Combined computational and experimental investigation of the refractory properties of $\text{La}_2\text{Zr}_2\text{O}_7$

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Abstract

We demonstrate how key material properties that provide guidance in the design of refractory materials can be accurately determined via *ab initio* thermodynamic calculations in conjunction with experimental techniques based on synchrotron X-ray diffraction and thermal analysis under laser-heated aerodynamic levitation. The properties considered include melting point, heat of fusion, heat capacity, thermal expansion coefficients, thermal stability and sublattice disordering, as illustrated in a motivating example of lanthanum zirconate ($\text{La}_2\text{Zr}_2\text{O}_7$). This work also sheds light on the unresolved controversy of possible phase transition before melting and identifies specific mechanisms responsible for the material's high melting point. This study benefits from the use of two very recent techniques: (i) a new small-cell coexistence method that enables the accurate and efficient determination of the melting points from *ab initio* calculations alone; (ii) the experimental determination of solid structure at high temperatures by high temperature synchrotron X-ray diffraction on laser heated aerodynamically levitated samples.

Keywords: lanthanum zirconate, heat of fusion, melting temperature, disorder, thermal expansion and heat capacity

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1. Introduction

Lanthanum zirconate is being investigated for a wide range of applications, including solid oxide fuel cell electrodes [1, 2], fluorescence screens [3, 4], catalysts [5, 6] and high-temperature superconducting coated conductors [7, 8]. In particular, $\text{La}_2\text{Zr}_2\text{O}_7$ is proposed as a promising thermal-barrier coating (TBC) material [9, 10, 11, 12, 13, 14, 15, 16, 17, 18] to replace the most-commonly used yttria-stabilized zirconia (YSZ), for the following reasons: (i) $\text{La}_2\text{Zr}_2\text{O}_7$ coating has high phase stability against thermal treatment, thus it is capable to function under higher temperatures, far beyond the limited operation temperature (1200 °C) of YSZ [19]; (ii) $\text{La}_2\text{Zr}_2\text{O}_7$ has a lower thermal conductivity, which provides better thermal insulation for the components from large and prolonged heat loads; (iii) $\text{La}_2\text{Zr}_2\text{O}_7$ has a lower oxygen ion diffusivity (less oxygen-transparent), so it protects the body coat from oxidation. The major drawback of $\text{La}_2\text{Zr}_2\text{O}_7$ as a TBC coating is its small thermal expansion coefficient, which does not match that of the superalloy in the body coat.

The assessment of novel refractory materials, such as lanthanum zirconate, demands the determination of a number of physical, chemical and mechanical properties. We demonstrate how *ab initio* calculations can be used in conjunction with advanced experimental techniques (synchrotron X-ray diffraction on laser heated aerodynamically levitated samples and thermal analysis above 2000 °C) to provide a more complete and accurate picture of thermal properties. Our combined computational and experimental investigation determines key material properties, ranging from enthalpy of fusion, melting temperature, to thermal expansion and heat capacity. We also investigate the possibility of high-temperature sublattice disordering.

Some properties are more directly obtained via computational means. For instance, the heat of fusion, the heat capacity and the thermal expansion are straightforward to calculate, but clearly benefit from an experimental verification to ascertain the validity of the modeling assumptions (e.g., stable structure,

30 sources of entropy and the reliance on density functional theory). These mea-
 surements, while simple at low temperature, become challenging above 1500 °C,
 as considered in this work, because they necessitate development of new exper-
 imental techniques and calibration standards. In contrast, other properties are
 more easily accessible experimentally. The most striking example is the melt-
 35 ing point, where computational efforts via *ab initio* methods demand advanced
 techniques to reduce the computational burden[20, 21, 22, 23, 24, 25, 26, 27, 28].
 In this work, the recently proposed small-cell coexistence method [29] makes it
 feasible to calculate the melting point of a compound with a substantially more
 complex crystal structure than considered in prior *ab initio* computational stud-
 40 ies. Given the challenges associated with these calculations, experimental vali-
 dation is particularly important. Another important example of computational-
 experimental complementarity is the determination of the presence of sublattice
 disordering. While it is difficult to assess the state of order of the oxygen sublattice
 via X-ray diffraction (due to its small scattering factor), our computations
 45 can rather clearly establish the possibility of such a disordering transition since
 oxygen diffusion is visible in our simulations. Conversely, disordering on the
 cation sublattice is not as easily accessible in our simulations but would have
 been detected experimentally if it were present.

Overall, our results show very good agreement between experimental mea-
 50 surements and their computational counterparts, even in cases reaching the limit
 of today’s computational or experimental methods. This situation supports the
 validity of our thermodynamic description.

