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Infrared radiative properties of alumina up to the melting point: A first-principles study

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ABSTRACT

The high thermal emission of alumina dominates the radiative heat transfer of rocket exhaust plume. Yet numerous experimental measurements on radiative properties of alumina at high temperatures vary considerably from each other and cannot provide physical insight into the underlying mechanism. In this work, the ab initio molecular dynamics (AIMD) method and ab initio parameterized Drude model are combined to predict the radiative properties of alumina for temperatures up to 2327 K (the melting point) in the spectral range 1–12 μm. Contributed by different microscopic processes, the optical absorption of alumina in the spectral range 1–4 and 4–12 μm is described by two distinct methods. In the spectral range 4–12 μm, the multi-phonon process mainly contributes to optical absorption and can be simulated by the AIMD method based on the linear response theory. While in the spectral range 1–4 μm, the optical absorption is mainly caused by intrinsic carriers and can be effectively described by the ab initio parameterized Drude model. The first-principles calculations can successfully predict the infrared radiative properties of alumina at high temperatures and well reproduce the literature experiments. Moreover, the theoretical simulations verify that alumina can retain its semiconducting character even in the liquid phase and there emerges sharp increase in the near-infrared optical absorption of alumina upon melting.

1. Introduction

With the character of optical transparency, relatively high thermal conductivity and excellently mechanical strength, alumina demonstrates promising candidate as optical elements and window material [1]. Importantly, as the major component of solid-propellant rocket exhaust plume, the optical constants of alumina play a key role in determining the thermal radiative properties of rocket exhaust plume, which has great impact in Astronautics fields [2]. Moreover, since over 90% of plume thermal emission occurs in the near infrared spectrum, it's essential to characterize the infrared optical constants of alumina at high temperatures [1].

Due to some uncertainties such as two-phase flow field and thermal non-equilibrium between gas and particles, however, it's very difficult to directly measure the radiative properties of alumina via plume experiments [1]. Numerous experiments have been performed to directly measure the thermal radiative properties of alumina. Oppenheim et al. [3] measured the optical absorption coefficient of sapphire in the spectral range 1–6 μm and for temperatures up to 1273 K. Gryvnak and Burch [2] heated the alumina samples for temperature up to 2293 K with a H_2/O_2 torch and found the discontinuous increase in

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absorption coefficient when alumina melts. Simmons [4] obtained the absorption index of alumina for temperatures ranging from 1800 to 3000 K. Sarou-Kanian et al. [5] measured the spectral emissivity of alumina droplet in the liquid-to-solid phase and then provided the absorption index under different gaseous environment in the spectral range 2–6 μm. Though those literature experiments all predict the same trend of temperature-varying infrared optical properties of alumina, yet those measured results vary considerably from each other. Such difference may be caused by the inevitable experimental errors at high temperatures and possible different alumina samples [6]. Moreover, limited by present technologies, it's difficult to accurately measure the radiative properties of alumina near or at the melting temperatures [2]. Based on this, direct experiments have limitations in accurately determining infrared optical properties of alumina at high temperatures up to the melting point.

Thus, one needs to firstly understand the microscopic mechanism beneath the infrared optical properties of alumina and then predict its thermal radiative properties at high temperatures. Reed [1] stated that intrinsic free carriers dominated the optical absorption in the near-infrared range (1–4 μm) and multi-phonon process played a key role in the spectral range 4–12 μm. On one hand, the contribution of intrinsic free carriers to light absorption can be effectively described by the Drude model which bases on the free electron gas theory [7]. To apply the Drude model, the key is to obtaining the important parameters of plasma frequency and excitation energy. Yet those two parameters couldn't be accurately acquired by empirical models [1] and should be determined by first-principles. The ab initio parameterized Drude model can provide one route to accurately predict free carriers' contribution to infrared optical absorption. On the other hand, the multi-phonon process can be simulated by the ab initio molecular dynamics (AIMD) method. Based on linear response theory [8], the AIMD approach can calculate the time-varying polarization induced by incident photons during dynamics simulations and then obtains the infrared optical absorption via Fourier transforming its autocorrelation function [9]. Debernardi et al. [10] implemented the AIMD method to successfully reproduce the infrared dielectric spectra of amorphous silicon at normal conditions. Yang et al. [11] predicted the infrared radiative properties of MgO crystal at 1950 K by AIMD and the calculated results demonstrated good agreement with literature infrared-reflectivity experiments.

