Prediction of new thermodynamically stable aluminum oxides

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Recently, it has been shown that under pressure, unexpected and counterintuitive chemical compounds become stable. Laser shock experiments (A. Rode, unpublished) on alumina (Al$_2$O$_3$) have shown non-equilibrium decomposition of alumina with the formation of free Al and a mysterious transparent phase. Inspired by these observations, we have explored the possibility of the formation of new chemical compounds in the system Al-O. Using the variable-composition structure prediction algorithm USPEX, in addition to the well-known Al$_2$O$_3$, we have found two extraordinary compounds Al$_4$O and AlO$_2$ to be thermodynamically stable in the pressure ranges 330–443 GPa and above 332 GPa, respectively. Both of these compounds at the same time contain oxide O$^{2-}$ and peroxy O$_2$$^{2-}$ ions, and both are insulating. Peroxo-groups are responsible for gap states, which significantly reduce the electronic band gap of both Al$_4$O$_2$ and AlO$_2$.

Aluminum and oxygen are among the most abundant elements in the universe. Their only stable compound, alumina Al$_2$O$_3$, is widely used due to its mechanical properties (e.g. as an abrasive material) and due to its very wide band gap (for example, as an optical window material in shock-wave experiments).

Al$_2$O$_3$ in the corundum structure (space group R3c) is an important mineral in the Earth’s crust. Alumina is easily incorporated into many silicates and significantly affects their physical properties (e.g. due to the large electronegativity difference, 1.8 on the Pauling scale), and the only possible oxidation states being +3 and −2 for Al and O, respectively, the only possible stable compound seems to be Al$_2$O$_3$. Of course, one can also imagine a peroxy with composition Al$_2$(O$_2$)$_2$=AlO$_2$, but such a compound has never been reported.

While no other stable oxides are known, there is evidence for metastable AlO$_2$, which was shown to form by an interfacial reaction in the presence of a kinetic constraint during diffusion-bonding of Pt and α-Al$_2$O$_3$. Raman spectroscopy has provided strong evidence for the presence of AlO$_2^-$, which formed after heating for 24 hours in the temperature range 1200–1400 °C. AlO$_2$ is a “peroxide oxide”, i.e. contains peroxy (O$_2$$^{2-}$) and oxide (O$^{2-}$) ions. It was not clear whether AlO$_2$ or other unusual oxides are stable at any pressure-temperature conditions.

Very recently, it has been shown that even in seemingly extremely simple systems, such as Na-Cl, totally unexpected compounds (Na$_2$Cl, Na$_2$O$_2$/NaCl$_2$, NaCl$_3$ and NaCl$_4$) become stable under pressure – these have been predicted using evolutionary crystal structure prediction method USPEX and verified by experiments. If such unusual compounds exist in the “trivial” Na-Cl system, one can expect similarly unusual compounds in nearly any other system under pressure. Here we test this hypothesis on the Al-O system, and indeed predict that Al$_4$O$_2$ and AlO$_2$ become thermodynamically stable under high pressure.

**Computational Methodology**

To predict stable Al-O oxides and their structures, we used the evolutionary algorithm USPEX in its variable-composition mode at pressures 0, 50, 100, 150, 200, 300, 400, 500 GPa. The reliability of USPEX has been demonstrated many times before – e.g. Ref. 9, 14–18. Modern methods have shown remarkable power to predict novel unexpected compounds – e.g. in the Na-CT, Mn-B$^{2+}$, Mg-C$^{2+}$ and Na-Si$^{2+}$ systems. Stable compositions were determined using the convex hull construction: a compound is thermodynamically stable when its enthalpy of formation from the elements and from any other compounds is negative. Enthalpy calculations and structure relaxations were
done using density functional theory (DFT) within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA)22, as implemented in the VASP code23. These calculations were based on the all-electron projector-augmented wave (PAW) method24 and plane wave basis sets with the kinetic energy cutoff of 600 eV and uniform Γ-centered k-point meshes with reciprocal-space resolution of $2\pi r_0 = 2\pi 0.02 \text{Å}^{-1}$. The first generation of structures/compositions was produced randomly with the use of space group symmetries (using algorithm12); the lowest-fitness 60% of the structures/compositions were allowed to produce child structures/compositions (fitness being defined as the difference between enthalpy of the structure and the convex hull). Initial structures were allowed to have up to 20 atoms in the unit cell, but this range was allowed to change in subsequent generations as a result of evolution. Child structures/compositions were created in the following manner: 20% by random symmetric generator, 40% by heredity, 20% by softmutation, and 20% by atomic transmutation. In this work, we first performed searches in the entire Al-O system with up to 20 atoms/cell, and have found only Al2O3 and oxygen-enriched phases Al4O7 and AlO2. Then we did additional focused searches in a narrower compositional range Al2O3-O, and obtained the same result.