This paper is organized as follows. The detailed computational and experi-
 mental approaches are first described in Section 2. Results and discussions are
 55 presented in Section 3.

2. Methods

Pyrochlore $\text{La}_2\text{Zr}_2\text{O}_7$ structure has the space group of $Fd\bar{3}m$ that derives
 from the fluorite-like arrangement of atoms. The cubic pyrochlore structure of

$\text{La}_2\text{Zr}_2\text{O}_7$ has been discussed in detail [30, 31, 32, 33]. As shown in Fig. 1,
 the La^{3+} ions occupy the special site $16d$ ($1/2, 1/2, 1/2$) and the Zr^{4+} ions oc-
 60 cupy the special site $16c$ ($0, 0, 0$). The oxygen atoms are located at sites $48f$
 ($x, 1/8, 1/8$) and $8b$ ($3/8, 3/8, 3/8$), and the oxygen vacancies at $8a$ ($1/8, 1/8, 1/8$).
 Table 1 lists the lattice parameter and the value of x from both calculation and
 experiment. The primitive unit of $\text{La}_2\text{Zr}_2\text{O}_7$ consists of 4 La, 4 Zr and 14 O
 65 atoms. There are 88 atoms in a face-centered cubic (fcc) conventional unit cell.
 $\text{La}_2\text{Zr}_2\text{O}_7$ is also reported in the defect fluorite ($Fm\bar{3}m$) structure as transitory
 during radiation damage and from low temperature synthesis. The defect fluo-
 rite structure can be derived from pyrochlore by disordering on both cation and
 anion sublattices.

70 2.1. Computational

We employ first-principles density functional theory [34, 35, 36] to model
 $\text{La}_2\text{Zr}_2\text{O}_7$. All electronic structures are calculated by the Vienna *Ab-initio*
 Simulation Package (VASP) [37, 38, 39], with the projector-augmented-wave
 (PAW) [40] implementation and the generalized gradient approximation (GGA)
 75 for exchange-correlation energy, in the form known as Perdew-Burke-Ernzerhof
 (PBE) [41]. For Lanthanum, the inner core $5s$ and $5p$ electrons are relaxed for

Figure 1: Pyrochlore structure of $\text{La}_2\text{Zr}_2\text{O}_7$.

electronic structure optimization. The electronic temperature is accounted for by imposing a Fermi distribution of the electrons on the energy level density of states, so it is consistent with the ionic temperature.

80 First-principles molecular dynamics (MD) techniques are utilized to simulate atomic movements and trajectories of $\text{La}_2\text{Zr}_2\text{O}_7$, in order to compute various properties. Specifically, MD simulations are carried out under constant number of atoms, pressure and temperature condition (NPT , isothermal-isobaric ensemble). Here the thermostat is conducted under the Nose-Hoover chain formalism [42, 43, 44, 45]. The barostat is realized by adjusting volume every 200
85 steps according to average pressure. Although this does not formally generate an isobaric ensemble, this approach has been shown to provide an effective way to change volume smoothly and to avoid the unphysical large oscillation caused by commonly used barostats [29]. The $\text{La}_2\text{Zr}_2\text{O}_7$ pyrochlore structure is taken
90 as a starting point for all MD simulations of the solid phase.

2.2. Experimental

Laser melting of $\text{La}_2\text{Zr}_2\text{O}_7$ for diffraction and thermal analysis experiments causes some loss of La resulting in $\text{La}_{1.96}\text{Zr}_{2.03}\text{O}_7$ stoichiometry, as determined by microprobe analysis. Thermal analysis is performed in sealed tungsten crucibles in Setaram Setsys 2400 instrument modified to enable sample temperature
95 monitoring with spectropyrrometer [46, 47]. High temperature X-ray diffraction experiments are performed on an aerodynamic levitator at beamline 11-ID-C at the Advanced Photon Source, Argonne National Laboratory. A detailed description of experimental setups is published elsewhere [48]. Processing of diffraction
100 data is performed with GSAS-II software [49]. Splat quenching of lanthanum

Table 1: Comparison between experimental and calculated data of $\text{La}_2\text{Zr}_2\text{O}_7$.

method	Expt.	PBE	HSE	HF
$a(\text{\AA})$	10.805	10.880	10.833	10.728
x	0.4200	0.4172	0.4171	0.4170

Figure 2: Melting and crystallization of $\text{La}_{1.96}\text{Zr}_{2.03}\text{O}_7$ in thermal analyzer at $10^\circ\text{C}/\text{min}$ heating/cooling rate. 150°C undercooling is evident. Integration of peaks in heat flow (blue trace) on melting and crystallization gives similar values indicating direct crystallization of pyrochlore phase.

zirconate melt is performed in UC Davis using custom built splittable nozzle aerodynamic levitator with CO_2 laser heating.

