

# Theoretical structure determination of $\kappa$ -Al<sub>2</sub>O<sub>3</sub> phase by first principle

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The aim of this work was to investigate possible structure models of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> phase. In order to identify all the possible structure models a notation for the different positions in the unit cell was developed. The calculation for determining most stable structure model for  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> was performed by first principles study within density functional theory using full potential linearized augmented plane wave (FP-LAPW) method with generalized gradient approximation (GGA). The stacking of the oxygen ion plans in the (001) direction is most definitely as ABAC sequence. The calculated results for bulk modules, total energy, band gap and total density of state show that the aluminum ions (lower case) which are between oxygen layers and must be in the octahedral positions as  $Ac^\beta c^\gamma Bc^\alpha c^\gamma Ab^\gamma b^\beta Cb^\alpha b^\beta$  stacking sequence.

(Received November 20, 2013; accepted July 10, 2014)

*Keywords:* Density functional theory, bulk modulus, Energy gap, Total energy

## 1. Introduction

Aluminum oxide is a highly insulating material that has a great number of technological applications: as a catalyst support, in electronic-device fabrication, as a cutting-tool material, etc. Aluminum oxide is one of the most widespread materials due to its special structure and properties. It has been the subject of extensive research in recent years [1–4]. Alumina exhibits a number of different phases, such as  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\kappa$ ,  $\theta$  and  $\chi$ . The  $\alpha$ -phase is the stable one, often used as a structural, optical, and electronic material, for instance as a substrate for epitaxial growth of Si in electronic-device fabrication [5, 6]. Both  $\alpha$  and  $\kappa$ -phase of Al<sub>2</sub>O<sub>3</sub> are used as wear-resistant coatings on cemented carbides in cutting-tool materials. The  $\kappa$ -phase can be produced by heat treatment of hydrated aluminas but is technologically most often produced by chemical vapor deposition (CVD). The advantages of the  $\kappa$ -phase over  $\alpha$ -phase is its smaller grain size, lower pore density, and epitaxial growth when produced using CVD. Despite a large amount of efforts at understanding the properties of the alumina phases, many questions still remain unanswered, especially at the fundamental atomistic level, including their crystal structures, their stability and bonding nature, and their phase transformation mechanisms. In particular, a good theoretical description and understanding of the crystal structure of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub>, is desirable. To date, the most studied phase of Al<sub>2</sub>O<sub>3</sub> is the stable  $\alpha$  phase. This is presumably due to the stability and the less complex structure of this phase, as compared to the metastable  $\kappa$ -Al<sub>2</sub>O<sub>3</sub>. In spite of their technological relevance, a fundamental understanding of the properties crystal structure of the metastable aluminas is still largely lacking. Experimentally, investigations on metastable aluminas are hampered by metastability, poor crystallinity, difficulty in obtaining pure-phase samples, and possible surface-energy stabilization. At the same time, theoretical

investigations are made difficult by the need for a high accuracy to describe the small energy differences occurring between the many and often very similar structural possibilities [7]. Simple semiempirical methods have shown to be inadequate, which makes first-principles methods at the quantum-mechanical level invaluable tools. However, relatively complex atomic structures make the first-principles methods computationally demanding, putting limits on the applicability of such methods for metastable aluminas. Because of this, there is still a lack of uncontroversial structural information on the metastable aluminas, which renders accurate theoretical studies on their properties hard to perform. In this study we want to determine crystal structure of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> by first principles problem.

## 2. Structure

Recent transmission electron microscopy (TEM) and X-ray diffraction (XRD) studies have shown  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> to belong to the space group Pna<sub>21</sub> and the orthorhombic crystal system with the mm2 point group [8-10]. Based on these experimental observations, the unit cell can be considered to be comprised of 40 atoms in total, 24 oxygen atoms and 16 aluminum atoms. There are four layers in the oxygen sublattice, each comprising six oxygen atoms, exhibiting a close-packed ABAC stacking sequence along the c-axis of the unit cell. Due to the stoichiometry of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub>, the aluminum sublattice has four layers with four atoms, lying interstitially between the oxygen layers. Because of the Pna<sub>21</sub> space group, there are four symmetry related positions in the unit cell: (x, y, z), (1/2-x, 1/2+y, 1/2+z), (1/2+x, 1/2-y, z), and (-x, -y, 1/2+z). For  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> this means that the unit cell can be described using 10 independent atomic positions. For every independent starting coordinate a second is generated

