Prediction of an U$_2$S$_3$-type polymorph of Al$_2$O$_3$ at 3.7 Mbar

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We predict by first principles a phase transition in alumina at ~3.7 Mbar and room temperature from the CaIrO$_3$-type polymorph to another with the U$_2$S$_3$-type structure. Because alumina is used as window material in shock-wave experiments, this transformation should be important for the analysis of shock data in this pressure range. Comparison of our results on all high-pressure phases of alumina with shock data suggests the presence of two phase transitions in shock experiments: the corundum to Rh$_2$O$_3$(II)-type structure and the Rh$_2$O$_3$(II)-type to CaIrO$_3$-type structure. The transformation to the U$_2$S$_3$-type polymorph is in the pressure range reached in the mantle of recently discovered terrestrial exoplanets and suggests that the multi-megabar crystal chemistry of planet-forming minerals might be related to that of the rare-earth sulfides.

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Alumina, Al$_2$O$_3$, is an important compound in high-pressure technology and geophysics. It is used as window material in shock-wave experiments (1). Ruby, Al$_2$O$_3$ doped with chromium, serves as a pressure-calibrant in diamond-anvil-cell experiments (2). In the Earth’s mantle, Al$_2$O$_3$ is a major chemical component in solid solution with Mg$_2$SiO$_3$ garnet, perovskite (PV), and impurities in Mg$_2$SiO$_3$, etc. (e.g., refs. 3–9).

The experimental and theoretical literature on phase transitions in Al$_2$O$_3$ is quite extensive (10–19). Two pressure-induced dissociation transformation; in Mg$_2$SiO$_3$ and NaMgF$_3$, the U$_2$S$_3$-products (22).

Alumina has a high bulk modulus, ~310 GPa at room temperature and pressure (20), which is about 3.5 times the bulk modulus of bulk Mg$_2$SiO$_3$. This leads to the expectation of a rather high pressure of ~3.7 Mbar at which the experimentally reported high-pressure phases (21) pass through an enthalpy minimum (10). In this paper, we present the first-principles prediction of a phase transition in Al$_2$O$_3$ from the CaIrO$_3$-type polymorph to another with the U$_2$S$_3$-type structure.

Computational Details. Calculations were performed by using the local-density (LDA) (23) and generalized-gradient approximations (GGA) (24). The valence electronic configurations used for the generation of Vanderbilt ultrasoft pseudopotentials (25) are $3s^23p^63d^1$ and $2s^22p^6$ for Al and O, respectively. Their cutoff radii are 1.8, 1.8, and 2.0 a.u. for Al and 1.0 and 1.0 a.u. for O. The plane-wave cutoff energy is 150 Ry. We used variable-cell-shape molecular dynamics (26, 27) for structural optimization under arbitrary pressures. Dynamical matrices were computed at wave vectors $\mathbf{q}$ by using density-functional perturbation theory (28, 29). The numbers of formula units in the unit cells, $k$ points in the irreducible wedge, and $q$ points are (2, 10, 4) for corundum, (4, 4, 8) for Rh$_2$O$_3$(II)-type, (2, 24, 6) for CaIrO$_3$-type, and (4, 3, 8) for U$_2$S$_3$-type Al$_2$O$_3$. Force constants are extracted to build dynamical matrices at arbitrary phonon $q$ vectors. Vibrational contributions to the free energy are calculated by the quasi-harmonic approximation (QHA) (30). In this approximation, the free energy is

$$F(V, T) = E_0(V) + \frac{1}{2} \sum_{i \neq q} h_{i-q}(V) + \sum_{i \neq q} k_BT \log \left( 1 - \exp \left( - \frac{h_{i-q}(V)}{k_BT} \right) \right), \tag{1}$$

where $E_0(V)$ is the static total energy and $h_{i-q}(V)$ are the phonon frequencies. The numbers of $q$ points in the irreducible Brillouin zone used for the summation in Eq. 1 are 116, 196, 124, and 112 for corundum, Rh$_2$O$_3$(II)-type, CaIrO$_3$-type, and U$_2$S$_3$-type Al$_2$O$_3$ respectively. Calculations were done using the Quantum-ESPRESSO package (31).

