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Study of Raman spectra for γ-Al_2O_3 models by using first-principles method

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ABSTRACT

The Raman spectra of spinel and nonspinel models for γ-Al_2O_3 were calculated by using a first principles method and an assignment on the basis of the proposed symmetry was established. The IR spectra were also calculated to validate the method. The results show that the Raman spectra are sensitive to the structural differences between the spinel and nonspinel models. The spinel model provides more medium peaks at the lower wave number range while the nonspinel model is much more flat. The Born effective charges, electron localization function, and dielectric tensors were also discussed briefly. These results provide valuable information for further insight into the structural properties of γ-Al_2O_3 in atomic scales.

1. Introduction

Alumina (Al_2O_3), as an important ceramic material, has attracted much attention because of its wide applications in industrial fields, such as electronics, optics, and mechanical engineering [1–3]. During the process of obtaining α-Al_2O_3 (corundum), which is the most thermodynamically stable form, a series of metastable structures (the so-called transition aluminas) are also obtained, including the β-, γ-, η-, θ-, κ-, and χ-phases [4]. Among them, γ-Al_2O_3 is the most widely used as a catalyst and a catalyst support [5,6].

γ-Al_2O_3 is usually described as a defective spinel with *Fd*-3*m* symmetry. That is, in the cubic spinel cell containing 8 AB_2O_4 formula units, γ-Al_2O_3 has a tetrahedral cation site (A) and an octahedral cation site (B). Al atoms take all A and B sites and create a few vacancies. To satisfy the Al_2O_3 stoichiometry, an average of 8/3 Al vacancies per spinel cubic cell are required. The locations of the vacancies have been extensively investigated by experimental methods [7–11]; however, the structural characterization of γ-Al_2O_3 is hampered by the fact that the samples obtained are usually porous with a large surface rather than single crystals. Therefore, no conclusive results have been obtained as to whether vacancies are entirely at octahedral sites, entirely at tetrahedral sites, or at both sites with a specific proportion.

On the basis of the spinel model, Gutiérrez and co-workers demonstrated that where 2 Al vacancies are located at octahedral sites, maximizing the distance between them gives the most energetically stable structure by using a first-principles method [12]. This model provides a compact unit cell containing 40 atoms. Previous structure models were defined with fractional occupation numbers that do not allow atomic simulations, because the unit cell has to be enlarged to obtain a cell containing hundreds of atoms. Therefore, Gutiérrez's model is widely used to perform theoretical calculations of the bulk and surface properties of γ-Al_2O_3 [13]. Recently, using a hierarchy of geometric analysis and ab initio calculations, Paglia et al. proposed a model to achieve the best fit to neutron scattering data, but the unit cell is very large, containing 160 atoms with tetragonal symmetry (space-group $I4_1/amd$) [7]. Another nonspinel model, provided by Krokidis [11], was obtained for dehydration of boehmite. This proposed structure benefits from ease of slab model establishment for use in surface calculations [14]. However, theoretical calculations [15,16] recently showed its infrared (IR) spectra have less agreement with the experimental [17] data compared with the spinel model. The results also indicate that the 160-atom super-cell model presents a rather structure-less density of state (DOS) [16]. Therefore, rational understanding of γ-Al_2O_3 in the atomic scale and a confident model depicting γ-Al_2O_3 are still lacking.

Raman spectra can provide much insight into the phonon vibration behaviors to help with structural characterization [18]. Despite the amount of researches devoted to γ-Al_2O_3, it is

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surprising that little work has been done using Raman scattering analysis and vibration mode assignment, partially resulting from that the fluorescent background covers the Raman spectra of γ-Al2O3 [19]. In the current study, the vibration properties of the spinel and nonspinel γ-Al_2O_3 models (40-atom unit cell) were examined and analyzed by using a first-principles method. The Raman spectra including both the frequency positions and intensities were calculated by using the density functional perturbation theory (DFPT) [20]. The Born effective charges, dielectric tensors, and IR spectra were also calculated and discussed briefly. The α-Al_2O_3 phase was considered to validate the theoretical method. Although the calculations did not involve the surface effects and the dispersion of the defects or impurities in γ-Al_2O_3, our results provide foundational data to enable the validation of the proposed γ-Al_2O_3 model, by comparing them with experimental results, and lead to further insight into the lattice dynamics of γ-Al_2O_3.

