Journal of the European Ceramic Society 36 (2016) 1073–1079

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Theoretical predictions of composition-dependent structure and properties of alumina-rich spinel

Bingtian Tu, Hao Wang*, Xin Liu, Weimin Wang, Zhengyi Fu

State Key Lab of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

ARTICLE INFO

Article history:
Received 4 April 2015
Received in revised form
13 November 2015
Accepted 28 November 2015
Available online 7 December 2015

Keywords:
Alumina-rich spinel
First-principles calculation
Composition-dependence
Optical properties
Mechanical properties

ABSTRACT

Alumina-rich spinel ($MgO{\cdot}nAl_2O_3$, $n \geq 1$) was described as a solid solution of $MgAl_2O_4$ and $Al_{8/3}O_4$ (γ-Al_2O_3) with formula of $Mg_{1-x}Al_{2(1+x/3)}O_4$ ($0 \leq x \leq 1$). Five redefined supercell models of $MgO{\cdot}nAl_2O_3$ were constructed to investigate the composition-dependence of structural, electronic, optical and mechanical properties. The first-principles calculations were developed with high accuracy to evaluate the lattice constant, electronic structure, dielectric function and elastic constants. The detailed structural information was presented by analyzing the variations in lattice constant, interstitial volume and anion parameter with the content of γ-Al_2O_3. The composition-dependent bulk modulus, shear modulus and electronic structure of alumina-rich spinel were well discussed. As increased the content of Al, the mechanical properties showed an increasing trend, while the optical absorption in the UV region presented a blue-shift of ~1.2 eV. These theoretical results provided a basis for understanding the crystal structure and intrinsic properties of alumina-rich spinel.

1. Introduction

Magnesium aluminate spinel ($MgAl_2O_4$), as a technologically important advanced ceramic material, has attracted a great deal of attention for its outstanding thermal–mechanical properties, chemical inertness and thermal shock resistance [1,2]. Fully dense $MgAl_2O_4$ ceramic has excellent optically transparent property in the range from ultraviolet (UV) to mid wave infrared (MWIR) light. Applications of transparent spinel ceramic include domes for missiles, transparent armors, lenses, point of sale (POS) scanning windows, UV lithography windows, etc. Transparent spinel ceramic, which is one of the limited materials with both high transparency in UV–MWIR range and sufficiently high mechanical properties, could be used as a candidate for sapphire [3].

Although $MgAl_2O_4$ is the only one ternary phase with a temperature below 1300 K in the MgO–Al_2O_3 phase diagram, the system does possess a spinel type solid solution $MgO{\cdot}nAl_2O_3$ ($0.6 \leq n \leq 9.1$) [4]. The spinel structure consists of a pseudo-*cubic closed-packed* (ccp) oxygen arrangement where the Mg and Al cations locate at 1/8 of the tetrahedral interstices and 1/2 of the octahedral interstice, respectively. In addition, an exchange is observed between Mg and Al cations in spinel crystal structure. This situation is always described by the inversion parameter, *i*. However, the degree of inversion in natural spinel is close to zero [5]. Similar to previous studies [6–8], our theoretical investigation does not take the inverse phenomena in the alumina-rich spinel solid solution into consideration.

Alumina-rich spinel containing excess Al is charge-compensated by cationic vacancies. There were considerable debates about whether the cationic vacancies distribute on octahedral [9–12], tetrahedral sites [13], or both [14]. Most of the recent experimental studies tended to support that the vacancies distributing on the octahedral site is more probable than a random distribution on both sites. According to the definition of solid solution, the spinel on the alumina-rich side could be described as the solid solution of $Al_{8/3}\square_{1/3}O_4$ (the defect spinel type γ-Al_2O_3, where $\square$ denotes the cation vacancy) and $MgAl_2O_4$ with the formula of $Mg_{1-x}Al_{2(1+x/3)}\square_{x/3}O_4$ ($0 \leq x \leq 1$).