within the same plane and a second pair is located two planes below, i.e. in the  $n+2$  plane. The room temperature lattice parameters of the  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> unit cell have been determined to be  $a=4.8351\text{\AA}$ ,  $b=8.3109\text{\AA}$  and  $c=8.9363\text{\AA}$  [11]. For distinguishing between alternative possible configurations of structure, a system of notation is required. In this examination of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub>, a structure notation scheme identical to that of the Halvarsson et al. [8] study is used, where the oxygen and aluminum positions are described by the type of stacking. For each stacking letters, there are three different ways to position a pair of ions in a closed-packed layer because of the symmetry relationships. We label these  $\alpha$ ,  $\beta$  and  $\gamma$  in such a way that the two ideal positions for an  $\alpha$  pair are at  $y=0$  and  $y=1/2$ , while those for  $\beta$  and  $\gamma$  are at  $0 < y < 1/2$  and  $1/2 < y < 1$ , respectively. Each symmetry related pair of position can be uniquely labeled by two letters: stacking and pair type. Because the oxygen sublattice is well known it can be fixed in one position while the possible configurations are considered for the interstitial Al ions. Each structure candidate is labeled with notation of the type  $Aa^\alpha c^\gamma Bc^\alpha c^\gamma$ ; the stacking and pair types of the first two oxygen and aluminum layers (layers  $n$  and  $n+1$ ) in the unit cell, allowing each possible unit cell to be implicitly described. This is achieved as a consequence of the symmetry, which allows the structure to be described using 10 independent atomic positions as the starting coordinates for the symmetry operators. A, B (and C) in the  $Aa^\alpha c^\gamma Bc^\alpha c^\gamma$ -type notation represent the layers of oxygen ions in accordance with the ABAC stacking sequence. The lower case letters,  $a$ ,  $b$ , and  $c$  and their associated subscripts,  $\alpha$ ,  $\beta$  and  $\gamma$  represent Al pair positions within the layer, as shown in Fig. 1, where the ideal positions for each pair between the A and B layers are illustrated. Each oxygen layer is composed of six ions per unit cell. Therefore there are no vacancies in the oxygen layers and the oxygen can be labeled only with their stacking letter. On the other hand the aluminum layers are composed of four ions, that is two ions pairs. The  $a^\alpha c^\gamma$  configuration representing the 2 Al pairs in the layer  $n$  is generated by applying the first two symmetry operators of the  $Pna_21$  space group. Applying the remaining two symmetry operators yields  $a^\alpha b^\beta$  in the  $n+2$  layer. Similarly, the  $c^\alpha c^\gamma$  configuration in the  $n+1$  layer leads to  $b^\alpha b^\beta$  pairs in the  $n+3$  layer. Hence the  $Aa^\alpha c^\gamma Bc^\alpha c^\gamma$ -type notation can be extended to  $Aa^\alpha c^\gamma Bc^\alpha c^\gamma Aa^\alpha b^\beta Cb^\alpha b^\beta$  in order to explicitly describe the unit cell.

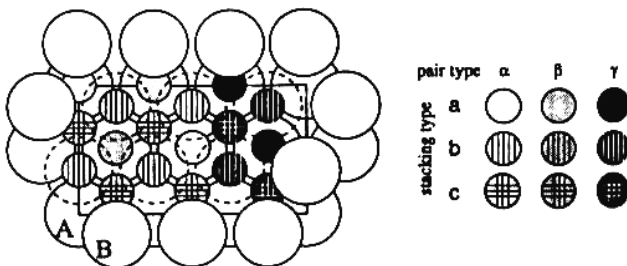


Fig. 1. Stacking sequence and Al pair positions within the layer.

