Comparison of Electronic and Optical Properties of the $\alpha$ and $\kappa$ Phases of Alumina Using Density Functional Theory

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$\kappa$-$\text{Al}_2\text{O}_3$ is a metastable phase of alumina. We have investigated the electronic structure and optical properties of $\kappa$-$\text{Al}_2\text{O}_3$ by a first-principles calculation in the framework of density functional theory (DFT) and the full potential linearized augmented plane wave (FP-LAPW) with three different potentials: the generalized gradient approximation (GGA), the local density approximation (LDA), and the Engle-Vosco approximation (EVA). The results were compared with the stable phase $\alpha$-$\text{Al}_2\text{O}_3$. Our calculated value for the direct band gap of $\alpha$-$\text{Al}_2\text{O}_3$ is 7.2 eV, which is very close to its experimental measurement. A direct band gap of 5.95 is obtained for $\kappa$-$\text{Al}_2\text{O}_3$ which is about 1.25 eV smaller than that of $\alpha$-$\text{Al}_2\text{O}_3$. The calculated optical reflectivity, optical conductivity, and electron energy loss spectrum for $\alpha$- and $\kappa$-$\text{Al}_2\text{O}_3$ are similar on the whole, and for $\alpha$-$\text{Al}_2\text{O}_3$ are in excellent agreement with the experimental measurements.

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I. INTRODUCTION

Alumina ($\text{Al}_2\text{O}_3$) is one of the most important ceramic materials, having exceptional properties. It has many industrial and technological applications because of its hardness, abrasion resistance, mechanical strength, corrosion resistance, good electrical insulation, useful optical properties, fine particle size, large surface area, and catalytic surface activity. Besides the stable phase $\alpha$-$\text{Al}_2\text{O}_3$, alumina exhibits a number of different metastable or transition phases, such as $\gamma$, $\kappa$, $\lambda$, $\eta$, $\theta$, and $\chi$ alumina. The metastable alumina can be divided into two major groups, depending on the stacking of their O anions: face-centered cubic (fcc) packing ($\gamma$, $\theta$, $\eta$, and $\lambda$) and hexagonal close packing (hcp) ($\kappa$ and $\chi$) [1].

The electronic structure of alumina ($\text{Al}_2\text{O}_3$) is increasingly of interest for its variety of applications in optical, electronic, and structural devices. For instance, $\alpha$-$\text{Al}_2\text{O}_3$ is used in electronics and $\kappa$-$\text{Al}_2\text{O}_3$ in wear-resistant coatings on cemented-carbide cutting tools. The $\kappa$-phase can be produced by heat treatments of hydrated aluminas, but is technologically most often produced by chemical vapor deposition (CVD). The advantages of the $\kappa$-phase over $\alpha$-$\text{Al}_2\text{O}_3$ are its smaller grain size, lower pore density, and epitaxial growth when produced using CVD. Although metastable, $\kappa$-$\text{Al}_2\text{O}_3$ appears to be very stable, maintaining
its structural identity up to temperatures of \( \sim 1200 \) K, where it transforms to \( \alpha-\text{Al}_2\text{O}_3 \) \[2, 3, 4\].

The modeling of the structural and electrical properties by means of first principles calculation has become a very useful tool for understanding the properties of materials such as \( \text{Al}_2\text{O}_3 \). There has been some efforts made in determining experimentally and theoretically the structural and optical properties of the \( \alpha-\text{Al}_2\text{O}_3 \) phase \[5, 6, 7, 8, 9\]. Despite these works, there has not been reported an accurate and good comparison between the \( \alpha- \) and \( \kappa-\text{Al}_2\text{O}_3 \) results. \( \alpha-\text{Al}_2\text{O}_3 \) is an insulator, and the measured value of its direct band gap is 8.8 eV \[10\]. The best calculated value for the band gap which has been reported is 6.6 eV \[11\]. Our calculated band gap, density of state, and optical properties for \( \alpha-\text{Al}_2\text{O}_3 \) are very close to the experimental measurements. Unfortunately for the \( \kappa-\text{Al}_2\text{O}_3 \) phase there are no good experimental results. But the very close agreement with the experimental values of our calculation for the \( \alpha-\text{Al}_2\text{O}_3 \) phase provides a good confirmation of the reliability of our calculations for \( \kappa-\text{Al}_2\text{O}_3 \).