Results and Discussion

The U$_2$S$_3$-type structure (Fig. 1) is closely related to the CaIrO$_3$-type structure (32). The space group of the U$_2$S$_3$-type phase is Pmcm (or Pnma in the standard setting), which is a subgroup of Cmcm, CaIrO$_3$-type phase’s space group. During the transformation the octahedral layers of the latter connect and produce the U$_2$S$_3$-type structure with a continuous 3D network of Al–O bonds. The calculated equations of states shown in Table 1 are consistent with those of previous studies (16–18). Static enthalpy calculations (Fig. 2) clearly show the sequence of stable phases.

The static transition pressures using the LDA (GGA) are 82 (88), 137 (145), and 373 (380) GPa for corundum-to-Rh$_2$O$_3$(II)-type,}
Rh$_2$O$_3$(II)-type-to-CaIrO$_3$-type, and CaIrO$_3$-type-to-U$_2$S$_3$-type transitions, respectively. These pressures are consistent with results from other calculations (16–18). A transition to the P6$_3$/mmc structure, another candidate form for a post-PPV phase, was not found in Al$_2$O$_3$ up to 700 GPa. In NaMgF$_3$ the U$_2$S$_3$-type phase is produced by a soft Rh$_2$O$_3$(II)-type to CaIrO$_3$-type phase boundary has a positive slope of $+9.3$ MPa/K at 1,000 K. This positive slope can be understood on the basis of the vibrational density of states (VDOS). Fig. 5 shows that peaks at low frequencies shift upward across the post-PPV transition, reflecting the shorter average Al$_{1}$–O distances in the U$_2$S$_3$-type phase. This decreases the vibrational entropy change across the transitions and the relative stability of Rh$_2$O$_3$(II)-type to CaIrO$_3$-type phase boundaries have negative Clapeyron slopes (17, 18), $dP/dT = -\Delta S/\Delta V$. In contrast, the CaIrO$_3$-type–U$_2$S$_3$-type phase boundary has a positive slope of $+9.3$ MPa/K at 1,000 K.

The quasi-harmonic phase boundaries in the Al$_2$O$_3$ system are displayed in Fig. 4. The corundum-to-Rh$_2$O$_3$(II)-type and

![Crystal structures of CaIrO$_3$-type (A) and U$_2$S$_3$-type Al$_2$O$_3$ (B). Blue and red spheres denote aluminum and oxygen, respectively. Al$_1$ and Al$_2$ are aluminum in the A and B sites, respectively. Polyhedra are drawn only around aluminum in the A and B sites, respectively.](image)

**Table 1. The third-order Birch–Murnaghan equation of states for Al$_2$O$_3$ polymorphs calculated by LDA**

<table>
<thead>
<tr>
<th>Phase Source</th>
<th>$V$, a.u.$^3$</th>
<th>$B$, GPa</th>
<th>$B'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corundum</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 GPa, static</td>
<td>Present calc. 283.46 259.8 4.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calc. (16)</td>
<td>273.30 248 4.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calc. (17)</td>
<td>286.32 252.6 4.237</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 GPa, 300 K</td>
<td>Present calc. 286.73 251.0 4.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calc. (18)</td>
<td>286.23 240.5 3.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exp. (33)</td>
<td>287.81 254.4 4.275</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh$_2$O$_3$(II)-type</td>
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</tr>
<tr>
<td>0 GPa, static</td>
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<tr>
<td>Calc. (16)</td>
<td>267.57 252 4.07</td>
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<tr>
<td>Calc. (17)</td>
<td>279.53 258.2 4.140</td>
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<td></td>
</tr>
<tr>
<td>80 GPa, 300 K</td>
<td>Present calc. 227.62 544.8 3.37</td>
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<td></td>
</tr>
<tr>
<td>Calc. (18)</td>
<td>225.94 530.2 3.33</td>
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</tr>
<tr>
<td>CaIrO$_3$-type</td>
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<tr>
<td>0 GPa, static</td>
<td>Present calc. 269.42 251.6 4.11</td>
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<td>Calc. (16)</td>
<td>261.70 231 4.38</td>
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<td>Calc. (17)</td>
<td>271.90 241.6 4.464</td>
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<td>150 GPa, 300 K</td>
<td>Present calc. 198.38 786.8 3.24</td>
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<tr>
<td>Calc. (18)</td>
<td>196.68 762.6 3.31</td>
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<tr>
<td>U$_2$S$_3$-type</td>
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<td></td>
</tr>
<tr>
<td>400 GPa, static</td>
<td>Present calc. 155.83 1,562 3.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calc. (16)</td>
<td>156.56 1,552 3.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400 GPa, 300 K</td>
<td>Present calc. 155.83 1,562 3.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calc. (18)</td>
<td>156.56 1,552 3.00</td>
<td></td>
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</tbody>
</table>

