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The role of low-lying optical phonons in lattice thermal conductance of rare-earth pyrochlores: A first-principle study

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Abstract—Rare-earth pyrochlores, commonly exhibiting remarkably low lattice thermal conductivities, are considered as promising topcoat materials for thermal barrier coatings. However the structural origin underlying their low thermal conductivities remains unclear. In the present study, we investigated the phonon properties of two groups of RE pyrochlores, $Ln_2Zr_2O_7$ (Ln = La, Nd, Sm, Gd) and $Gd_2T_2O_7$ (T = Zr, Hf, Sn, Pb) employing density functional theory and quasi harmonic approximation. Through the relaxation time approximation (RTA) with Debye model, the thermal conductivities of those RE pyrochlores were predicted, showing good agreement with experimental measurements. The low thermal conductivities of RE pyrochlores were shown to largely come from the interference between the low-lying optical branches and acoustic branches. The structural origin underlying the low-lying optical branches was then clarified and the competition between scattering processes in transverse and longitude acoustic branches was discussed.

Keywords: Rare-earth; Pyrochlores; Phonon dispersion; Thermal conductivity; Density functional theory

1. Introduction

Thermal barrier coating (TBC) [1–3] is an essential constituent in gas turbine engines. It is applied to surfaces of superalloy components in the engine, shielding them from the hot gas to allow an operating temperature much higher than their melting temperatures. The thermal insulation from TBC is determined by the outmost ceramic topcoat [1–3]. Currently the common material used for the top coat is 7 wt.% yttria stabilized zirconia (7YSZ) because of its relatively low thermal conductivity (2.0–3.0 $W\,m^{-1}\,K^{-1}$) [4,5], good toughness [6,7] and thermochemical compatibility with the underlying TGO [4,8]. However, 7YSZ suffers from accelerated sintering kinetics [9,10] and destabilization of the desirable metastable t' phase at elevated temperatures [11], and susceptibility to calcium-magnesium aluminosilicate (CMAS) penetration [12,13], which significantly degrades its insulating efficiency, strain tolerance and intrinsic toughness, being greatly detrimental to its performance and durability. These limitations necessitate innovation to develop alternative coating materials.

Rare-earth (RE) pyrochlores recently emerge as potential candidate materials for the next-generation top coat given their low intrinsic thermal conductivities (i.e., 1–2 $Wm^{-1}\,K^{-1}$) [14–19]. The RE pyrochlore also exhibits high temperature stability [4], similar thermal expansion coefficient as its beneath substrate [20,21], and can react with the CMAS melt to seal the surface against further infiltration [22]. In addition, RE pyrochlores can well preserve the pore content and architecture owing to their sluggish sintering kinetics [23]. The thermal properties of various RE pyrochlores were well characterized in many experimental studies [14–19]. It was postulated in some studies [24,25] that the abnormally low thermal conductivities of these pyrochlores may be attributed to the abundance of intrinsic oxygen vacancies and low-lying optical phonons due to RE element rattling. However the exact structural origin and phonon characteristics, particularly at the atomic level, remain largely unknown. Recently a few studies attempted to model and understand the thermal transport in pyrochlores. Liu et al. [26] and Feng et al. [27,28] investigated the thermal conductivities of $Ln_2Zr_2O_7$, $Ln_2Sn_2O_7$ (Ln = La, Nd, Sm, Gd) and $La_2T_2O_7$ (T = Ge, Ti, Sn Zr, Hf) systems using density functional theory (DFT). In their studies, several physical properties, including elastic constants, lattice spacing and density, were computed from first-principles calculations, and subsequently combined with the simple formulas suggested by Clarke [29], Slack [30] and Cahill et al. [31] to estimate the minimum thermal conductivity. The estimated values yield good ball-park agreements with experimental measurements. Nonetheless, those studies fail to distinguish different RE pyrochlores in terms of thermal conductivity and thus do not reveal the mechanistic origin of lattice heat conduction.

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In this paper, we employ the approach of relaxation-time approximation (RTA) together with the Debye model [32] to study the high-temperature thermal conductivities of several RE pyrochlores. Different from the simple models invoked in those previous modeling studies of pyrochlore oxides [26–28,33], this approach allows direct considerations of phonon scattering processes and anharmonic relaxation times, and is evidenced by a few studies to an accurate method to predict the thermal conductivity for a wide variety of solid-state materials [32,34–36]. We focused on two sets of RE pyrochlores, $Ln_2Zr_2O_7$ (Ln = La, Nd, Sm, Gd) and $Gd_2T_2O_7$ (T = Zr, Hf, Sn, Pb). Through first-principle DFT calculations, the ground-state crystal structures and corresponding elastic constants of those pyrochlores were obtained. Meanwhile the harmonic and anharmonic vibrational properties, including phonon density of states (DOS), phonon dispersion and Grüneisen parameters, are thoroughly investigated by DFT phonon calculations within the quasi harmonic approximation (QHA) [37]. Using the information obtained from DFT, the thermal conductivities of the RE pyrochlores considered were evaluated within RTA along with the Debye approximation, and compared with the ones estimated from Clarke's and Cahill's models. The predictions from RTA along with the Debye approximation were demonstrated to effectively differentiate between different RE pyrochlores and yield much more consistent agreement with experimental data. Finally, the atomic vibration patterns contributing to the low-lying optical modes that scatter the acoustic modes were investigated to clarify the mechanistic origin of the low thermal conductivity of RE pyrochlores.

