pressure transmitting medium and also as a thermal insulator. The sample was compressed to 70 GPa at room temperature and then heated at 1800 K for half an hour by using a YLF laser. The sample of $FeAlO_3$ itself works as a laser absorber. Temperature was measured on one side of the sample using the spectroradiometric technique.[12] After heating treatment, the laser power was switched off, and the temperature was quenched at the pressure.

Angle-dispersive X-ray diffraction measurements were performed on the sample in DAC at BL13A in Photon Factory, Japan. A monochromatic incident beam at a wavelength of about 0.42 Å was used and was collimated to a diameter of 30 μm. A diffraction image was recorded on an imaging plate. The recorded two-dimensional image data were integrated along each Debye−Scherrer ring and converted to a one-dimensional diffraction pattern by the software PIP.[13]

3. Results and Discussion

An X-ray diffraction pattern obtained at 72 GPa and 300 K after heating at about 1800 K was totally different from that of the $FeGaO_3$ type of $FeAlO_3$ (See Figure 2a). Characteristic triplet

TABLE 1: Observed and Calculated X-ray Diffraction Pattern of the Orthorhombic Phase at 72 GPa and 300 K[a]

h	k	l	d (obsd)	d (calcd)	d (obsd)/d (calcd) − 1
0	1	1	3.6991	3.6964	0.0007
0	2	0	3.2689	3.2674	0.0004
1	1	1	2.9256	2.9252	0.0001
2	0	0	2.3897	2.3925	−0.0012
1	2	1	2.3205	2.3118	0.0038
0	0	2	2.2379	2.2412	−0.0015
1	3	1	1.8180	1.8131	0.0027
2	2	1	1.7757	1.7729	0.0016
1	2	2	1.7250	1.7241	0.0005
0	4	0	1.6303	1.6337	−0.0021
2	1	2	1.5852	1.5867	−0.0009
3	1	1	1.4640	1.4645	−0.0003

[a] Indexed by an orthorhombic symmetry with a = 4.785(5) Å, b = 6.535(7) Å, c = 4.482(7) Å, and V = 140.2(3) Å^3. Standard deviations are shown in parentheses. The unit of d is Å.

TABLE 2: Observed and Calculated X-ray Diffraction Pattern of the Trigonal Phase at Ambient Conditions[a]

h	k	l	d (obsd)	d (calcd)	d (obsd)/d (calcd) − 1
0	1	2	3.5872	3.5884	−0.0003
1	0	4	2.6247	2.6255	−0.0003
1	1	0	2.4599	2.4576	0.0009
1	1	3	2.1501	2.1510	−0.0004
0	2	4	1.7943	1.7942	0.0000
1	1	6	1.6487	1.6489	−0.0001
2	1	4	1.4497	1.4491	0.0004
3	0	0	1.4185	1.4189	−0.0003

[a] Indexed by a trigonal symmetry with a = 4.915(1) Å, c = 13.34(7) Å, and V = 279.2(1) Å^3. Standard deviations are shown in parentheses. The unit of d is Å.

of diffraction peaks appeared between 2.2 and 2.4 Å, and at first sight, the features of the diffraction pattern appeared quite similar to those of the $GdFeO_3$-type orthorhombic perovskite, such as $MgSiO_3$ perovskite. Indeed, all peaks could be indexed on an orthorhombic cell in Table 1. The unit cell parameters are a = 4.785(5) Å, b = 6.535(7) Å, c = 4.482(7) Å, and V = 140.2(3) Å^3. Rietveld refinement on the basis of the $GdFeO_3$-type perovskite structure has failed, partly because some NaCl peaks overlap some sample peaks, and in addition, peak profiles measured are a little broad. Further identification of this orthorhombic structure will be discussed later in this communication.

The X-ray diffraction pattern was also measured after the pressure was fully released in Figure 2b. This diffraction pattern appeared to be significantly different from the diffraction pattern measured at 72 GPa (See Figure 2a). Surprisingly, the diffraction peaks could neither be indexed by the high-pressure orthorhombic phase nor by the $FeGaO_3$-type structure. The diffraction peaks could be assigned as a trigonal cell in Table 2. We can propose candidate structures including (i) $LiNbO_3$ ($R3c$), (ii) corundum (R-$3c$), and (iii) ilmenite (R-3), which are difficult to distinguish only from the powder diffraction data. However, since systematic data on the c/a ratio of these structures has been known,[14] the possible structure would be discussed on the basis of the c/a ratio. The c/a ratio is about 2.63 for the $LiNbO_3$ structure (cf. $LiNbO_3$, $MnTiO_3$) and about 2.73 for the corundum structure (cf. Al_2O_3, Fe_2O_3). The c/a ratios of the ilmenite structure vary around 2.8 (cf. $FeTiO_3$, 2.77; $ZnGeO_3$, 2.80; $MgSiO_3$, 2.87), and the scattering of the c/a ratios for the ilmenite structure is possibly due to the different disordered state of cations. Thus, it is clear that the c/a ratio of 2.71 for the trigonal phase observed in this study is close to that for the corundum structure. To compare with the corundum and
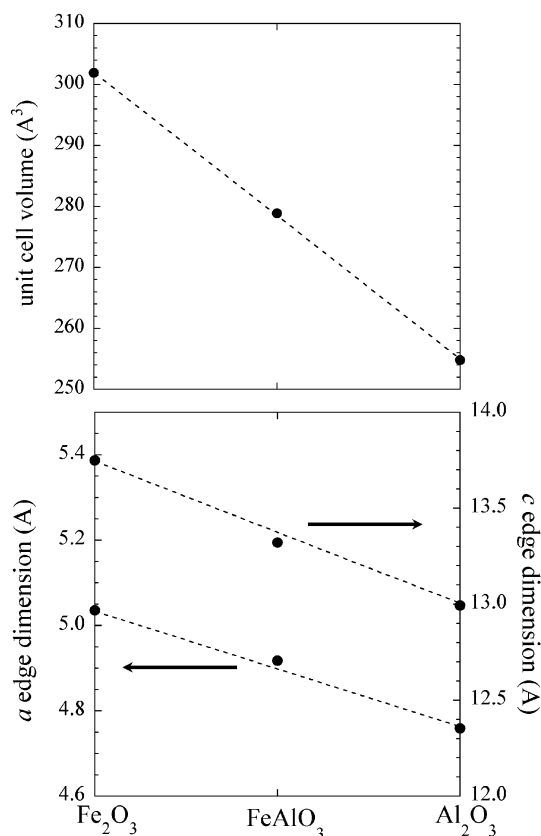
Figure 3. Unit cell edge dimensions and volumes of the trigonal phase are plotted in comparison with those of corundum (Al_2O_3) and hematite (Fe_2O_3). Dotted lines were just to connect the values between corundum and hematite.

