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Predictions of thermal expansion coefficients of rare-earth zirconate pyrochlores: A quasi-harmonic approximation based on stable phonon modes

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Rare-earth (RE) pyrochlores are considered as promising candidate materials for the thermal barrier coating. In this study, we performed first-principles calculations, augmented by quasi-harmonic phonon calculations, to investigate the thermal expansion behaviors of several RE2Zr2O7 (RE = La, Nd, Sm, Gd) pyrochlores. Our findings show that RE2Zr2O7 pyrochlores exhibit low-lying optical phonon frequencies that correspond to RE-cation rattling vibrational modes. These frequencies become imaginary upon volume expansion, preventing correct determination of the free energy versus volume relation and thereby quantification of thermal expansion using QH phonon calculations. To address this challenge, we proposed a QH approximation approach based on stable phonon modes where the RE-cation rattling modes were systematically eliminated. This approach is shown to provide accurate predictions of the coefficients of thermal expansion (CTEs) of RE2Zr2O7 pyrochlores, in good agreement with experimental measurements and data from first-principles molecular dynamics simulations. In addition, we showed that the QH Debye model considerably overestimates the magnitudes and wrongly predicts the trend for the CTEs of RE2Zr2O7 pyrochlores. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4954280]

I. INTRODUCTION

The efficient use of energy in turbine engines demands high combustion temperature, often much beyond the melting temperature of the superalloy used in the turbine blades.1 This high-temperature operation is enabled by the application of a multilayer coating, i.e., thermal barrier coating (TBC)2–4 on the turbine blades that shields the underlying superalloy from the hot combustion gas. The capacity of TBC in shielding heat is attributed to its outmost layer, i.e., the top coat, being a ceramic oxide of low thermal conductivity. Consequently the development of new top coat materials of lower thermal conductivities has always been central in the continuous pursuit of higher energy efficiency for turbine engines. Besides the apparent need for low thermal conductivity, one must also consider the strain compliance of the ceramic top coat with respect to the underlying metallic bond coat. Close coefficients of thermal expansion (CTEs) between the top coat and bond coat are thus required to minimize the mismatch strain during thermal cycling in order to ensure mechanical stability and prevent exacerbated coating failure.5,6

Currently, the material commonly used for the top coat is ~7 wt. % Y2O3-stabilized ZrO2 (7YSZ) due to their lower inherent thermal conductivities,7,8 high CTEs9 that match the CTE of the metallic bond coat9 well to avoid top coat spallation.9 Nonetheless the performance of 7YSZ is discounted by accelerated sintering kinetics10,11 and phase destabilization12,13 at elevated temperatures, and susceptibility to calcium-magnesium aluminosilicate (CMAS) penetration.14,15 and therefore alternative top coat materials are sought. In the search of alternatives for 7YSZ, rare-earth (RE) pyrochlores recently emerge as potential candidate materials, given their low intrinsic thermal conductivities (i.e., 1–2 W m⁻¹ K⁻¹),16–18 and their sluggish sintering kinetics19 as well as their ability to moderate CMAS infiltration.20 To assess the strain compliance of the RE pyrochlores, a series of experiments were carried out to measure their thermal expansions.21–25 In parallel to these experimental measurements, lately several theoretical studies25–28 were also performed, trying to predict the CTEs using computational methods to aid the experiments. For instance, Qun-bo et al.28 studied the CTEs of several RE2Zr2O7 systems using classical molecular dynamics (MD) simulations with a Buckingham-type pair-wise potential. Yet apparently, it is unlikely for such a simple potential that only accounts for the short-range interactions to be sufficient to accurately describe the interatomic interactions within the RE2Zr2O7 system. In the studies by Feng et al.,27,28 a quasi-harmonic (QH) Debye model was used to examine heat capacities and CTEs of a few RE2Zr2O7 and RE2Sn2O7 systems. However in those studies, the phonon dispersion was simply assumed to be linear with the wave vector,27,28 which may be enough to approximate some simple systems, but very much questionable for RE pyrochlores with complex phonon dispersions. As such, further work is necessary to explore the full phonon dispersions and improve our theoretical capacity to provide more accurate prediction of CTEs of RE pyrochlores in order to facilitate the material exploration.