On each independent layer there are 18 possible configurations for the two Al pairs. We have considered to all possible combinations of the Al pairs between the two independent layers. In the closed packed structure of the oxygen sub-lattice, there are two different type of interstices, octahedral and tetrahedral positions. This can be seen in Fig. 2, where three different Al-ions have been placed in a-, b- and c- positions between two oxygen layers, one in A- and one in B- position. Al ion in the c-position is bounded by six oxygen ions which are the corners of an octahedron, thus the Al ion is in an octahedral position. Similarly, the Al ion in the- and b-positions are in tetrahedral positions.

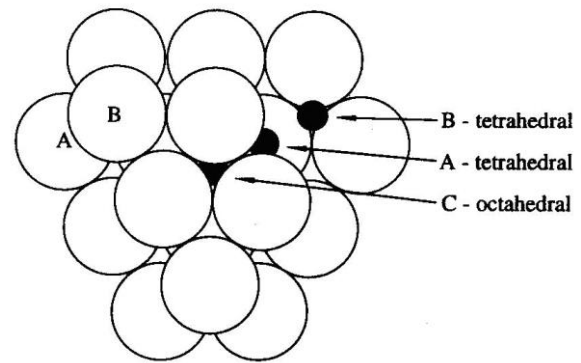


Fig. 2. Octahedral and tetrahedral positions of Al ions.

The aluminum layers can be categorized in accordance with their Al pair coordination and we denoted the Al ions positions by O, T and M letters in which O reflects all Al ions being situated in octahedral sites, T indicates complete tetrahedral site occupancy, and M (mixed) represents one pair in the octahedral and the other pair in tetrahedral positions. This allows independent structural possibilities to be grouped in nine ways: OOOO, OMOM, MOMO, MMMM, TOTO, OTOT, MTMT, TMTM and TTTT, depending on the type of coordination in the first four layers. For simplicity we call these groups as group 1, 2 ... and finally group 9, respectively.

### 3. Methods and calculations

Calculation of structural, electric properties of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> was carried out by self-consistent scheme by solving the Kohn-Sham equations. Using a full potential linearized augmented plan wave (FP-LAPW) method in the framework of the density functional theory (DFT) along with the generalized gradient approximation (GGA), [13-15] using Wien2k codes [16]. In the first step of the calculation,  $Rk_{\max}$ ,  $G_{\max}$  and number of k point which are the internal parameter of Wien2k codes must be optimized. So that, calculation was performed with 300 k-points and  $Rk_{\max}=7$  ( $R$  is the smallest muffin-tin radius and  $k_{\max}$  is the cut-off wave vector of the plane-wave basis set) for the convergence parameter for which the calculation stabilize and convergence in terms of the energy are achieved. The values of other parameters are  $G_{\max}=14 \text{ au}^{-1}$

( $G_{\max}$  is the magnitude of largest vector in charge density Fourier expansion or the plane wave cutoff and  $au$  is the Bohr radius),  $R_{\text{MT}}(\text{Al})=1.6au$  and  $R_{\text{MT}}(\text{O})=1.7au$  (muffin-tin radius). When the difference charge density was less than  $0.0001e$  between steps as convergence criterion the iterations were halted. The cut-off energy, which defines the separation of the valence and core states, was chosen  $-8 \text{ Ry}$ .

From 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 and can be written as follows:

$$B = -V \frac{\partial P}{\partial V} \quad (1)$$

In term of energy, the bulk modulus is also defined by equation of state (EOS) and evaluated at the minimum:

$$B = V \frac{\partial^2 E}{\partial V^2} \quad (2)$$

The position of the minimum of 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 total energy was calculated. From such results the equilibrium volume, bulk modulus and its pressure derivative was derived. A series of total energy calculations as a function of volume can be fitted to an equation of states according to Murnaghan [17];

$$E(V) = E_0 + \frac{B_0 V}{B'_0} \left[ \frac{(V_0/V)^{B'_0}}{B'_0} + 1 \right] - \frac{B_0 V_0}{B'_0 - 1} \quad (3)$$

$B_0$  is an equilibrium bulk modulus that effectively measures the curvature of the energy versus volume curve about the relaxed volume  $V_0$ , and  $B'_0$  is the derivative of the bulk modulus.

