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Structural, elastic, vibrational and electronic properties of amorphous Al₂O₃ from ab initio calculations

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Molecular Dynamics simulations

Inicial conditions: \( \{ r_i(t_0), v_i(t_0) \}_N \)

Choice of interatomic potential → forces

Numerical solution to the eqs. of motion

Physical properties: temporal average over configurations: \( \langle ........ \rangle_t \)

\[ V(r) = \frac{q_i q_j}{r} - \frac{C_{ij}}{r^6} + B \exp(ar) \]

- empirical pot
- ab-initio \( \varepsilon(R) \)

Verlet

\( \Delta t: 10^{-15} \) s: time step

Termodynamics prop.
- structural properties
- dynamical prop.
Basic diagnostics

- Pair distribution function
- Angular distribution
- Coordination numbers

- Vibrational density of states $D(\omega)$

- Direct visualization

\[ Z_{\alpha(\beta)}(t) = \left\langle \sum_{i=1}^{N} m_{i\alpha} \vec{v}_{i\alpha}(0) \cdot \vec{v}_{i\alpha}(t) \right\rangle \]

\[ D_{\alpha(\beta)}(\omega) = \frac{1}{\sqrt{2\pi}} \int \frac{Z_{\alpha(\beta)}(t)}{Z_{\alpha(\beta)}(0)} \exp(-i\omega t) \, dt \]

VACF
Ceramic material with several technological applications due to high melting point (2327 K), extreme hardness (Moh 9) and low electrical conductivity.

Structural phase transitions:
- liquid $\rightarrow$ $\gamma$ $\rightarrow$ $\delta$, $\theta$ $\rightarrow$ $\alpha$-alumina
- amorphous (a.o) $\rightarrow$ $\gamma$ $\rightarrow$ $\theta$ $\rightarrow$ $\alpha$-alumina
Amorphous $\text{Al}_2\text{O}_3$

- $\text{Al}_2\text{O}_3$-$\text{SiO}_2$ glass is one of the the most important systems in ceramics science
- Many technological applications: catalysis, dielectric, optical devices, microelectronics and thin films devices
- It is present in the surface of aluminum in contact to air (oxidation and passivation phenomena)
- Most alumina thin films are amorphous: they are composed by porous amorphous alumina, but its atomic properties are not well understood so far
**Procedure**

- **Combined use of classical and *ab initio* Molecular Dynamics:**

  - **Crystalline sample (80 atoms)**
  - **Classical Molecular Dynamics**
  - **Amorphous Sample**

  - **ab-initio MD**

  - **Relaxation**

  - **Electronic properties**
  - **Elastic properties**

  - **Structural and Dynamical properties**
Computational details

- *ab initio* MD by using VASP (Vienna Ab Initio Simulation Package)
- Density Functional Theory with LDA (local density approximation)
- Ultrasoft pseudopotentials
- Energy cutoff $E_{cut} = 296.77$ eV (21.81 Ry)
- Only gamma point, $\Gamma = (0,0,0)$
- Time step of 3 fs for atomic motion
Pair distribution function

Neutron static structure factor: experiments and simulation

## Interatomic distances and coordination numbers

<table>
<thead>
<tr>
<th>Results</th>
<th>$R_{\text{Al-Al}}$ (Å)</th>
<th>$R_{\text{Al-O}}$ (Å)</th>
<th>$R_{\text{O-O}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lamparter y Kniep</td>
<td>3.2 ± 0.55</td>
<td>1.8 ± 0.21</td>
<td>2.8 ± 0.58</td>
</tr>
<tr>
<td>Classical MD</td>
<td>3.24</td>
<td>1.74</td>
<td>2.77</td>
</tr>
<tr>
<td>$ab$ initio MD</td>
<td>3.27</td>
<td>1.80</td>
<td>2.91</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Results</th>
<th>$n_{\text{Al-Al}}$</th>
<th>$n_{\text{Al-O}}$</th>
<th>$n_{\text{O-Al}}$</th>
<th>$n_{\text{O-O}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classical MD</td>
<td>9.1</td>
<td>3.97</td>
<td>2.65</td>
<td>16.85</td>
</tr>
<tr>
<td>$ab$ initio MD</td>
<td>8.9</td>
<td>4.49</td>
<td>2.99</td>
<td>16.46</td>
</tr>
</tbody>
</table>
Angular distribution