The aim of this paper is to determine some of the basic structural, electronic, and optical properties of the \( \alpha- \) and \( \kappa-\text{Al}_2\text{O}_3 \) phases, and compare them, by first principles methods based on density functional theory (DFT), with the full potential linearized augmented plane wave (FP-LAPW) method and with three different exchange-correlation potentials: the generalized gradient approximation (GGA), the local density approximation (LDA), and the Engel-Vosco approximation (EVA)\[12, 13, 14, 15, 16\].

II. STRUCTURE

The unit cell of \( \alpha-\text{Al}_2\text{O}_3 \) is rhombohedral, composed of two \( \text{Al}_2\text{O}_3 \) molecular units (i.e., 10 atoms). It can be more easily visualized, however, with a trigonal unit cell, that is, a hexagonal coordinate system, composed of six molecular units (30 atoms). The crystal structure of \( \alpha-\text{Al}_2\text{O}_3 \) is described as an almost close-packed ABAB stacking of oxygen ions in planes that are perpendicular to the [0001] direction (the \( c \) axes of the hexagonal coordinate system). Smaller aluminum ions occupy two thirds of the six-foldly coordinated interstitial sites present between the oxygen layers. Then \( \alpha-\text{Al}_2\text{O}_3 \) belongs to the trigonal crystal system and has a rhombohedral lattice with space group \( R\bar{3}c \). A summary of \( \alpha-\text{Al}_2\text{O}_3 \) crystallographic specifications is given in Table I. Transmission electron microscopy (TEM) and X-ray diffraction studies have shown that \( \kappa-\text{Al}_2\text{O}_3 \) belongs to the space group \( pna2_1 \) \[17, 18\]. The \( \kappa-\text{Al}_2\text{O}_3 \) has an orthorhombic crystal structure, containing eight \( \text{Al}_2\text{O}_3 \) formula units per unit cell.

The unit cell consists of four oxygen layers in close-packed ABAC stacking sequence and four aluminum layers along the \( c \)-axes, with each oxygen layer comprising six oxygen atoms. The unit cell contains 40 atoms in total, where the number of oxygens is 24 atoms and for aluminum it is 16 atoms \[19, 20, 21\].

A study by Olliver et al. based on XRD, TEM, and SEM concluded that the aluminum atoms to be inserted between the oxygen layer in both octahedral and tetrahedral positions are in a 3:1 ratio \[22\]. The crystal four-fold symmetry (mm2) results in 10 independent
TABLE I: Crystallographic specifications of the $\alpha$- and $\kappa$-Al$_2$O$_3$ phases.

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$-Al$_2$O$_3$</th>
<th>$\kappa$-Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>$D_3^1 = R3c$</td>
<td>Pna2$_1$</td>
</tr>
<tr>
<td>Point group</td>
<td></td>
<td>mm2</td>
</tr>
<tr>
<td>Unit cell</td>
<td>Rhombohedral or Trigonal</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Molecular units</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Lattice parameter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$(Å)</td>
<td>5.128</td>
<td>4.759</td>
</tr>
<tr>
<td>$b$(Å)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$c$(Å)</td>
<td>-</td>
<td>12.992</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>55.28°</td>
<td></td>
</tr>
</tbody>
</table>

atomic positions. The pna2$_1$ symmetry is as follows: $(x, y, z)$, $(-x, -y, z + 1/2)$, $(x + 1/2, -y + 1/2, z)$, $(-x + 1/2, y + 1/2, z + 1/2)$. A summary of the $\kappa$-Al$_2$O$_3$ crystallographic specifications is given in Table I.