In the present study, we utilize the quasi-harmonic (QH) phonon calculations, which have been proven to be a powerful tool for investigating thermal properties of many materials,30,31 to investigate thermal expansion of RE
pyrochlores. The RE$_2$Zr$_2$O$_7$ (RE = La, Nd, Sm, Gd) pyrochlore group are chosen as the model systems for our study. The phonon dispersion spectra as the pyrochlore volume varies were computed employing the density-functional perturbation theory (DFPT).\textsuperscript{32} We found RE pyrochlores exhibit low-lying optical branches that correspond to relaxation rattling vibrational modes. Lattice expansion was found to induce softening of these rattling modes, resulting in unphysical irregularities in the free energy versus volume relation determined from the QH phonon calculations. To address this challenge, we proposed a QH approximation approach based on stable phonon modes where the relaxation rattling modes were eliminated. This approach was shown to correctly produce the free energy versus volume relation and accurately predict the CTEs of RE pyrochlores, verified by comparison with experimental measurements. Meanwhile, the QH Debye model and the first-principles molecular dynamics (FPMD) simulations were also employed to predict the thermal expansion behaviors of the RE pyrochlores. The predictions from FPMD simulations also show good agreement with experimental data, albeit being slightly higher than the ones predicted from our proposed QH approximation approach. On the other hand, the QH Debye model not only considerably overestimates the CTEs of RE pyrochlores, but also yields a different trend as the one observed in experiments.

II. METHODOLOGY

A. Free energy minimization and quasi-harmonic (QH) approximation

For an ensemble of a volume $V$, held at a fixed temperature $T$ and without any applied pressure, the equilibrium volume can be obtained by minimizing the total free energy

$$F_{\text{total}}(V, T) = F_e(V, T) + F_{\text{vib}}(V, T),$$

where $F_e(V, T)$ is the free energy of electronic structure and $F_{\text{vib}}(V, T)$ is the vibrational Helmholtz free energy. With the electronic entropy contribution being negligible for insulators,\textsuperscript{32} $F_e(V, T) \approx F_e(V, 0)$, which can be readily obtained from first principles calculations. $F_{\text{vib}}(V, T)$, on the other hand, can be approximated by two methods, described as follows. One method is to perform QH phonon calculations,\textsuperscript{32,33} with $F_{\text{vib}}(V, T)$ expressed as

$$F_{\text{vib}}(V, T) = \frac{9}{8} k_B \Theta_D + k_B T \left\{ 3 \ln \left[ 1 - \exp \left( -\Theta_D / T \right) \right] - D \left( \frac{\Theta_D}{T} \right) \right\},$$

where $D(\Theta_D / T)$ is the Debye integral given by

$$D(y) = 3 / y^3 \int_0^y x^3 / (e^x - 1) dx,$

with $M$ being the mass per cell, $B$ being the adiabatic bulk modulus, $\nu$ being the Poisson ratio, and $f(\nu)$ given by

$$f(\nu) = \left\{ 3 \left( \frac{2 + 3\nu + \nu^2}{1 - 2\nu} \right)^{3/2} + \left( \frac{11 + 3\nu}{3 - 4\nu} \right)^{3/2} \right\}^{-1}. $$