2. Methodology

2.1. Density functional theory and phonon calculations

DFT calculations were performed using the Vienna ab initio simulation package (VASP) [39,40] with Perdew–Burke–Ernzerhof GGA approach [41] based on plane-wave basis sets. Valence configurations of the elements used in this study are as follows: La-$5s^2$ $5p^6$ $5d^1$ $6s^2$, Nd-$5s^2$ $5p^6$ $4f^4$ $6s^2$ ($4f^3$ frozen in the core), Sm-$5s^2$ $5p^6$ $4f^4$ $6s^2$ ($4f^5$ frozen in the core), Gd-$4f^7$ $5s^2$ $5p^6$ $5d^1$ $6s^2$, Zr-$4s^2$ $4p^6$ $5d^2$ $5s^2$, Hf-$5s^2$ $5p^6$ $5d^2$ $6s^2$, Sn-$5s^2$ $5p^2$, Pb-$6s^2$ $6p^2$, and O-$2s^2$ $2p^4$. The values of the Hubbard energy U [42,43] for Gd $4f$ valence electrons were set following Ref. [27]. The electron–core interaction was described by the Blöchl's projector augmented wave method (PAW) within the frozen-core approximation [44]. For the structural optimization and computation of elastic constants, a conventional pyrochlore cubic unit cell containing 88 atoms was constructed, and a $2 \times 2 \times 2$ Monkhorst–Pack (MP) k–mesh for Brillouin-zone integrations and a cutoff energy of 450 eV for the plane-wave basis set were used in the DFT calculations with convergence criteria for energy and force on each ion set as 10^{-9} eV and 10^{-6} eV Å^{-1}, respectively. The real-space force constants were obtained with the density-functional perturbation theory (DFPT) [45] using $2 \times 2 \times 2$ supercells (176 atoms) constructed from the pyrochlore primitive cell (22 atoms). The phonon properties were evaluated using PHONOPY [46] on $23 \times 23 \times 23$ q grid for all the RE pyrochlore systems. In the phonon calculations within QHA, the cell volume was varied by ±0.75% with respect to the equilibrium volume.

2.2. Models for lattice thermal conductivity

2.2.1. Minimum thermal conductivity based on Clarke's and Cahill's model

The concept of minimum thermal conductivity, $\kappa_{\min}$, was developed by Slack [47], stating that for a material there is a lower limit for the intrinsic thermal conductivity. It is of great technological importance to the TBC material research and has been widely used to predict the plateau thermal conductivities of poly-ion ceramic oxides at high temperature. Clarke et al. [29] proposed an expression of $\kappa_{\min}$, assuming that the phonon mean free path is identical to the inter-atomic spacing and the specific heat approaches $3k_B$ (k_B being the Boltzmann's constant) per atom above the Debye temperature:

$$\kappa_{\min} = 0.87 k_B \overline{M}^{-2/3} E^{1/2} \rho^{1/6}, \tag{1}$$

where $\overline{M}$ is the average mass of per atom, E is Young's modulus and ρ is the density. In the work by Cahill et al. [31], in accordance with Einstein's notion of lattice vibration, they assume that individual oscillators vibrate independently of one another and the phonon scattering time is one half the period of vibration. Under those assumptions, $\kappa_{\min}$ at high temperature limit can be expressed as

$$\kappa_{\min} = \frac{k_B}{2.48} p^{2/3} (v_l + 2v_t) \tag{2}$$

where p is the density of number of atoms per volume, and v_l and v_t are the average longitudinal and transverse sound velocities respectively. As apparently illustrated in Eqs. (1) and (2), both Clarke's and Cahill's models predict that lower $\kappa_{\min}$ requires smaller modulus (or sound velocity) and larger size of the unit cell.

2.2.2. Relaxation-time approximation (RTA) with the Debye model

RTA is commonly invoked in the treatment of Boltzmann transport equation (BTE) [32]. Given that it is usually difficult to consider various phonon scattering relaxation times for the full phonon dispersions, RTA is often augmented by the Debye model to simplify the phonon branches.

Phonon dispersion curves normally consist of low-frequency acoustic and high-frequency optical branches [32]. Generally, only acoustic phonons are effective for heat conduction, whereas optical phonons contribute very little to heat transport [32]. Consequently the total thermal conductivity, κ can be simplified as just a sum of contributions from two transverse (κ_{TA} and $\kappa_{TA'}$) and one longitudinal (κ_{LA}) acoustic phonon branches as discussed in Refs [34–36]:

$$\kappa = \kappa_{TA} + \kappa_{TA'} + \kappa_{LA}. \tag{3}$$

These partial conductivities κ_i (i = TA, TA′ or LA stands for two transverse and one longitudinal acoustic phonon branches, respectively) are given by RTA with Debye approximation [32] as:

$$\kappa_i = \frac{k_B}{2\pi^2 v_i} \left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\tilde{\Theta}_i/T} \tau_q \frac{x^4 e^x}{(e^x - 1)^2} dx \tag{4}$$

where $\hbar$ is the reduced Plank constant, T is temperature, v_i is corresponding acoustic phonon velocity, and $x = \hbar w / k_B T$ is a dimensionless quantity with ω being the phonon frequency. $\tilde{\Theta}_i$ is the reduced Debye temperature determined from the conventional Debye temperature, Θ_i, given in