III. METHOD OF CALCULATION

We have calculated the structural and electrical properties of the $\alpha$- and $\kappa$-Al$_2$O$_3$ phases by a self-consistent scheme, solving the Kohn-Sham equations in the framework of density functional theory (DFT) by means of the full potential augmented plane wave method (FP-LAPW) with three different potentials: the generalized gradient approximation (GGA), the local density approximation (LDA), and the Engle-Vosco approximation (EVA) [15]. In the full potential method, space is divided into two regions, a spherical muffin-tin (MT) around the nuclei and an interstitial region between the muffin-tin spheres (I). In the first region the radial solution of the Schrödinger equation and their energy derivatives are used as basis functions, and for the interstitial region the basis set consists of plane waves. Core states are treated fully relativistically, while valence and semi-core states are treated semirelativistically.

The calculation was performed with 2000 $k$ points and $RK_{\text{max}} = 8.0$ is the convergence parameter for which the calculation stabilizes and the convergence in terms of energy is achieved. The calculations were performed by the Wien2k codes [23]. For both phases the iteration was halted when the charge density difference was less than 0.00001e between steps, which was used as a convergence criterion. The core cut-off energy, which defines the separation of the core and valence electrons, was chosen as $-8.0$ Ryd.
IV. RESULTS AND DISCUSSION

IV-1. Electronic structure

Many aspects of the crystalline behavior can be understood when the total energy of the system is known, or more often, when the energy difference between two or more electronic or nuclear configurations are known as a function of some parameters. The calculations were first carried out applying the experimental data for lattice constants, then, by minimizing the ratio of the total energy of the crystal to its volume (volume optimization), the theoretical lattice constants were obtained. $\kappa$-$\text{Al}_2\text{O}_3$ is classified as a medium hard material, and it can be used as a wear-resistant coating on cemented-carbide cutting tools, thus the hardness, bulk modulus, and shear modulus are important parameters for estimating the hardness of the material in order to assess its use as a cutting tool. From the literature, we know that the bulk elastic properties of a material determine how much it will compress under a given amount of external pressure. The ratio of the change in pressure to the fractional volume compression is called the bulk modulus ($B$) of the material. In terms of energy, the bulk modulus is also defined from a derivative of the equation of state (EOS) evaluated at the minimum.

$$B = V \frac{\partial^2 E}{\partial V^2}.$$

The position of the minimum of the EOS defines the equilibrium lattice parameter and unit cell volume at zero pressure. In this calculation from a series of strained lattices, the static lattice potential corresponding to the total energy was calculated. From such results the equilibrium volume, bulk modulus, and its pressure derivative were derived. A series of total energy calculations as a function of volume can be fitted to an equation of state according to Murnaghan [24].

Figure 1 shows the total energy with respect to volume of the unit cell after optimization for the $\alpha$-$\text{Al}_2\text{O}_3$ and $\kappa$-$\text{Al}_2\text{O}_3$ phases.

![Figure 1: Variation of energy with volume for (a) $\alpha$-$\text{Al}_2\text{O}_3$ and (b) $\kappa$-$\text{Al}_2\text{O}_3$.](image)

In Table II., we have presented the calculated and experimental values for the equilibrium volume, axial ratios, and bulk moduli for the $\alpha$- and $\kappa$-phases. Our calculated values
were obtained from the equations of state (EOS).

### TABLE II: Unit cell volume, lattice constants ratio, and bulk modulus for $\alpha$-Al$_2$O$_3$ and $\kappa$-Al$_2$O$_3$.

