Physics Letters A 378 (2014) 1867–1870

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

# First-principles calculations of the dielectric and vibrational properties of ferroelectric and paraelectric $BaAl_2O_4$

Congwei Xie [a], Qingfeng Zeng [a,*], Dong Dong [a], Shuang Gao [a], Yongqing Cai [b], Artem R. Oganov [c,d,e]

[a] Science and Technology on Thermostructural Composite Materials Laboratory, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China
[b] Institute of High Performance Computing, 1 Fusionopolis Way, Singapore 138632, Singapore
[c] Department of Geosciences, Center for Materials by Design, and Institute for Advanced Computational Science, State University of New York, Stony Brook, NY 11794-2100, USA
[d] Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region 141700, Russia
[e] School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, Shaanxi 710072, PR China

## ARTICLE INFO

*Article history:*
Received 12 December 2013
Received in revised form 17 April 2014
Accepted 24 April 2014
Available online 1 May 2014
Communicated by R. Wu

*Keywords:*
First-principles
Dielectric properties
$BaAl_2O_4$ polymorphs
Transparent materials

## ABSTRACT

First-principles calculations have been conducted to study the structural, dielectric, and vibrational properties of ferroelectric and paraelectric $BaAl_2O_4$. High-frequency and static dielectric constants, and phonon frequencies at the Brillouin zone center are reported. Both $BaAl_2O_4$ polymorphs are promising infrared-transparent materials due to their low electronic dielectric constants. The ferroelectric and paraelectric $BaAl_2O_4$ have much smaller permittivity compared to the classical ferroelectric materials. From an atomic nanostructure standpoint, the abnormally low permittivity of $BaAl_2O_4$ polymorphs is mainly related to low coordination numbers of Ba (9) and Al (4).

## 1. Introduction

$BaAl_2O_4$ has attracted a great attention due to its intriguing optical properties and exciton effect evidenced by strong photoluminescence emission [1,2]. This material also shows excellent dielectric and pyroelectric properties. However, as a typical complex oxide, $BaAl_2O_4$ has a much smaller dielectric constant than classical ferroelectric materials like $BaTiO_3$ (average static dielectric constant can reach 2450 [3]). The origin of this unexpectedly low dielectric constant of $BaAl_2O_4$ is still unclear. Understanding the polarization mechanism and ionic contribution to the dielectric constant is critically important for its optoelectronic applications.

$BaAl_2O_4$ exhibits a paraelectric–ferroelectric (PE–FE) phase transition over a wide temperature range (400–670 K) [4]. In both structures, corner-sharing $AlO_4$ tetrahedra form a three-dimensional network with hexagonal channels which are filled with $Ba^{2+}$ cations [4,5]. The crystal structure of low-temperature FE phase has been determined by single-crystal [6] and powder [7] X-ray diffraction, respectively. The FE phase adopts a hexagonal structure (space group $P6_3$) [6,7]. The crystal structure of the PE phase was proposed by Huang et al. [7], who suggested that PE phase has a $P6_322$ symmetry, which was confirmed by high resolution electron microscopy study performed by Abakumov et al. [4].

First-principles calculations are capable of predicting the material properties using no empirical data, and this gives the promise to speed up materials research [8,9]. This work aims to investigate the dielectric and vibrational properties of $BaAl_2O_4$ polymorphs using first-principles calculations. The crystal structures of FE and PE phases in this study are from the data of Huang et al. [7] and Abakumov et al. [4], respectively.