One early report showed that the oxygen diffusivity in alumina-rich spinel is higher than that in stoichiometric sample [15]. The enhanced diffusion could promote sintering and have a positive influence on the densification. There were several studies of $MgO{\cdot}nAl_2O_3$ polycrystalline ceramics with high level of light transmission (>80%) throughout the visible wavelength region [16–18]. Krell et al. [19,20] studied the impacts of Al composition on the sintering and hardness of alumina-rich spinel. Navrotsky et al. [9] also investigated the thermochemistry and crystal structure of alumina-rich spinels. So far, the processing, elastic strength,

* Corresponding author. Fax: +86 2787160401.
E-mail address: shswangh@whut.edu.cn (H. Wang).

http://dx.doi.org/10.1016/j.jeurceramsoc.2015.11.043
0955-2219/

optical transparent properties and thermodynamics of spinel transparent ceramics have been well summarized [1,19], but relatively few researches have focused on the composition-dependent crystal structure and intrinsic properties in alumina-rich spinel.

The first-principles calculations based on the density functional theory (DFT) [21,22] have been widely used for studying the structure and properties of materials. In some solid solutions, such as $Al_{4+2x}Si_{2-2x}O_{10-x}$, $Zn_{1-x}Cd_xO$, $Cd_{1-x}Ca_xO$ and $Al_{(8+x)/3}O_{4-x}N_x$ (γ-alon), the first-principles calculations have been successfully performed to investigate the effect of varying composition on structure and intrinsic properties [23–26]. In stoichiometric spinel $MgAl_2O_4$, the structure, electronic, optical and mechanical properties were widely studied by DFT calculations [7,8,27–32]. Nevertheless, a lack of systematic investigations on the structure, electronic, optical and mechanical properties of alumina-rich spinel, has motivated the exploration of composition-dependent crystal structure and properties by theoretical means.

In this work, five models of alumina-rich spinel ($Mg_{1-x}Al_{2(1+x/3)}O_4$, $x = 0$, 0.25, 0.5, 0.75 and 1), corresponding to $MgAl_2O_4$, $MgO{\cdot}1.44Al_2O_3$, $MgO{\cdot}2.33Al_2O_3$, $MgO{\cdot}5Al_2O_3$ and γ-Al_2O_3, were chosen for theoretical investigations. The composition-dependence of crystal structure, electronic structure, optical and mechanical properties were presented and discussed. The calculated results provided a basis for understanding the crystal structure and intrinsic properties of alumina-rich spinel.

2. Model and computational details

In the defect cubic spinel structure (*Fd* 3*m*) of $MgO{\cdot}1.44Al_2O_3$, $MgO{\cdot}2.33Al_2O_3$, $MgO{\cdot}5Al_2O_3$ and γ-Al_2O_3, the 2/3, 4/3, 6/3 and 8/3 cationic vacancies per unit cell were required to maintain the electroneutrality. Starting from the stoichiometric spinel structure ($MgAl_2O_4$), a redefined cell ($Mg_6Al_{12}O_{24}$) was constructed in terms of the basis vectors of its cubic unit cell, ***a***, ***b*** and ***c***, such that $\boldsymbol{a}' = 1.5\boldsymbol{a} + 0.5\boldsymbol{b}$, $\boldsymbol{b}' = -0.5\boldsymbol{b} + 0.5\boldsymbol{c}$, $\boldsymbol{c}' = -0.5\boldsymbol{b} - 0.5\boldsymbol{c}$, where ***a'***, ***b'*** and ***c'*** are the unit vectors of the redefined cell [33]. The redefined cell was three quarters the size of a conventional cell. Based on the $1 \times 2 \times 1$ redefined supercell, structural models of $MgAl_2O_4$, $MgO \cdot 1.44Al_2O_3$, $MgO{\cdot}2.33Al_2O_3$, $MgO{\cdot}5Al_2O_3$ and γ-Al_2O_3, which contain 84, 83, 82, 81 and 80 atoms respectively, were constructed. The numbers of formula unit in these supercells, *Z'*, were all 12. More than fifteen possible structural models for each of $MgO{\cdot}1.44Al_2O_3$, $MgO{\cdot}2.33Al_2O_3$ and $MgO{\cdot}5Al_2O_3$ were constructed to carry out the full geometry optimization. As shown in Fig. 1, the structural models with the lowest total energy were subsequently used for further calculations.

The calculations based on density functional theory were performed using the Cambridge Serial Total Energy Package (CASTEP) codes [34]. The generalized gradient approximation (GGA) parameterized by Perdew, Burke and Ernzerhof (PBE) was used to describe the electronic exchange-correlation (XC) potential [35]. Ultrasoft pseudopotential [36] was used with $2s^22p^4$, $3s^23p^0$ and $3s^23p^1$ as the valence-electron configurations for O, Mg and Al atoms respectively, to describe the interactions between ions and electrons. With convergence testing, the plane-wave cutoff energy of 380 eV is sufficient for all structural models. The Brillouin zone was sampled with $2 \times 2 \times 5$ *k*-points meshes for all models according to the Monkhorst–Pack scheme. The geometries of the configurations were optimized using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimizer in the CASTEP package with the following default convergence tolerances: 5.0×10^{-6} eV for energy change, 0.01 eV/Å for maximum force, and 5.0×10^{-4} Å for maximum displacement.