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$-Al$_2$O$_3$</th>
<th>$\kappa$-Al$_2$O$_3$</th>
</tr>
</thead>
</table>
|      | $V(\text{Å}^3)$ | $b/a$ | $c/a$ | $B(\text{GPa})$ | $V(\text{Å}^3)$ | $b/a$ | $c/a$ | $B(\text{GPa})$
| FP-LAPW-GGA | 256.93 | 1.67 | 7.2 | 243.4 | 361.4 | 1.71 | 1.84 | 224 |
| FP-LAPW-LDA | 262.97 | 1.73 | 7.7 | 230.8 | 262.8 | 1.72 | 1.85 | 239 |
| FP-LAPW-EVA | 262.8 | 1.73 | 7.7 | 231.4 | 262.2 | 1.73 | 1.84 | 234 |
| EXPT.$^d$ | 255 | 1.73 | 7.7 | 239 | 359.1 | 1.72 | 1.85 | 246.7 |
| EXPT.$^f$ | 255 | 1.73 | 7.7 | 239 | 352 | 1.72 | 1.85 | 246.7 |

$^a,b,c$This work. $^d$Reference 26. $^f$Reference 11. $^g$Reference 19.

The band structures for the $\alpha$ and $\kappa$ phases have been calculated with the FP-LAPW-GGA, FP-LAPW-LDA, and FP-LAPW-EVA methods. The calculated band structures for the $\alpha$ and $\kappa$ phases along the high-symmetry lines of the Brillouin-zone (BZ) by the FP-LAPW-EV method are better than those of other methods and are shown in Fig. (2a, b), respectively.

For the case of $\alpha$-Al$_2$O$_3$, there is a direct band gap which separates the valence and conduction bands with 7.2 eV at the $\Gamma$ point. The experimental value for the direct band gap of $\alpha$-Al$_2$O$_3$ is 8.8 eV, found by French [10]. Our calculated value for the band gap is very close to the experimental value, and is very much better than other theoretically
calculated values that have been reported. (For comparison, please see Table III). Our calculations with DFT are fundamentally ground-state calculations and, therefore, tend to underestimate the band gap energy, since this energy corresponds to a transition to a higher-energy exited state of the solid [30].

For the case of \( \kappa \)-Al\(_2\)O\(_3\) we obtained a direct band gap of 6.0 eV at the \( \Gamma \) point, which is 1.2 eV smaller than that for \( \alpha \)-Al\(_2\)O\(_3\). Comparison of the theoretical and experimental results for \( \alpha \)-Al\(_2\)O\(_3\) serves to give an indication of the accuracy of our prediction for the \( \kappa \)-Al\(_2\)O\(_3\) phases.

As with the case of \( \alpha \)-Al\(_2\)O\(_3\), the top of the valence bands (VB) is very flat, indicating a very large effective hole mass. On the other hand conduction bands show a large curvature, especially at the \( \Gamma \) point, indicating a good mobility for electrons if they only could be exited across the wide band gap.

Fig. 3 compares the calculated total density of state (DOS) of \( \alpha \)-Al\(_2\)O\(_3\) and \( \kappa \)-Al\(_2\)O\(_3\). The general features of the two DOS curves are similar since they all reflect Al-O bonding.

The width of the upper valence bands (UVB) are about 6.7 eV and 6.53 eV for \( \alpha \)- and \( \kappa \)-Al\(_2\)O\(_3\) respectively. There are many peaks in this region, which are the sources of electrons that can make transitions to the conduction band. The width of LVB is calculated to be 3.1 eV and 3.0 eV for the \( \alpha \) and \( \kappa \)-Al\(_2\)O\(_3\) phases, respectively. The experimental value for the LVB width for \( \alpha \)-Al\(_2\)O\(_3\) is about 6.0 eV, and thus the LVB difference may be due to correlation effects in these deep-lying semicore-like states. The LVB has two peaks that are located at around 16.5 eV and 19.0 eV for \( \alpha \)-Al\(_2\)O\(_3\), and at 16.0 eV and 17.5 eV for \( \kappa \)-Al\(_2\)O\(_3\). The width between the UVB and LVB is calculated to be 6.0 eV, and thus the LVB difference may be due to correlation effects in these deep-lying semicore-like states. The region between the upper and lower valence bands is referred to as the ionicity gap, and the lack of any electronic states in these regions is a demonstration of the ionicity of both \( \alpha \)-Al\(_2\)O\(_3\) and \( \kappa \)-Al\(_2\)O\(_3\).