## 2. Computational methodology

The present first-principles calculations were carried out using the CASTEP code [10] with norm-conserving pseudopotentials [11]. Modified Perdew–Burke–Ernzerhof GGA functional for solids (PBEsol) [12] was applied to describe the exchange and correlation potentials. The kinetic energy cutoff for the plane waves was 900 eV. To sample the Brillouin-zones, a $2 \times 2 \times 2$ ($5 \times 5 \times 3$) Monkhorst–Pack grid of $k$-points [13] was adopted for a primitive cell of FE phase (PE phase). The convergence tolerance of energy change, maximum force on each atom and stress of the optimized

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* Corresponding author. Tel.: +86 29 88495619; fax: +86 29 88494620.
*E-mail address:* qfzeng@nwpu.edu.cn (Q. Zeng).

http://dx.doi.org/10.1016/j.physleta.2014.04.047
0375-9601/

**Table 1**
Optimized lattice constants and the internal atom coordinates of the FE-$BaAl_2O_4$ and PE-$BaAl_2O_4$.

| Compound | Space group (No.) | Lattice constants (Å) | Atom position (Wyckoff position) |
|---|---|---|---|
| FE-$BaAl_2O_4$ | $P6_3$<br>(173) | $a = 10.264$<br>$c = 8.656$<br>$a = 10.449$ [7]<br>$c = 8.793$ [7]<br>$a = 10.369$ [1]<br>$c = 8.807$ [1] | Ba1(2a) (0, 0, 0.247)<br>Ba2(6c) (0.506, 0.005, 0.258)<br>Al1(6c) (0.157, 0.332, 0.063)<br>Al2(6c) (0.155, 0.329, 0.451)<br>Al3(2b) (1/3, 2/3, 0.947)<br>Al4(2b) (1/3, 2/3, 0.550)<br>O1(6c) (0.180, −0.002, 0.984)<br>O2(6c) (0.686, −0.001, 0.039)<br>O3(6c) (0.497, 0.184, −0.006)<br>O4(6c) (0.181, 0.501, 1.002)<br>O5(6c) (0.121, 0.324, 0.257)<br>O6(2b) (1/3, 2/3, 0.749) |
| PE-$BaAl_2O_4$ | $P6_322$<br>(182) | $a = 5.113$<br>$c = 8.730$<br>$a = 5.224$ [4]<br>$c = 8.793$ [4] | Ba(2b) (0, 0, 1/4)<br>Al(4f) (1/3, 2/3, 0.054)<br>O1(6g) (0.359, 0, 0)<br>O2(2c) (1/3, 2/3, 1/4) |

structure was $1 \times 10^{-5}$ eV/atom, 0.01 eV/Å, and 0.05 GPa, respectively.

The calculation of vibrational and dielectric properties were performed using density functional perturbation theory (DFPT) [14]. $\Gamma$-phonon frequencies and dielectric tensors were computed as second derivatives of the total energy with respect to atomic displacements or external electric field [15,16]. The longitudinal-optical/transverse-optical (LO/TO) splitting of zone center optical modes was investigated parallel and perpendicular to the (001) direction approaching to $\Gamma$-point.

## 3. Results and discussions

### 3.1. Structure optimization

The crystal structure of FE-$BaAl_2O_4$, containing 56 atoms in its unit cell, is a hexagonal structure with space group $P6_3$. Figs. 1a and 1b represent $b$–$c$ and $a$–$b$ plane of the unit cell, respectively. Three-dimensional tridymite-like framework is made of $AlO_4$ tetrahedra with Ba atoms situated in the hexagonal channels. The structure of the FE-$BaAl_2O_4$ contains four symmetrically inequivalent Al atoms with clearly distinct coordination environment (Fig. 1c). Both the $(Al3)O_4$ tetrahedron and $(Al4)O_4$ tetrahedron have a three-fold symmetry axis, and the two tetrahedra share the same oxygen atom (O6). The (Al3)–(O6)–(Al4) bond angle is 180°. At the same time, the $(Al1)O_4$ and $(Al2)O_4$ tetrahedra are distorted, and the (Al1)–(O5)–(Al2) bond angle is 155.3°. Figs. 2a and 2b show that the $b$–$c$ and $a$–$b$ plane of the $2 \times 2 \times 1$ superstructure of PE-$BaAl_2O_4$, respectively. PE- and FE-$BaAl_2O_4$ display group–subgroup relations: their structural topology is the same, with the FE phase being symmetry-broken. FE-$BaAl_2O_4$ also has a larger cell (a $2 \times 2 \times 1$ supercell of PE-$BaAl_2O_4$). All Ba atoms in PE-$BaAl_2O_4$ are symmetrically equivalent. All Al atoms in PE-$BaAl_2O_4$ are also symmetrically equivalent and the (Al)–(O2)–(Al) bond angle is 180° (Fig. 2c).