To compute $F_{\text{vib}}(V, T)$ (using QH phonon calculations or QH Debye model), first-principles density functional theory (DFT) calculations using the Vienna \textit{ab initio} simulation package (VASP)\textsuperscript{35,36} with Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA)\textsuperscript{37} approach based on plane-wave basis sets were performed on RE$_2$Zr$_2$O$_7$ (RE = La, Nd, Sm, Gd) pyrochlore group. The $f$-electrons for RE elements Nd, Sm, and Gd are not treated explicitly, but are kept frozen in the cores. The electron–core interaction was described by the Blöchl’s projector augmented wave method (PAW) within the frozen-core approximation.\textsuperscript{38} The pyrochlore crystal structure is of space group $Fm\bar{3}m$, consisting of $\text{RE}^{3+}$ cations at $16d$ ($1/2$, $1/2$, $1/2$), $\text{Zr}^{4+}$ cations at $16c$ (0, 0, 0), $\text{O}^{2-}$ anions at $48f$ ($x$, $1/8$, $1/8$), and $\text{O}^{2-}$ anions at $8b$ (3/8, 3/8, 3/8) in the primitive cell.\textsuperscript{39} A pyrochlore cubic conventional cell of 88 atoms (see illustration later in Fig. 3(c)) was used in DFT calculations. A 2 x 2 x 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, which gives an energy convergence of less than $10^{-3}$ eV/atom. The convergence criteria for total energy and force on each ion were set as $10^{-9}$ eV and $10^{-6}$ eV Å$^{-1}$, respectively. The optimized lattice constants were obtained to be 10.58 Å, 10.66, 10.74, and 10.83 Å for Gd$_2$Zr$_2$O$_7$, Sm$_2$Zr$_2$O$_7$, Nd$_2$Zr$_2$O$_7$, and La$_2$Zr$_2$O$_7$, respectively, all within <1% deviation from experimental values.\textsuperscript{40} For the phonon calculations, the real-space force constants were obtained with the DFPT\textsuperscript{32} calculations using 2 x 2 x 2 supercells (176 atoms) constructed from the pyrochlore primitive cell (22 atoms) with a 1 x 1 x 1 MP $k$-mesh. The phonon properties were calculated using PHONOPY\textsuperscript{41} on $23 \times 23 \times 23$ q grid for all RE pyrochlores considered. In the QH phonon calculations, the crystal lattice parameter was varied by $\pm 5\%$ with respect to the equilibrium lattice parameter. With $F_{\text{vib}}(V, T)$ and subsequently $F_{\text{total}}(V, T)$ at different volumes determined, free energy minimization can be performed to obtain the equilibrium volume $V(T)$ of the material system at
temperature \( T \). The strain variation of \( \pm 5\% \) is used to ensure sufficient precision in the fitting of \( F_{\text{total}}(V, T) \) to determine \( V(T) \).

### B. First-principles molecular dynamics simulations

Besides the afore-mentioned methods based on quasi-harmonic approximation, the equilibrium volume of a RE pyrochlore can also be directly obtained via first-principles molecular dynamics (FPMD) simulations. A pyrochlore conventional cell of 88 atoms was constructed for the FPMD simulations. The canonical ensemble (NVT) with Langevin thermostat\(^{42-44} \) was employed to achieve the desired temperature in simulations. A \( 2 \times 2 \times 2 \) \( k \)-mesh grid and a time step of 1 fs were used. Specifically, FPMD simulations were performed at \( T = 300 \), 600, 900, 1200, and 1500 K, on simulation cells of different cell volumes that correspond to isotropic lattice strains ranging from \( -5\% \) to \( +3\% \). In each simulation, the system was equilibrated for 0.4–1.6 ps, and the pressure was monitored.\(^{45} \) In general, more simulation time is required for the system to attain equilibrium as the temperature increases. From the above simulations, the evolution of average pressure \( (p) \) versus the cell volumes \( (V) \) at each temperature was obtained. By fitting the \( (p, V) \) data with respect to the Murnaghan equation of state (EOS),\(^{46} \) the equilibrium cell volume \( V(T) \) corresponding to \( p = 0 \) at temperature \( T \) can then be determined.

### C. Quantification of thermal expansion

With the equilibrium volumes at different temperatures known, the volumetric CTE \( \alpha \) can be determined as

\[
\alpha = \frac{1}{V(T)} \frac{dV(T)}{dT}.
\]

Besides the volumetric CTE, another measure often conveniently adopted in experiments to quantify thermal expansion is the expansion ratio,\(^{21-25} \) denoted as \( R_{\text{ex}} \) and defined as

\[
R_{\text{ex}} = \frac{V(V)}{V_{\text{RT}}}^{1/3} - \frac{V(T)}{V_{\text{RT}}}^{1/3},
\]

with \( V_{\text{RT}} \) being the value of \( V(T) \) at room temperature, 298 K. Below when we compare our model predictions with experimental measurements, this measure of expansion ratio is adopted to represent CTE.

### III. RESULTS AND DISCUSSION

#### A. Predictions of thermal expansion from QH phonon calculations

1. **Phonon dispersion spectrums and imaginary frequencies**

To determine \( F_{\text{vib}} \) and \( F_{\text{total}} \) (cf. Eqs. (1) and (2)) from the QH phonon calculations, we examine the phonon properties of RE pyrochlores at different volumes. To avoid redundancy, below in our phonon and free energy analyses, we use the Gd\(_2\)Zr\(_2\)O\(_7\) system as the representation (while the results of other RE\(_2\)Zr\(_2\)O\(_7\) systems are presented in the supplementary material\(^{47} \)). The phonon dispersion spectra along high-symmetry directions in their Brillouin zones (BZ) and partial density of states (PDOS) of the Gd\(_2\)Zr\(_2\)O\(_7\) system of different cell sizes are shown in Fig. 1. Here, the difference in the cell size is quantitatively represented by an isotropic lattice strain \( \varepsilon_L \), defined with respect to the equilibrium lattice parameter at 0 K.