The partial DOS of \( \alpha \)- and \( \kappa \)-Al\(_2\)O\(_3\) for aluminum and oxygen atoms are shown in Fig. 4 and Fig. 5, respectively. The electronic states below the fermi level for \( \alpha \)- and \( \kappa \)-
Al$_2$O$_3$ are dominated by oxygen states. The lower valence bands (LVB) are composed of the O-2s orbital, and the upper valence bands (UVB) consist mostly of the O-2p orbital, with a small mixing from the Al-3s, -3p, and -3d hybridized orbitals. The upper part of the UVB corresponds to the O-2p nonbonding states, and the lower part is the O-2p bonding states. All states contribute mainly to the conduction band (CB) DOS.

FIG. 4: Partial DOS of the $\alpha$-Al$_2$O$_3$ and $\kappa$-Al$_2$O$_3$ phases for aluminum atoms.

FIG. 5: Partial DOS of the $\alpha$-Al$_2$O$_3$ and $\kappa$-Al$_2$O$_3$ phases for oxygen atoms.

To our knowledge, experimental measurements for the $\kappa$-Al$_2$O$_3$ phase have not yet been determined. This is because it is hard to obtain pure, isotropic specimens that are large enough for experimental investigations. Table III summarizes the band structure properties of the $\alpha$- and $\kappa$-A$_2$O$_3$ phases.
TABLE III: Band structure properties of the $\alpha$-Al$_2$O$_3$ and $\kappa$-Al$_2$O$_3$ phases. The experimental and theoretical values for the energy gap ($E_g$), upper valence band width (UVBW), lower valence band width (LVBW), and upper valence to lower valence band width (UV to LV) are listed.

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$-Al$_2$O$_3$</th>
<th>$\kappa$-Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EXPT.</td>
<td>GGA$^a$</td>
</tr>
<tr>
<td>$E_g$</td>
<td>8.8$^g$</td>
<td>6.32</td>
</tr>
<tr>
<td>UVBW</td>
<td>8.0$^h$</td>
<td>7.3</td>
</tr>
<tr>
<td>LVBW</td>
<td>6.0$^i$</td>
<td>3.24</td>
</tr>
<tr>
<td>UV to LV</td>
<td>6.0$^i$</td>
<td>8.87</td>
</tr>
</tbody>
</table>

$^a,b,c$This work $^d$Reference 19. $^e$Reference 11. $^f$Reference 9. $^g$Reference 27. 29. $^h$Reference 28.

IV-2. Optical properties

Optical properties of both $\alpha$- and $\kappa$-Al$_2$O$_3$ have been calculated with the FP-LAPW-GGA method. There are no experimental results for the optical properties of the $\kappa$-Al$_2$O$_3$ phases, but, with the aim of experimental results for the $\alpha$-Al$_2$O$_3$ phase, a comparison of the theoretical and experimental results for the $\alpha$-phase serves to give an indication of the accuracy of our predictions for the $\kappa$-phase.

Figure 6a shows the reflectivity spectrum for $\alpha$-Al$_2$O$_3$ and $\kappa$-Al$_2$O$_3$. Reflectance also probes the many-body excitations, such as excitons (bound electron-hole pairs), providing a valuable probe of how electrons and holes interact in the lattice.

The measured spectrum of reflectivity shows an excitonic peak at 9.0 eV. This peak is closely associated with the band gap of Al$_2$O$_3$. Peak 2, at 12.6 eV, is due to direct interband transitions and shows anisotropic features. In our calculated reflectivity spectrum (Fig. 6b), there is a shoulder at about 8.0 eV, which can be related to the excitonic peak. Other peaks are located at about 12.5, 21.0, and 33.0 eV. The peak seen at 32 eV in the measured spectrum, or at 32.0 eV in our calculated spectrum, arises from transitions from the O-2s lower valence band to the conduction band. However, all the features of the experimental spectrum (i.e., peaks at 9.0, 12.6, and 32.0 eV) are well represented in our calculations. For the case of $\kappa$-Al$_2$O$_3$ (Fig. 6c), all the features of the spectrum are similar to the $\alpha$-phase. There is a shoulder at about 7.0 eV, and the reflectance is high from the band gap energy to about 24.0 eV, where it falls off rapidly because of the exhaustion of the upper valence-to-conduction band transition.