2. Computational details

The first principles density-functional theory (DFT) calculations were performed within the local density approximation (LDA). Optimized Fritz–Haber-Institute (FHI) pseudopotentials [21] with Troullier–Martins scheme [22] were used for all atoms. Al (3*s*, 3*p*) and O (2*s*, 2*p*) orbits were considered and expanded by plane waves with a cut-off energy of 55 Hartree. The $4\times4\times2$ and $4\times4\times4$ Monkhorst – Pack's meshes were employed to perform integrations in reciprocal space for spinel and nonspinel γ-Al_2O_3, and a $3\times3\times3$ mesh for α-Al_2O_3. The Hellmann – Feynman forces were limited to less than 10^{-6} Hartree/Bohr ($\approx 5\times10^{-5}$ eV/Å) to perform the structural optimizations. The phonon frequencies, dielectric tensors, and Bohn effective charges were calculated in the framework of the density-functional perturbation theory (DFPT) [23].

Considering the Al_2O_3 samples obtained were not usually bulk crystals, the vibration mode spectra of polycrystalline powders were simulated in this work. The IR absorptions are governed by [24]

$$S(m)=\sum_{\alpha}\left|\sum_{s\beta}Z_s^{*\alpha\beta}U_s^{\beta}(m)\right|^2 \tag{1}$$

where $Z_s^{*\alpha\beta}$ represents the Born effective charge tensor of the atom s in the directions α and β, and $U_s^{\beta}(m)$ is the eigendisplacement of the atom s in the direction β corresponding to the vibration mode m. The Raman spectra of powders can be

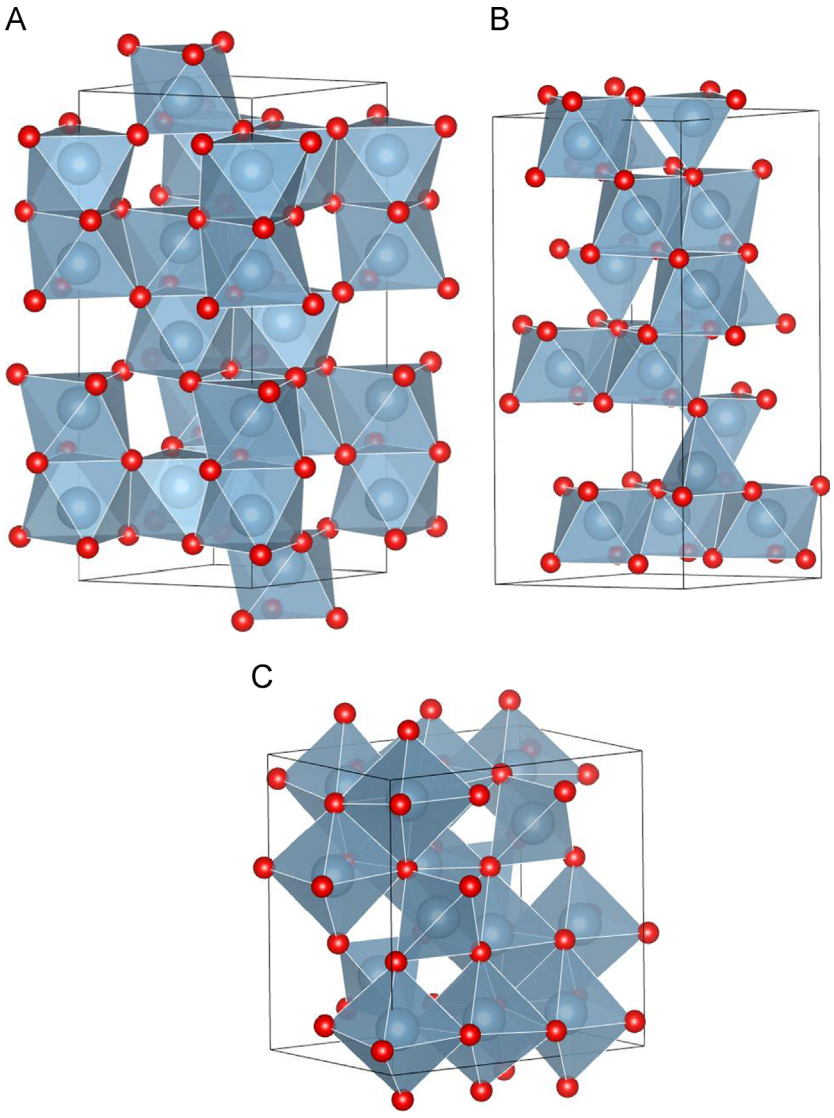

Fig. 1. (Color online) Schematic illustration of alumina (Al, gray; O, red). (A) α-Al2O3; (B) spinel γ-Al_2O_3; (C) nonspinelγ-Al_2O_3.