As seen in Fig. 1, we see all the phonon branches descend with the increasing in tensile strain, which is expected given that lattice expansion results in weaker interatomic bonding. Meanwhile, we note that certain frequencies become imaginary under tensile straining (i.e., \( \varepsilon_L > 0 \)). The number of imaginary branches increases as \( \varepsilon_L \) increases and settles at eight under large \( \varepsilon_L \) values (see supplementary material\(^{47} \)).

2. **Rattling modes and strain-induced softening**

Those imaginary branches bring immediate challenge for QH phonon calculations. As seen in Eq. (2), the imaginary frequencies cannot be accounted for in the evaluation of \( F_{\text{vib}}(V, T) \). Consequently, as the volume (and simultaneously the strain \( \varepsilon_L \)) varies, the set of phonon branches included in the evaluation of \( F_{\text{vib}}(V, T) \) is not consistent, as more phonon branches are omitted\(^{48} \) as \( \varepsilon_L \) increases (in the tensile regime) where we can see that more phonon branches are omitted as \( \varepsilon_L \) increases (in the tensile regime). This inconsistency leads to irregularities in the free energy evolution as illustrated in Fig. 2(a) (i.e., the \( F_{\text{total}} \) versus \( V \) curves in open symbols), preventing accurate determination of the equilibrium volumes at different temperatures and subsequently the prediction of CTE.\(^{49} \)

The above challenge necessitates a more refined approach towards the treatment of different phonon branches. In this regard, it is important to first understand the mechanistic origin underlying the imaginary frequencies. From the PDOS plot in Fig. 1, it is clear that the imaginary branches come from the localized low-lying rattling phonon modes attributed to vibration of the RE cation, which are softened under tensile straining. This softening suggests that the RE cation be not stable at its original location upon tensile straining. In this regard, we examine vibrational motions of atoms associated with these rattling phonon modes at high-symmetry points, \( \Gamma \) and \( L \), as representatives. In the example case of Gd\(_2\)Zr\(_2\)O\(_7\) (see Fig. 3(c) for the atomic configuration), we found that Gd atom exhibits dominant vibrational magnitude in the rattling phonon modes, while O’ (8b) atom shows near zero vibration, and Zr and O (48f) atoms show very small amplitudes of vibration, mostly being lesser than 15% of that of the Gd atom. The above observation is consistent with the PDOS shown in Fig. 1. Hence, we further examined the corresponding vibrational patterns of Gd atoms in details. Fig. 3 shows two vibration patterns corresponding to the lowest bands at high-symmetry points \( \Gamma \) and \( L \) as representatives.\(^{50} \) The directions and relative magnitudes of vibrational motions of Gd at \( \Gamma \) and \( L \) are schematically illustrated in Figs. 3(a) and 3(b) respectively. We can see that the motions are highly localized at RE atoms.

A close examination reveals that all these vibrational motions lay within the plane perpendicular to the Gd-O’
bond. This can be attributed to the fact that the Gd-O’ bond is
the strongest one among all bonds Gd forms with its neigh-
bors. As a consequence, the resistance is less when the motion
direction is perpendicular to the Gd-O’ bond. Overall, we can
treat these vibrational patterns as Gd-tetrahedral rotations
around the O’ atom. In particular, the vibrational positions
corresponding to $U$ and $L$ can be categorized as $96g$
(in-plane
displacement towards the adjacent O atom) and $96h$
in-plane
displacement toward the nearest Zr atom) sites in space group
$Fm\bar{3}m$, respectively (see Fig. 3(c)).

Accompanying the vibration, atoms deviate from their
original lattice positions. Consequently, the lattice potential
is necessarily modified. In Fig. 4, we plotted the change in
the lattice potential, i.e., $\Delta E$, with respect to the phonon nor-
mal mode amplitude at different $\varepsilon_L$ values for the two vibra-
tion patterns shown in Fig. 3. The normal mode amplitude