hematite structures, unit cell dimensions and volume of the trigonal phase are plotted in Figure 3. These values could be plotted almost on the line between corundum and hematite. This evidence supports the corundum type of $FeAlO_3$. It is important that Fe^{3+} and Al^{3+} should occupy a single cation site in the corundum structure of $FeAlO_3$ in disorderly manner, since there is a single cation site in corundum structure. However, disorder of Fe^{3+} and Al^{3+} is not so trivial from the viewpoint of their similar ionic radii. Their ionic radii in an octahedral site are 0.63 Å for Fe^{3+} and 0.61 Å for Al^{3+}.[15] In addition, it may be noted that Fe^{3+} has no crystal field stabilization energy. At this moment, since another interesting issue is whether the corundum type of $FeAlO_3$ is a thermodynamically stable phase, it will be necessary to perform more detailed study of the P–T phase diagram on $FeAlO_3$.

It was recently reported that corundum and hematite transform into the $Rh_2O_3(II)$ structure at high pressure and high temperature.[16,17] It is known that the powder diffraction pattern for the $Rh_2O_3(II)$ structure is quite similar to that for the $GdFeO_3$-type orthorhombic perovskite structure. Both the $Rh_2O_3(II)$ structure of Al_2O_3 and Fe_2O_3 could not be recovered and back-transformed into the corundum structure on release of pressure. On the other hand, some oxides with the $GdFeO_3$-type orthorhombic perovskite structure, which are stabilized at high pressure and high temperature, transform into the $LiNbO_3$ structure during decompression.[14,18,19] From this evidence, it could be pointed out that the order–disorder-type transition of cations would not occur during decompression at room temperature, since there is a single cation site in corundum and the $Rh_2O_3(II)$ structure and two cation sites in perovskite and the $LiNbO_3$ structure. Thus, our conclusion that the recovered

trigonal phase could have the corundum structure suggests the high-pressure orthorhombic phase to probably be the $Rh_2O_3(II)$ structure rather than the $GdFeO_3$-type orthorhombic perovskite structure.

Frost and Langenhorst[10] measured the Fe^{3+} solubility into (Mg, Fe)SiO_3 perovskite in the Al-bearing system and showed that increasing the Al_2O_3 content of silicate perovskite only increases the Fe^{3+} solubility. The variation in Fe^{3+} solubility with the Al_2O_3 content is close to linear at higher Al_2O_3 content, and this implies that the substitution mechanism involved in the incorporation of Fe^{3+} and Al^{3+} into the silicate perovskite plays an important role at higher Al_2O_3 content. An atomic computer simulation study also suggested the $FeAlO_3$–$MgSiO_3$ type of substitution mechanism to be energetically favorable at lower mantle conditions.[8] Although the maximum solubility of the $FeAlO_3$ component into $MgSiO_3$ perovskite at lower mantle conditions has been hitherto unknown, it is expected that a substantial amount of the $FeAlO_3$ component can dissolve in $MgSiO_3$ perovskite, or in an extreme case, a continuous solid solution of (Mg, Fe^{3+})(Al^{3+}, Si)O_3 may appear, if the isostructural $FeAlO_3$ perovskite is stabilized at lower mantle conditions. However, since our conclusion indicates that the $FeAlO_3$ component would be stabilized with the $Rh_2O_3(II)$ structure rather than the $MgSiO_3$ perovskite structure at lower mantle conditions, it is reasonable that there is a maximum solubility of the $FeAlO_3$ component into $MgSiO_3$ perovskite at lower mantle conditions.[20]

4. Summary

Synchrotron X-ray diffraction measurements were carried out on $FeAlO_3$ prepared under high-pressure and high-temperature experiments using a double-sided YLF laser-heated diamond anvil cell technique. A new polymorph of $FeAlO_3$ could be synthesized at 72 GPa and 1800 K that exhibited a $Rh_2O_3(II)$-type structure. This phase further transformed into $FeAlO_3$ with corundum structure during decompression.

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