![Relative static LDA enthalpies of Al$_2$O$_3$ polymorphs with respect to the CaIrO$_3$-type phase. Dashed vertical lines denote corundum-Rh$_2$O$_3$(II)-type, Rh$_2$O$_3$(II)-type to CaIrO$_3$-type, and CaIrO$_3$-type to U$_2$S$_3$-type transition pressures, respectively. The perovskite form of Al$_2$O$_3$ does not have a stability field, consistent with previous calculations (16–18).](image)
the \(U_2S_3\)-type phase with increasing temperature. The downward shift of the high-frequency peak reflects the increase of the average Al\(_2\)-O distances, increasing the entropy. The influence of the low-frequency modes is predominant in the entropy and the Clapeyron slope remains positive even at high temperatures. However, this downward frequency shift at high frequencies produces a peculiar phase boundary with positive slope but slightly negative curvature; the Clapeyron slopes at 1,500 K and 2,000 K are \(+8.2\) and \(+7.7\) MPa/K, respectively.

\(\text{Al}_2\text{O}_3\) is important for dynamic compression technology, because it is used as window material. In raw shock data to 340 GPa, no direct evidence of phase transition was noticed, although there was an atypical relationship between shock velocity \((u_s)\) and particle velocity \((u_p)\): \(u_s = C + S u_p\), in which \(S\) (0.957) is unusually small, implying a possibility of sluggish phase transformations (34). However, a comparison between our static LDA results on \(\text{Al}_2\text{O}_3\) and raw shock data to 340 GPa (34, 35) strongly suggests the presence of all three phases stable below 340 GPa in the shock data (Fig. 6). With shock data alone, it is difficult to resolve phase transitions accompanied by small density changes that could be comparable to the limit of detectability. The transition pressures in shock data are much higher than the calculated ones. This suggests that the phase transitions in \(\text{Al}_2\text{O}_3\) have considerable hysteresis. This is consistent with observations from static compression experiments in which sample annealing was necessary for phase transitions (15, 17, 19). According to Fig. 6, the transition pressure from the corundum to \(\text{Rh}_2\text{O}_3(\text{II})\)-type phase in shock experiments should be \(\approx 120\) GPa. It is interesting to note that this transition pressure is close to the pressure at which optical transparency (36) and electrical resistivity (37) were reduced in shock compression, implying a strong relationship between these reductions and the corundum-to-\(\text{Rh}_2\text{O}_3(\text{II})\)-type phase transition that may induce more defects. A recent comparative study of shock-compressed materials suggested that \(\text{Al}_2\text{O}_3\) with an unusually small \(S\) might collapse into a more incompressible phase above 340 GPa (38). The \(U_2S_3\)-type phase is denser than the \(\text{CaIrO}_3\)-type phase by \(\approx 1.6\%\) at 400 GPa and 300 K. However, their bulk moduli are very similar: 1,558 GPa and 1,552 GPa in the \(\text{CaIrO}_3\)-type and the \(U_2S_3\)-type phases, respectively. This contrasts with the case of \(\text{NaMgF}_3\). Through the post-PPV transition in \(\text{NaMgF}_3\), charge densities between Na and F increase and bonding between MgF\(_6\) layers by Na atoms is strengthened (22). As a consequence, the compressibility of the \(b\) axis, which is perpendicular to the Mg-F
layers, decreases and the bulk modulus increases from 282 to 292 GPa at 50 GPa. In contrast, in Al2O3, the charge density between Al2 and O atoms is already high in the CaIrO3-type phase. There is no significant increase/decrease of charge density between the Al2-O layers through the transition (Fig. 7), although the distance between layers decreases.