The measured optical conductivity, which is proportional to the number of electronic interband transitions, for the $\alpha$-Al$_2$O$_3$ phase is shown in Figure 7a. This figure shows
many peaks that are located at about 9.0, 12.5, 17.5, and 31.5 eV. The peak at 9.0 eV is excitonic. In comparison, our calculated optical conductivity (Fig. 7b) has similar features and is much better than other calculated spectrums that have been reported. The optical conductivity spectrum for $\kappa$-Al$_2$O$_3$ is also shown in Figure 7c. Observe that the calculated positions of the features are very similar for both phases.

The electron energy loss spectrum function (EELS) can be deduced from the following relation: [25]
\[ -\text{Im}(\varepsilon^{-1}) = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2}. \]  

This function is proportional to the probability that electrons traversing the bulk material will lose energy. It has the advantage of covering the complete energy range, including non-scattered and elastically scattered electrons (zero loss) electrons, which excite the atom’s electrons of the outer shell (valence loss) or valence interband transitions. Figure 8a shows the measured EELS for \(\alpha\)-\(\text{Al}_2\text{O}_3\). The energy of the main maximum of \(-\text{Im}(\varepsilon^{-1})\) is assigned to the energy of the volume plasmon, \(\eta \omega_p\), and is equal to 26 eV. From Figure 8b it is clear that the value of the plasmon energy is equal to 26.0 eV, which is equal to its experimental value, so a very excellent agreement between the experimental measurement and our calculated results has been obtained. In Figure 8c the energy loss function is plotted for \(\kappa\)-\(\text{Al}_2\text{O}_3\). The plasmon energy is equal to 24.5 eV. With the aim of accuracy of our results for \(\alpha\)-\(\text{Al}_2\text{O}_3\), we can conclude that our results for \(\kappa\)-\(\text{Al}_2\text{O}_3\) are very accurate.

V. CONCLUSION

We have calculated the band structure and optical properties of \(-\text{Al}_2\text{O}_3\) using the full potential linearized augmented plane wave (FP-LAPW) with three different potentials: the generalized gradient approximation (GGA), the local density approximation (LDA), and the Engle-Vosco approximation (EVA) in the framework of density functional theory (DFT). Our calculated results for \(\alpha\)-\(\text{Al}_2\text{O}_3\) shows a very good agreement with the experimental measurements, that gives us confidence for our calculation for \(\kappa\)-\(\text{Al}_2\text{O}_3\). The total density

FIG. 8: Variation of EELS with energy for the \(\alpha\)-\(\text{Al}_2\text{O}_3\): (a) experimental, (b) theoretical, and (c) \(\kappa\)-\(\text{Al}_2\text{O}_3\) phases.
of state calculations show that, for both $\alpha$- and $\kappa$-$\text{Al}_2\text{O}_3$ below the Fermi level, O-2p and O-2s states are dominate. The calculations show a direct band gap of 5.95 eV for the $\kappa$-phase, which is 1.25 eV smaller than that of the $\alpha$-$\text{Al}_2\text{O}_3$ phase. The calculated bulk modulus for the $\alpha$-phase is smaller than that for the $\kappa$-phase, so the $\kappa$-phase must be harder than the $\alpha$-phase. The calculated optical reflectivity, optical conductivity, and electron energy loss spectrum for $\alpha$-$\text{Al}_2\text{O}_3$ are very close to the experimental measurements, and all their features are similar to those for $\kappa$-$\text{Al}_2\text{O}_3$.

References

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