#### 4. Results and discussion

In order to investigate the most stable and best model for structure of  $\kappa\text{-Al}_2\text{O}_3$  we have calculated some of the important parameter for nine structures candidate of  $\kappa\text{-Al}_2\text{O}_3$ . The calculation 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 for all groups. Finally, we relaxed the structure for finding the equilibrium position of each ion in the structure for all of the nine groups.

Table 1 and 2 are summarizes the results obtained after structural relaxation for group 1, as well as results of experimental work for comparison [11].

Table 1. Lattice constants of  $\kappa\text{-Al}_2\text{O}_3$ .

Lattice constant In (Å)	Calculated This work FP-LAPW (GGA06)	Expriment [11]
a	4.8435	4.8351
b	8.2224	8.3109
c	9.0011	8.9363

In Table 2, the relaxed atomic positions of each atom after the residual forces on each atom after relaxation were less than  $1 \text{ mRy/Bohr}$  are given. The final calculation was performed with the theoretical lattice constant and relaxed structure.

Table 2. Atomic positions of  $\kappa\text{-Al}_2\text{O}_3$ .

Atoms	Calculated (this work) FP-LAPW (GGA06)			Experimental [11]		
	x	y	z	x	y	z
Al(1)	0.6711	0.8340		0.6787	0.8416	
Al(2)		0.0012			0.0000	
Al(3)	0.1755	0.3400		0.1846	0.3432	
Al(4)		0.7884			0.7868	
O(1)	0.8220	0.6395		0.8115	0.6489	
O(2)		0.6970			0.6972	
O(3)	0.6621	0.4552		0.6677	0.4696	
O(4)		0.9885			0.9993	
O(5)	0.3310	0.8372		0.3290	0.8313	
O(6)		0.8999			0.8927	
	0.0311	0.4955		0.0248	0.4908	
		0.6322			0.6292	
	0.4800	0.6678		0.4717	0.6647	
		0.6451			0.6381	
	0.5203	0.6789		0.5145	0.6728	
		0.1308			0.1212	
	0.8613	0.3215		0.8608	0.3301	
		0.8615			0.8662	
	0.3376	0.4934		0.3360	0.4992	
		0.0015			0.0009	

Fig. 3 shows the values of energy and volume for each group. It is clear that the energy of groups 1 and 2 are less than other groups. In other word, when the Al ions are in octahedral positions, the total energy of unit cell is lower than other situations.

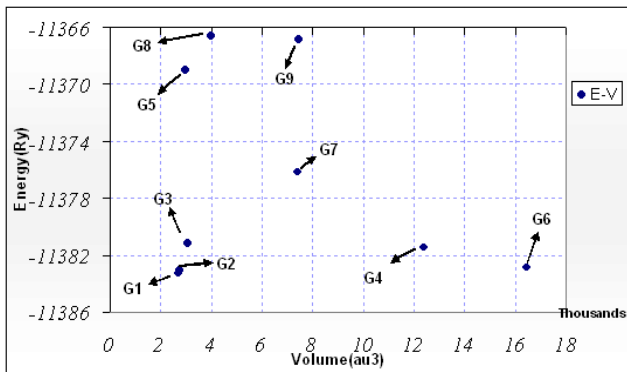


Fig. 3. The total energy and volume of nine groups.

The calculated bulk modulus and total energy for nine groups of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> are summarized in Table 3.

From the literature we know that the bulk modulus of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> is about 240 (GPa) and experimental measurements show that the bulk modulus of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> is in order of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [12]. It can be seen from Table 3 that the G1 group satisfies this situation. On the other hand by comparison of total energy of nine groups we can see that total energy of group G1 is less than other groups so that this group is more stable than the other groups.