In this work, the AIMD method and ab initio parameterized Drude model are combined to predict the high temperature optical absorption of alpha phase alumina (α-Al_2O_3) in the spectral range 1–12 μm for temperatures up to the melting point (2327 K). The choice of alpha phase is based on the experimental observation that alumina collected from sea-level rocket firings are predominantly alpha [1]. In the ab initio parameterized Drude model, the plasma frequencies and thermal excitation energy of alumina were determined by first-principles and then applied to predict the intrinsic free carrier's contribution to the near-infrared (1–4 μm) optical absorption. To implement the AIMD method, the time-varying polarization induced by incident electromagnetic wave were collected to predict multi-phonons' contribution to light absorption in the spectral range 4–12 μm. To validate first-principles method, the theoretically predicted radiative properties of alumina were compared with literature experiments.

2. Computational methods

The infrared optical absorption of alumina mainly arises from two contributions: intrinsic free carriers and multi-phonon process [1,12]. In the spectral range 4–12 μm, multi-phonon process tends to couple with incident photons and results in photon's absorption, which can be simulated by the AIMD method based on linear response theory. While in the spectral range 1–4 μm, the incident photons are absorbed by intrinsic free carriers and can be described by ab initio parameterized Drude model.

2.1. Multi-phonon process by AIMD

In the spectral range 4–12 μm, the incident photon tends to couple with lattice vibration and thus induces dielectric polarization. Based on linear response theory, it's feasible to obtain the imaginary part of infrared dielectric function by Fourier transforming the autocorrelation function of the induced polarization in the classic limit [9]

$$\varepsilon_2(\omega)=\frac{2\pi\omega}{3VK_BT}\int_{-\infty}^{\infty}dte^{-i\omega t}\langle M(t)\times M(0)\rangle \tag{1}$$

where V is the volume, T is the temperature and M is the total dipole moment, respectively. The real part ε_1 can be obtained from ε_2 using Kramers–Kronig dispersion relations by [13].

$$\varepsilon_1(\omega)=\frac{2}{\pi}\int_0^{\infty}d\omega'\frac{\omega'\varepsilon_2(\omega')}{\omega'^2-\omega^2}+1 \tag{2}$$

With the calculated dielectric functions, it's capable of obtaining the radiative properties, such as absorption index k and absorption coefficient α, of solids by [14]

$$k=\sqrt{\left(\sqrt{\varepsilon_1{}^2+\varepsilon_2{}^2}-\varepsilon_1\right)/2} \tag{3}$$

$$\alpha=4\pi k/\lambda \tag{4}$$

To predict the infrared optical properties of α-Al_2O_3 crystal by AIMD, the Car-Parrinello molecular dynamics (CPMD) software package [15] was applied. The α-Al_2O_3 crystal was modeled by a $2\times2\times1$ conventional hexagonal unit cell containing 60 atoms with periodic boundary conditions. The conventional hexagonal structure of α-Al_2O_3 crystal consists of hexagonal close packing of aluminum cations, with oxygen anions occupying 2/3 of the octahedral sites, as shown in Fig. 1. The relaxed room temperature lattice parameters of hexagonal unit cell $a=b=4.759$ Å and $c=12.99$ Å, in good agreement with experiment (within 1%) [16]. Each hexagonal unit cell containing 18 O atoms and 12 Al atoms and the mass of O and Al atom is 2.657×10^{-26} kg and 4.482×10^{-26} kg,