The formation enthalpy is generally calculated to verify the stabilities of compound in first-principles investigations [37,38]. At ambient condition with $T = 0$ K and $p = 0$ Pa, the formation enthalpy of alumina-rich spinel could be obtained using the following formula whereby the zero-point vibration contribution is ignored:

$$\Delta H_f = E[Mg_{1-x}Al_{2(1+x/3)}O_4] - \left[(1-x)\mu_{Mg} + \frac{2x+2}{3}\mu_{Al} + 4\mu_O\right], \quad (1)$$

where μ_{Mg}, μ_{Al} and μ_O are the total energy per atom of the elements of Mg, Al and O in their elemental reference phase, $E(Mg_{1-x}Al_{2(1+x/3)}O_4)$ denotes the total energy per formula unit of $Mg_{1-x}Al_{2(1+x/3)}O_4$ ($x = 0$, 0.25, 0.5, 0.75 and 1).

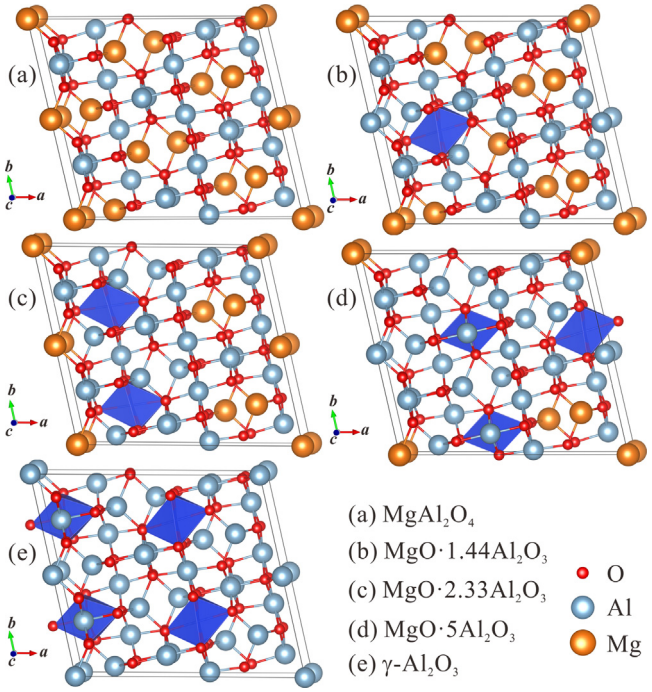

Fig. 1. Supercell model of $MgAl_2O_4$, $MgO{\cdot}1.44Al_2O_3$, $MgO{\cdot}2.33Al_2O_3$, $MgO{\cdot}5Al_2O_3$, and γ-Al_2O_3, where the octahedrons indicate the sites of Al vacancies.

3. Results and discussion

3.1. Crystal structure

To investigate the ground-state crystal structure of alumina-rich spinel, both lattice constants and atomic positions were fully optimized at first. As indicated in Table 1, the optimized lattice parameters, average bond lengths and formation enthalpies of selected models are listed. The calculated formation enthalpies of all considered $Mg_{1-x}Al_{2(1+x/3)}O_4$ structures are negative, which indicates that the structures proposed in this work are thermodynamically stable. In view of the variation of formation energy with *x*, it is noticed that the alumina-rich spinel tend towards decreasing the stability as the increase of cationic vacancies, which is in good agreement with experimental reports [4,9]. The interatomic distance in 16*d* site slightly increased with the increase of Al content, while the bond length in 8*a* site presented an evident decrease. This is in good agreement with the experimental results reported by Lucchesi and Giusta [12]. According to Sickafus's investigations on the structure of spinel [39], the lattice parameter of alumina-rich spinel was estimated by following formula.

$$a = 2\left(\frac{V'}{Z'}\right)^{1/3}, \quad (2)$$

where V' is the volume of supercell after geometry optimizations, and Z' is the number of formula unit in these supercells. The lattice constant as a function of composition is plotted in Fig. 2, where the