Computed structural parameters of both phases are listed in Table 1 and values from other reports are also listed for comparison. Our calculated lattice constants of FE-$BaAl_2O_4$ are close to the experimental results [7] and other calculated results obtained by using GGA-PBE [1]. The present structural parameters of PE-$BaAl_2O_4$ are also comparable to the experimental results [4].

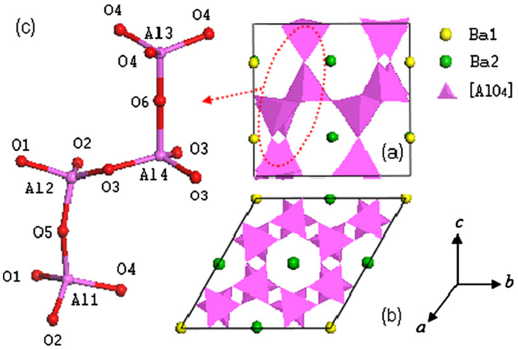

**Fig. 1.** Crystal structure of FE-$BaAl_2O_4$: (a) $b$–$c$ plane of the unit cell, (b) $a$–$b$ plane of the unit cell, and (c) coordination environments of Al atoms in the FE-$BaAl_2O_4$.

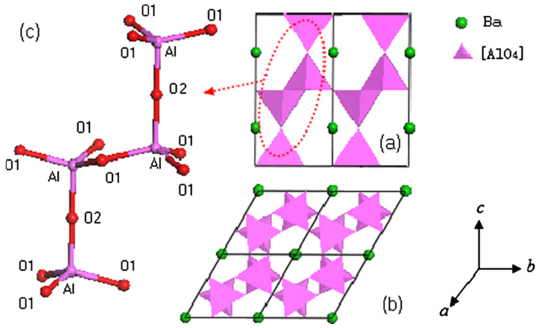

**Fig. 2.** Crystal structure of PE-$BaAl_2O_4$: (a) $b$–$c$ plane of the $2 \times 2 \times 1$ supercell, (b) $a$–$b$ plane of the $2 \times 2 \times 1$ supercell, and (c) coordination environments of Al atoms in the PE-$BaAl_2O_4$.

### 3.2. Electronic dielectric constants

Due to the anisotropic hexagonal symmetry of the $BaAl_2O_4$, the calculated dielectric tensor has two independent components $\varepsilon_{\perp c}$ and $\varepsilon_{\parallel c}$ (perpendicular to and parallel to the $c$ axis). Our present values of the electronic dielectric constants are $\varepsilon_{\infty,\perp c} = 3.12$ and $\varepsilon_{\infty,\parallel c} = 3.13$ for FE-$BaAl_2O_4$. The average permittivity $\bar{\varepsilon}_\infty$, obtained from the expression $\bar{\varepsilon}_\infty = (2\varepsilon_{\infty,\perp c} + \varepsilon_{\infty,\parallel c})/3$, is 3.12. The calculated values of $\varepsilon_{\infty,\perp c}$, $\varepsilon_{\infty,\parallel c}$ and $\bar{\varepsilon}_\infty$ for PE-$BaAl_2O_4$ are 3.12, 3.14 and 3.13, respectively, which are similar to those of FE-$BaAl_2O_4$.

Using the electronic dielectric constants, we can obtain some other properties such as the index of refraction $n$, the reflectivity $R$, and the optical transmittance $T$. These properties can also help us to confirm the accuracy of our calculations. For nonmagnetic materials, the index of refraction $n$ and reflectivity $R$ of $BaAl_2O_4$ can be calculated by $n = \varepsilon^{1/2}$ and $R = (n-1)^2/(n+1)^2$, respectively.