- Al-Al-Al = 120
- Al-Al-Al = 95, 120
- O-Al-O = 102
- O-Al-O = 85, 105
Basic building blocks

$O-Al-O = 109.5^\circ$

$O-Al-O = 90^\circ$

$\sim 52\%$ of $\text{AlO}_4$ terahedron

$\sim 40\%$ of $\text{AlO}_6$ octahedron
Connectivity of basic units

$\text{Al-O-Al} = 120^\circ$

$\text{Al-O-Al} = 95^\circ$
Vibrational density of states
Connectivity between basic units

Al-O-Al = 120°

Al-O-Al = 95°
Elastic properties

<table>
<thead>
<tr>
<th>phase</th>
<th>B (GPa)</th>
<th>G (GPa)</th>
<th>E (GPa)</th>
<th>ν</th>
</tr>
</thead>
<tbody>
<tr>
<td>amorph</td>
<td>193.4</td>
<td>141.0</td>
<td>340.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Alpha (Wefers &amp; Misra)</td>
<td>253</td>
<td>164</td>
<td>404</td>
<td>0.23</td>
</tr>
</tbody>
</table>
Electronic density of states

Energy gap
Exp 3.2 eV
Theo. 2.6 eV
Electronic density of states: comparison to γ-alumina

Electron localization function

Charge transfer calculated via Voronoi analysis:
Al ~ 2.89
O ~ -1.92
# Different alumina phases

<table>
<thead>
<tr>
<th>Phase</th>
<th>Density g/cm³</th>
<th>Al Coordination Number</th>
<th>Bond length Al-O (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>amorphous</td>
<td>3.17</td>
<td>4(76%), 5(22%)</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>3.9</td>
<td>4(23%), 5(51%), 6(21%)</td>
<td>1.77</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>4(15%), 5(21%), 6(64%)</td>
<td>1.79</td>
</tr>
<tr>
<td>a, ab-initio</td>
<td>3.17</td>
<td>4(50%), 5(42%), 6(5%)</td>
<td>1.81</td>
</tr>
<tr>
<td>liquid</td>
<td>3.17</td>
<td>3(13%), 4(66%), 5(20%)</td>
<td>1.76</td>
</tr>
<tr>
<td>gamma</td>
<td>3.66</td>
<td>4(37%), 6(63%)</td>
<td>1.94 +/- 0.3</td>
</tr>
<tr>
<td>theta</td>
<td>3.65</td>
<td>4(50%), 6(50%)</td>
<td>1.9 +/- 0.3</td>
</tr>
<tr>
<td>alpha</td>
<td>3.98</td>
<td>6 (100%)</td>
<td>1.97</td>
</tr>
</tbody>
</table>

a) PRE 61, 2723 (2000),  
c) PRB 65, 012101 (2002), PRB, 72, 035116 (2005)  
Conclusions

- Using of ab-initio MD appear new features, absent in (simple) empirical interatomic potential
- The building blocks of the system are \( \text{AlO}_4 \) and \( \text{AlO}_6 \)
- The connectivity of this units is both by the corners (majority) and by the edges (minority)
- The v-DOS present two bands. The low frequency band is related to the inter-unit vibrations, and the high band to the intra-unit vibrations
- \( B = 193 \text{ GPa} \), the lower of all polymorph
- The e-DOS is similar to the one of the crystalline \( \gamma-\text{Al}_2\text{O}_3 \), with a gap of 2.9 eV
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