This post-PPV transition in Al2O3 occurs at pressures exceeding those achieved in the Earth’s mantle (≈135 GPa at the core–mantle boundary) and should not alter our views of this region. However, it might affect our understanding of the rocky mantles of recently discovered terrestrial exoplanets (39–41) because it could change the solubility of Al2O3 in CaIrO3-type MgSiO3. The change in coordination from 6 to 7 in the B site suggests that Al2O3 might ex-solve from MgSiO3, in particular, from the smaller 6-fold B site occupied by silicon in the CaIrO3-type structure. The ex-solution of Al2O3 could affect the electrical and thermal conductivities of the CaIrO3-type solid solution, as the incorporation of Al2O3 affects the electrical conductivity of MgSiO3 perovskite in the presence of iron (4).

The prediction of the U2S3-type structure of Al2O3 suggests a likely close relationship between the multi-megabar crystal chemistry of planet-forming minerals and that of rare-earth sulfides, RR’S3 (R, R’ = lanthanoid or actinoid). Several crystal structures, including the corundum, CaIrO3-type, and U2S3-type structures, are produced in the RR’S3 family of compounds depending on atomic species and preparation conditions (42). In refs. 42 and 43, the structure corresponding to CaIrO3-type is referred to as NdYbS3-type.1 The perovskite structure (GdFeO3-type) also occurs in RR’S3 compounds. At high temperature, LaYbS3 is in the α phase with the GdFeO3-type structure, whereas at low temperatures it adopts the β phase with the NdYbS3-type (i.e., CaIrO3-type) structure (44, 45). This is reminiscent of the postperovskite transition in MgSiO3 with a positive Clapeyron slope (46–48). The relationship between these crystal structures and cation radii can be summarized as follows: the corundum structure occurs with small R and R’ radii (e.g., Yb2S3), the U2S3-type structure with large R and the CaIrO3-type and the GdFeO3-type structures with large R in the A site and small R’ in the B site (e.g., NdYbS3 and α-LaYbS3). This chemical-pressure effect produces a sequence of structures consistent with that produced by pressure in Al2O3. The ratios (V_A1 + V_A2)/V_A102O38, where V_A1 and V_A2 are polyhedral volumes around Al1 in the A site and Al2 in the B site and V_A102O38 is the formula unit volume, are 0.43, 0.62, and 0.68 in corundum, CaIrO3-type, and U2S3-type Al2O3. These are very close to corresponding ratios in Yb2S3 (0.42) (49), NdYbS3 (0.62) (43), and U2S3 (0.69) (50), respectively.

In calculating V_A1 and V_A2, the coordination numbers of Al2 at the A site and Al1 at the B site are set to be 6 and 8, and 6 and 8 for corundum (where there is no distinction between Al1 and Al2), CaIrO3-type, and U2S3-type Al2O3. Therefore, one can anticipate that other RR’S3 structures may also play an important role in stabilizing sequioxides analogous to Al2O3 under pressure, or solid solutions and intermediate compounds of Fe2O3, Al2O3, CaO, MgO, FeO, and SiO2 at multi-megabar pressures. This could have unexpected consequences for the internal structure and dynamics of exoplanets. In fact, Al2O3 in the α-GdS2-type structure, one of the major structures of RR’S3 compounds, and the U2S3-type polymorph have very similar enthalpies (see Fig. 2).

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The NdYbS3-type structure was first reported to have the B2212 symmetr which is nearly indistinguishable from the CaIrO3-type structure. The difference between them is very tiny; in the B2212 NdYbS3-type structure, the cation at the B site and one kind of sulfur are just slightly shifted from the CaIrO3-type structure (44). However the NdYbS3-type structure refined in the B2212 symmetry is nearly indistinguishable from the CaIrO3-type structure. The difference between them is very tiny; in the B2212 NdYbS3-type structure, the cation at the B site and one kind of sulfur are just slightly shifted from the CaIrO3-type structure. A recent x-ray diffraction study suggested the NdYbS3-type structure should have the Cmcm symmetry and be the same as the CaIrO3-type structure (44).

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