The  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> is an insulator and has a wide band gap about 6eV [4]. The total density of state of each group has been calculated and the results are shown in Fig 4. Calculated total density of state shows that, group G1 have a band gap about 5eV and group G2 about 3eV. However, the total density of state for the other groups didn't show wide band gap. By comparing the values of band gaps for

nine groups, one can select the group G1 with structure notation  $Ac^{\beta}c^{\gamma}Bc^{\alpha}c^{\gamma}Ab^{\gamma}b^{\beta}Cb^{\alpha}b^{\beta}$  or OOOO type, as the most suitable and stable structure for  $\kappa$ -Al<sub>2</sub>O<sub>3</sub>.

Table 3. The bulk modulus, volume and total energy for nine groups of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub>.

Groups	Energy (Ry)	Volume (au) <sup>3</sup>	Bulk modulus(GPa)
G1 OOOO	-11383.2823	2669.6795	250
G2 OMOM	-11383.0793	2715.313	230
G3 MOMO	-11381.1884	3074.8269	180
G4 MMMM	-11381.497	12403.6786	8
G5 TOTO	-11368.9791	2947.9231	195
G6 OTOT	-11382.8742	16425.6867	18
G7 MTMT	-11376.1722	7393.1598	12
G8 TMTM	-11366.8612	7431.4888	13
G9 TTTT	-11366.6083	3988.0230	117

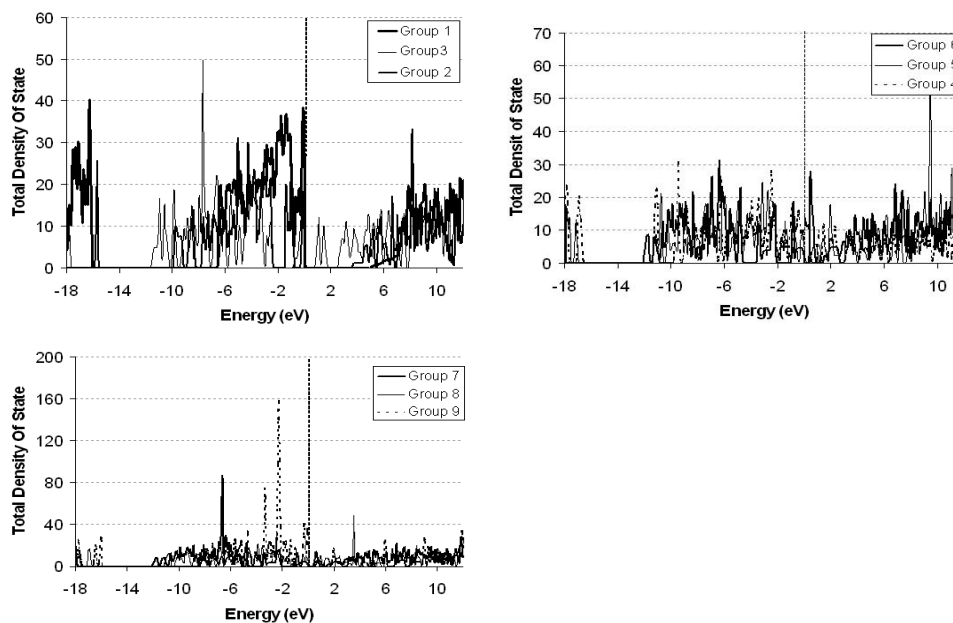


Fig. 4. Total density of state for nine candidates Groups of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub>.

## 5. Conclusion

The purpose of this study was to investigate the structure of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> by first principle study in the framework of density functional theory with the method of full potential linearized augmented plan wave (FP-LAPW) and by generalized gradient approximation (GGA). Nine different structures have been chosen for  $\kappa$ -Al<sub>2</sub>O<sub>3</sub>, with the possible arrangement of Al ions between the O ions layers. Based on the theoretical calculation we found that the total energy of group G1 is less than other groups. The bulk modulus of this group is 250 (GPa) and the calculated band gap value is 5eV. It can therefore be concluded that the most stable structure of  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> is of OOOO type coordination, with  $Ac^{\beta}c^{\gamma}Bc^{\alpha}c^{\gamma}Ab^{\gamma}b^{\beta}Cb^{\alpha}b^{\beta}$  configuration which all Al ions are in octahedral positions.

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