3. Results and discussions

3.1. Fusion enthalpy

105 Fusion enthalpy is calculated as the enthalpy difference between the solid and the liquid at 2500 K. We perform *NPT* MD simulation to generate a trajectory for each phase. The enthalpy is evaluated as an average over time during the MD trajectory.

We use a supercell containing 88 atoms ($8 \text{ La}_2\text{Zr}_2\text{O}_7$) for the pyrochlore 110 phase. Modeling liquid phase on a periodic cell is subject to relatively stronger finite-size effect, since the liquid is imposed by the unrealistic periodic boundary condition. So we choose a larger cell with 176 atoms to describe the liquid phase more accurately.

We perform further correction on the data from PBE to a more accurate hybrid functional of Heyd-Scuseria-Ernzerhof (HSE) [50]. For both the pyrochlore 115 and liquid phases, we compute energy differences between PBE and HSE on randomly chosen snapshots from MD trajectories, and then combine them as a correction on the fusion enthalpy.

The fusion enthalpy is calculated to be 0.26 eV/atom (270 kJ/mol). After
120 HSE correction, it is 0.28 eV/atom (300 kJ/mol). The major error is considered
to be the finite-size effect from the liquid phase. Based on study on different
system size (88 atoms versus 176 atoms), the error is estimated to be 0.02
eV/atom (20 kJ/mol).

First experimental measurement of fusion enthalpy for $\text{La}_2\text{Zr}_2\text{O}_7$ pyrochlore
125 was reported by Radha [17]. New set of measurements (Fig. 2) is performed
on laser melted $\text{La}_{1.96}\text{Zr}_{2.03}\text{O}_7$ in sealed tungsten crucibles to prevent carbon
contamination from furnace. Uncertainty in experimental measurements of fu-
sion enthalpy by thermal analysis is difficult to evaluate due to the absence of
enthalpy calibration standard above Al_2O_3 melting temperature (2054 °C). The
130 value 300 ± 50 kJ/mol can be taken as a conservative evaluation of both sets of
experimental measurements.

The close agreement between computation and experiment strongly supports
the validity of the results. We find the computational approach relatively easier
than its experimental counterpart in determining heat of fusion, when temper-
135 ature reaches far beyond the Al_2O_3 melting temperature (2054 °C). Enthalpy
calibration standard for higher temperature, e.g., Y_2O_3 (2430 °C), would in-
crease the accuracy of fusion enthalpy measurements by commercially available
thermal analyzers. We plan to work on it in the next step, using a combined
experimental and computational approach.

140 3.2. Melting temperature

We employ our small-size coexistence method to calculate the melting tem-
peratures. The result is shown in Fig. 3. The details of this method have been
described previously in Ref. [29], and here we briefly reiterate it. While tradi-
tional two-phase coexistence method accurately predicts melting temperature
based on stabilized coexistence, it is computationally prohibitive in the DFT
framework, due to large system size (usually at least 1,000 atoms) to stabilize
the interface. We reduce the cell size down to about 100 atoms, so it becomes
feasible to combine directly with DFT. Though coexistence can no longer be

stabilized in a small cell, we manage to obtain the melting temperature based on the statistical distribution of the final phases, i.e., we run multiple duplicates of small-cell coexistences to evaluate the probabilities of the final phases. Starting from solid-liquid coexistence, we monitor the system evolution until it reaches a pure final phase, either a solid or a liquid, and we calculate such probabilities based on the results from multiple duplicated simulations. We then fit the melting temperature from these probability distributions. It can be formally derived that the distribution, at a particular temperature, is

$$\frac{N_{\text{liquid}}}{N_{\text{solid}}} = \exp\left(-\beta G^{l-s} l_x / 2\right), \quad (1)$$

where $N_{\text{liquid}}/N_{\text{solid}}$ is the ratio of the number of MD runs that coexistence ends in either liquid or solid, G^{l-s} is the Gibbs free energy difference at temperature T , l_x is a finite-size parameter and β is $1/k_{\text{B}}T$. The Gibbs free energy difference is

$$H^s(T) = H^s(T_m) + C_p^s(T - T_m) \quad (2)$$

$$H^{l-s}(T) = H^{l-s}(T_m) + C_p^{l-s}(T - T_m) \quad (3)$$

$$G^{l-s}(T) = \frac{T_m - T}{T_m} H^{l-s}(T_m) - C_p^{l-s} \frac{(T - T_m)^2}{T_m}. \quad (4)$$

where T_m is melting temperature, H is enthalpy, H^{l-s} is heat of fusion, C_p is heat capacity. In Ref. [29], we validated this relation through various examples

Figure 3: The melting temperature of $\text{La}_2\text{Zr}_2\text{O}_7$ fitted according to Eqs. (1) to (4).