After USPEX predictions, we selected structures on the convex hull and close to it, and relaxed them carefully at pressures 0, 10, ..., 520 GPa. These calculations have confirmed stability of three oxides - well-known Al2O3 and non-classical AlO2 and Al4O7. For these compounds, we also computed their electronic band structures. For accurate estimates of the band gaps, we have used the HSE hybrid functional25. Phonon frequencies throughout the Brillouin zone were calculated using the finite displacement approach as implemented in the Phonopy code26,27, and these calculations confirmed that these phases are dynamically stable at pressure ranges where our enthalpy calculations predict their thermodynamic stability.

Results

Stable compounds in the Al-O system. At all pressures in the range 0–500 GPa, the known compound - Al2O3 - is found to be thermodynamically stable. In agreement with previous works we find the same sequence of phase transitions – from corundum to the Rh2O3(II)-type structure at 100 GPa, then to the CaIrO3-type structure at 130 GPa, and then to the U2S3-type phase at 394 GPa.

The computed thermodynamics of Al-O compounds are shown in Fig. 1. Al4O7 and AlO2 begin to show competitive enthalpies of formation at pressures above 300 GPa and have stability fields at

Figure 1 | Thermodynamics of the Al-O and Al2O3-O systems. For the end members we used the theoretically predicted lowest-enthalpy structures from this work and Ref. 27.

Figure 2 | Pressure-composition phase diagram of the Al2O3-O system.
The structure contains 7- and 8-coordinate Al atoms (coordination polyhedra are shown). Some layers of the structure contain only oxide O₂⁻ ions, other layers contain both oxide O₂⁻ and peroxide O₂²⁻ ions. Peroxo-ions have two O atoms connected by a bond; the O-O bond length is 1.43 Å.

The structure of AlO₂ at 500 GPa. Al atoms are in the 9-fold coordination (coordination polyhedra are shown). Oxide O₂⁻ and peroxide O₂²⁻ ions are arranged in alternating planes. Peroxo-ions have two O atoms connected by a bond; the O-O bond length is 1.38 Å.

### Table 1 | Crystal structures of Al₄O₇ at 400 GPa and AlO₂ at 500 GPa

**Al₄O₇:** Space group C2. Lattice parameters a = 4.598 Å, b = 9.670 Å, c = 5.094 Å, β = 153.5°

| Wyckoff symbol | x    | y     | z     |
|----------------|------|-------|-------|
| Al1            | 4c   | 0.2700| 0.0001| 0.5216|
| Al2            | 2a   | 0     | 0.2580| 0     |
| Al3            | 2a   | 0.5000| 0.2859| 0     |
| O1             | 2a   | 0     | 0.4399| 0     |
| O2             | 4c   | 0.2624| 0.1299| 0.9110|
| O3             | 4c   | 0.2534| 0.3140| 0.5046|
| O4             | 2b   | 0.5000| 0.1324| 0.5000|
| O5             | 2a   | 0.5000| 0.4568| 0     |