![Phonon dispersions and partial density of states (PDOS) for Gd$_2$Zr$_2$O$_7$ pyrochlores under strain values of $\varepsilon_L$ being (a) $-1\%$, (b) 0\%, (c) $+1\%$, and (d) $+2\%$ (positive and negative signs respectively indicate tension and compression), respectively. The eight rattling phonon branches that can become imaginary (i.e., negative frequencies) under tensile straining are indicated by red dashed line. For the PDOS, the blue solid, green dashed, yellow dashed-dotted, and red dotted curves denote those corresponding to Gd, Zr, O, and O’ atoms (see Fig. 3(c)), respectively.](image1)

![Calculated free energy, (a) $F_{\text{vib}}$ with full phonon branches and (b) $F_{\text{SM}}^\text{vib}$ with stable modes only as a function of primitive cell volume of Gd$_2$Zr$_2$O$_7$ (from QH phonon calculations, see Eqs. (2) and (8)), for $T=0$ K, 400 K, 800 K, 1200 K, and 1600 K.](image2)
that the degree of anharmonicity elevates as
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the overall expansion of the host lattice.\textsuperscript{54–56} It is however important to note that in the QHSM approach the free energy itself, i.e., $F_{\text{vib}}(V, T)$, is not predicted (which is certainly not possible with the imaginary frequencies). The above also hints a criterion regarding soft mode omission when examining thermal expansion, i.e., the soft modes to be omitted can only be associated with localized vibrations.

**B. Predictions of thermal expansion from the QH Debye model and FPMD simulations**

Besides QH phonon calculations, the volumetric CTE $\alpha$ and/or expansion ratio $R_{ex}$ of RE$_2$Zr$_2$O$_7$ pyrochlores are also calculated employing the QH Debye model\textsuperscript{34} and FPMD simulations, with the results also presented in Fig. 6. We see the $R_{ex}$ data from FPMD simulations generally agree well with experimental data, but are slightly higher than the ones predicted by the QHSM approach. This small discrepancy between FPMD and the QHSM approach predictions is expected as FPMD automatically includes contributions from the rattling modes which are omitted in the QHSM approach.

On the other hand, the QH Debye model significantly overestimates the thermal expansion. For instance, the $R_{ex}$ data predicted by the QH Debye model are 15%–35% higher than the experimental data for the RE$_2$Zr$_2$O$_7$ pyrochlores considered. In addition, the QH Debye model predicts...
Nd$_2$Zr$_2$O$_7$ \(>\) Gd$_2$Zr$_2$O$_7$ \(>\) Sm$_2$Zr$_2$O$_7$ \(>\) Nd$_2$Zr$_2$O$_7$ \(>\) La$_2$Zr$_2$O$_7$; different from the experimental observation of Gd$_2$Zr$_2$O$_7$ \(>\) Sm$_2$Zr$_2$O$_7$ \(>\) Nd$_2$Zr$_2$O$_7$ \(>\) La$_2$Zr$_2$O$_7$:

The poor predictability of the QH Debye model indicates the QH Debye model fails to account for certain fundamental lattice vibration characteristics of RE$_2$Zr$_2$O$_7$ pyrochlores. This is not surprising, given that $\Theta_D$ and $F_{vib}(V,T)$ are prescribed by average materials properties, i.e., $B$, $M$ and $\nu$ (see Eqs. (3)–(5)), and thus do not capture features of local lattice vibration.57

IV. SUMMARY AND DISCUSSION

In summary, we studied the thermal expansion behaviors of the RE$_2$Zr$_2$O$_7$ (RE = La, Nd, Sm, Gd) pyrochlores using first-principles calculations. The corresponding phonon dispersion spectra as the lattice strain varies were computed, and QH phonon calculations were performed to evaluate the free energy of the system. Imaginary frequencies were observed when the system is subject to tensile straining. These frequencies were shown to come from the low-lying optical branches that correspond to RE-cation rattling vibrational modes, and induce unphysical irregularities in the free energy evaluation using the QH phonon calculations. To mitigate the difficulties associated with the imaginary frequencies, we proposed a QH approximation approach based on stable phonon modes. This approach enables accurate predictions of the CTEs of RE$_2$Zr$_2$O$_7$ pyrochlores, evidenced by good agreement with experimental measurements and data from FPMD simulations. Meanwhile, we found that the QH Debye model not only considerably overestimates the CTEs of RE$_2$Zr$_2$O$_7$ pyrochlores, but also fails to predict the relative trend among different RE$_2$Zr$_2$O$_7$ pyrochlores. Albeit the success of the proposed approach in predicting the CTE, it is important to discuss possible consequences due to the omission of RE-cation rattling modes in the approach. One main consequence could be the underestimation of the CTE, which is hinted by the discrepancy, though very small, between predictions from the QHSM approach and data from FPMD simulations (cf. Fig. 6). In order to remedy the consequence, it is necessary to account for the contribution of the imaginary modes to the free energy. One possible route can be the independent anharmonic oscillator (IAO) approximation58–61 where the double-well anharmonic potential is fitted to a functional form (e.g., parabola-plus-Gaussian or 2–4 polynomial). Nonetheless, although the IAO method has been shown to be applicable in certain systems.
with few soft modes and simple crystal structures, it is rather challenging to directly apply it in complex systems like RE₂Zr₂O₇ pyrochlores, and thus necessitates further studies which will be pursued in our forthcoming research.⁶²