**AlO₂:** Space group P2₁/c. a = 4.664 Å, b = 2.304 Å, c = 4.726 Å, β = 90.75°

|      |      |      |      |
|------|------|------|------|
| Al   | 2a   | 0.2217| 0.2750| 0.6315|
| O1   | 2a   | 0.1339| 0.7582| 0.8768|
| O2   | 2a   | 0.5016| 0.1831| 0.3849|

Figure 5 | Phonon dispersion curves of AlO₂ (left) and Al₄O₇ (right) at 400 GPa.
330–443 GPa and at >332 GPa, respectively. From Fig. 1, one can see that at 500 GPa the enthalpy of formation of AlO2 from Al2O3 and O is impressively negative, −0.12 eV/atom. The predicted pressure-composition phase diagram is shown in Fig. 2. To assess the effect of temperature, we performed quasi-harmonic free energy calculations for AlO2, Al2O3 and O. We found that temperature and zero-point vibrations stabilize AlO2 and expand its stability field: at T = 300 K it becomes stable at 321 GPa, at T = 2060 K at 300 GPa, at T = 3200 K at 280 GPa.

Structures of stable compounds: Al4O7 and AlO2. Structures of the stable phases of Al2O3 have been discussed elsewhere, so here we focus only on the new compounds, Al4O7 and AlO2. Each of these compounds has only one stable structure up to 500 GPa, and both contain at the same time oxide O2− and peroxide [O-O]2− anions, i.e. both can be described as “oxide peroxides”. At normal conditions, the O–O bond lengths are 1.21 Å in the O2 molecule, 1.28 Å in the superoxide O2− ion, and 1.47 Å in the peroxide O2−2 ion. In Al4O7 the O–O bond length is 1.43 Å at 400 GPa, in AlO2 it is 1.38 Å at 500 GPa – clearly indicating the presence of peroxide-ions.

The chemical formulas of these compounds can be obtained from Al2O3 by consecutive replacement of O2− by O2−2 (which has the same charge): taking two formula units Al4O6 and replacing O2−2, we obtain Al4O5(O2) for Al4O7, and doing the same replacement again, we obtain Al4O4(O2)2 for AlO2. These are indeed the structural formulas: Al4O5(O2) for Al4O7, and Al4O4(O2)2 for AlO2. These structures are shown in Figs. 3 and 4, and their parameters are given in Table 1.

Discussion

Properties of the new phases. Phonon dispersion curves of Al4O7 and AlO2, computed at 400 and 500 GPa, respectively, are shown in Fig. 5. Both phases are dynamically stable and display a continuum of phonon energies, i.e. absence of decoupled O–O vibrational modes of peroxy-groups, because at high pressure Al–O modes have frequencies comparable to O–O modes. At the same time, in the electronic structure, there are clearly defined dispersive bands of peroxy-groups, and these play an important role, as we discuss below. Both phases are dynamically and mechanically stable, as shown by their computed phonons, elastic constants, and evolutionary metadynamics simulations, also enabled in the USPEX code and allowing one to explore possible phase transitions. We have confirmed that there are indeed no distortions or modulations that could lead to more stable structures.

All the predicted phases are insulating and show very distinct electronic structure compared with Al2O3. At 400 GPa, the computed DFT band gaps are 6.93 eV for Pnma-Al2O3, 2.51 eV for Al4O7, 2.92 eV for AlO2. We recall that DFT calculations significantly underestimate band gaps, while hybrid functionals and GW approximation give much better band gaps, typically within 5–10% of...
the true values. Fig. 6 shows band gaps as a function of pressure, computed using the GGA (PBE functional), hybrid HSE functional25 and GW approximation30,31; one can see that GGA band gaps are \(\sim 30\%\) underestimates; HSE band gaps practically coincide with the most accurate GW values for AlO\(_2\), but are 0.2–1.1 eV lower for Al\(_2\)O\(_3\) and Al\(_4\)O\(_7\). At all levels of theory, Al\(_2\)O\(_3\) and AlO\(_2\) come out to have band gaps \(\sim 2\) times lower than the band gap of Al\(_4\)O\(_7\).