In addition, there are two methods based on FPMD, i.e., the temperature-dependent effective potential approach (TPEP),⁶³ and the velocity-autocorrelation functions (VAF),⁶⁴ which were shown to provide avenues in mitigating the soft-mode issues. However, both methods suffer certain limitations when applying to complex oxides, such as pyrochlore oxides, elaborated in details as follows. In the TPEP approach, in order to minimize the computational cost, the variables in interatomic force constants (IFC) matrix were reduced using symmetry relations. To the best of our knowledge, only single-element systems with small number (10–40) of independent variables have been tested using this method in the literature. For complex oxides such as pyrochlore, the number of independent variables of harmonic IFC matrix is already rather large, e.g., ~400 for a $2 \times 2 \times 2$ pyrochlore supercell, not to mention the third order IFC matrix who has thousands of independent variables. Such a large number of variables in the IFC matrix render it is very challenging (or virtually impossible) to achieve a sound numerical fitting in the TPEP approach. For the VAF method, the phonon eigenvectors are assumed to be not altered by anharmonic effects. However, this assumption is not valid for certain complex systems containing many atoms in the primitive cell and with huge change of eigenvectors, such as pyrochlore oxides. Our preliminary results in applying VAF to the pyrochlore oxide shows that stable results cannot be obtained, especially at high temperatures. Therefore, although the TPEP and VAF methods based on FPMD may yield useful information about phonon properties, those constrains discussed above prevent their direct application to predict the thermal expansion coefficients for complex systems.

One may of course re-sorts to FPMD, which provides a brute-force approach to study the thermal expansion of materials. However, its application is bottlenecked by the heavy computational cost, which would grow exponentially to quickly become undesirable and even unbearable as the complexity and size of the system increases. The objective of our study is to identify an alternative based on the QHA approach, to provide a much more efficient route than FPMD. The QHSM approach we developed, though with certain aspects (e.g., the soft mode issue) that certainly necessitate further studies, has been demonstrated to have the capacity to obtain similar result as the ones yielded by FPMD, and can serve as a good utility for complex oxide systems.

**SUPPLEMENTARY MATERIAL**

See supplementary material⁴⁷ for additional phonon dispersions and potential wells at various strains for Sm₂Zr₂O₇, Nd₂Zr₂O₇, and La₂Zr₂O₇ pyrochlore oxides.

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The exact time duration for each simulation depends when stable temperature and pressure fluctuations are attained.


See supplementary material at http://dx.doi.org/10.1063/1.4954280 for additional phonon dispersions and potential wells at various strains for Sm$_2$Zr$_2$O$_7$, Nd$_2$Zr$_2$O$_7$, La$_2$Zr$_2$O$_7$ pyrochlore oxides.

The number of branches omitted converges to eight at large strains.

For instance, the inconsistency/irregularity induces an up-shift in those $F_{\text{total}}$ versus $V$ curves (in open symbols), and as a result the volume that corresponds to the lowest $F_{\text{total}}$ remains unchanged as temperature varies - a fictitious zero CTE phenomenon.

Vibration patterns of similar characteristics are observed for other low-lying branches.

Note that the correspondence between the normal mode amplitude and the maximum displacement of Gd, $d_{\text{Gd}}$, can be strain-dependent. However the difference is ignorable in the strain range considered. Here the correspondence shown in Fig. 4 is at $c_4 = 0$.


As apparently the omission of those rattling phonon branches does not lead to noticeable underestimation of the thermal expansion.


Although the IAO method has been shown to be applicable in certain systems with few soft modes and simple crystal structures, it is rather challenging (from some preliminary calculations we attempted) to directly employ it in complex systems like RE$_2$Zr$_2$O$_7$ pyrochlores.