This band gap reduction for Al\(_2\)O\(_3\) and AlO\(_2\) originates from the additional low conduction band in the middle of the band gap. Our calculations (Fig. 7) show that these low conduction bands can be unequivocally assigned to the peroxo-groups. In both Al\(_2\)O\(_3\) and AlO\(_2\), both gap states - the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) - come from peroxo-groups. Together with low compressibility of the peroxo-groups (between 300 GPa and 500 GPa, the O-O distance changes from 1.37 to 1.38 Å and from 1.46 to 1.42 Å in AlO\(_2\) and Al\(_4\)O\(_7\), respectively), this explains why the band gaps of Al\(_4\)O\(_7\) and especially AlO\(_2\) are practically independent of pressure in a wide pressure range (Fig. 6). As Fig. 8 shows, projected densities of states show only small contributions from Al, thus indicating a high degree of ionicity. Indeed, Bader charges32 are +2.44 of Al, −0.83 of O1 (peroxide anion) and −1.61 of O2 (oxide anion) in AlO\(_2\) at 400 GPa.

While the band gaps computed by DFT (PBE functional) are, as expected, significantly underestimated, the energetics are accurate. We have tested this by computing the energy and enthalpy of the reaction

\[
\text{Al}_2\text{O}_3 + \frac{1}{2}\text{O}_2 = 2\text{AlO}_2
\]

using the combined exact exchange (EXX) and random phase approximation (RPA) technique33–35. At 300 GPa we obtained the

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**Figure 8 | Projected electronic densities of states of AlO\(_2\) and Al\(_4\)O\(_7\).** (a) AlO\(_2\): O1 is a peroxide site and O2 is an oxide ion; (b) Al\(_4\)O\(_7\): O2 and O3 are atoms from two different peroxide ions, and O1, O4, O5 are oxide sites.
following energies (enthalpies) for this reaction: 0.1727 eV/atom (−0.0113 eV/atom) for the RPA+EXX method and 0.1782 eV/atom (0.0330 eV/atom) for PBE. At 500 GPa the results are 0.1284 eV (−0.1200 eV/atom) for RPA+EXX and 0.1371 eV (−0.1150 eV/atom) for PBE. These calculations fully confirm our findings and give additional insight:

1. In both PBE and EXX+RPA the new compounds are stabilized by the P^+V-term in the free energy, rather than by the internal energy. This originates from the low packing efficiency in elemental oxygen, which remains a molecular solid in the entire pressure range studied here. For this reason we can expect increased reactivity of oxygen, and stabilization of oxygen-rich compounds (such as peroxides) at high pressures.

2. The results of the PBE and EXX+RPA are quantitatively similar, especially at 500 GPa, where the difference is only 5 meV/atom.

3. At the EXX+RPA level of theory the new compounds predicted here are even more stable than at the PBE level.

Conclusions

Systematic search for stable compounds in the Al–O system at pressures up to 500 GPa revealed two new stable compounds (AlO_2 and Al_2O_3), which have stability fields that are above 332 GPa and in the range 330–443 GPa, respectively. Our analysis reveals that insulating compounds AlO_2 and Al_2O_3 exhibit significantly ionic character, both contain peroxide [O–O]^{2−} and oxide O^{−} anions and therefore belong to the exotic class of “peroxide oxides”. Electronic levels of the peroxide–group form gap states (“low conduction band”) that lead to a twofold lowering of the band gap relative to Al_2O_3. Our preliminary results show that the formation of perooxo–ions and stabilization of peroxides under pressure occur in many oxide systems, and this phenomenon may play an important role in planetary interiors, with their high pressures and abundance of oxygen atoms.

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Author contributions

Author contributions: Y.L., Q.Z., S.N.W. and G.K. performed and analyzed calculations. Y.L., S.N.W. and A.R.O. wrote the paper, X.D. provided technical assistance with calculations.

Additional information

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