Table 2: Details of HSE correction on the melting temperature.

T_m^{PBE}	2420 K
$\Delta\mu^s$	-2.634 eV
$\Delta\mu^l$	-2.610 eV
ΔH^{l-s}	0.28 eV
ΔT_m	210 K
T_m^{HSE}	2630 K

from empirical potentials. Finite size effect was studied systematically. We found we can usually control the error to be below 100 K, using a cell containing
145 around 100 atoms.

The simulations on $\text{La}_2\text{Zr}_2\text{O}_7$ are performed on a $1 \times 1 \times 2$ fcc supercell, which contains 176 atoms and measures approximately $11 \times 11 \times 22 \text{ \AA}^3$. The plane wave energy cutoff is set to 400 eV and it is further increased to 500 eV for pressure correction. *NPT* MD simulations are carried out to trace the evolution
150 of coexisting systems. Only Γ -point is used throughout the calculations. To estimate the error of using this single k-point, we compare with fully converged k-point grid and compute energy difference on randomly chosen configurations from both solid and liquid. The root mean square error is less than 1 meV/atom.

The melting temperature T_m is calculated to be 2420 ± 28 K, as shown in Fig. 3. We apply a correction based on the more accurate hybrid functional of HSE. First, free energy correction is made on each phase following the thermodynamic integration method.

$$\mu_\beta = \mu_\alpha + \frac{1}{N} \int_0^1 \langle H_\beta - H_\alpha \rangle_{H_\lambda} d\lambda, \quad (5)$$

where β is HSE, α is PBE. Due to the high computational cost of HSE, only $\lambda = 0$ is used for integration. Then the melting temperature correction is evaluated as

$$\Delta T_m = (\Delta\mu^l - \Delta\mu^s) \cdot \frac{T_m}{\Delta H^{l-s}}, \quad (6)$$

where $\Delta\mu^{l/s}$ are the corrections in free energies for the liquid and the solid,
155 ΔH^{l-s} is heat of fusion, and ΔT_m is melting temperature correction. Detailed

Table 3: **Comparison of the computational and** experimental data for the melting temperature of $\text{La}_2\text{Zr}_2\text{O}_7$.

T (C)	Reference
2150	this work, PBE
2360	this work, HSE
2260	this work, expt.
2295	Radha (2009) [17]
2340	Lakiza (2005) [51]
2230	Zoz (1978) [52]
2160	Portnoi (1972) [53]
2280	Rouanet (1971) [54]
2250	Lin (1964) [55]

data of the HSE correction on melting temperature are listed in Table 2. The melting temperature after HSE correction is 2630 K.

Experiment measures the melting temperature as 2260 °C (2530 K), which lies in the middle of the two theoretical predictions. Our results are in close
160 agreement with others in the literature, as shown in Table 3.

Our calculations enable us to identify the factors that contribute to a high melting point in $\text{La}_2\text{Zr}_2\text{O}_7$. It has a large fusion enthalpy of 0.28 eV/atom, which is a major contributor to the high melting point. Pyrochlore phase $\text{La}_2\text{Zr}_2\text{O}_7$ is further stabilized by its high entropy, in the following two respects. An inter-
165 esting behavior of the pyrochlore structure is **the formation of** soft vibrational modes upon thermal expansion. As shown in Fig. 4, thermal expansion not only softens **the certain zone-center phonon modes**, but also creates a new wide double-well feature, which significantly increases **the** accessible phase space. The high entropy of the solid phase also comes from diffusion of oxygen atoms. As
170 discussed in Section 3.3.1, the corresponding barrier is relatively low, so oxygen atoms visit their neighboring vacancies frequently. The likelihood to form an oxygen-disordered sublattice greatly increases **the** configurational entropy, which further stabilizes the solid phase.

Figure 4: Potential energy upon perturbation along a **zone-center soft phonon mode predominantly involving La motion along $\langle 123 \rangle$ and $\langle 110 \rangle$ directions** (blue: 0 K; red: 2% thermal expansion). The potential well not only softens, but also forms double-wells (**the curvature at the center turns negative after the thermal expansion**). This feature significantly increases the accessible phase space, which increases entropy as a result.

3.3. Disorder

The susceptibility of the pyrochlore structure to disordering is related to the resistance of these materials to radiation damage. Irradiation effects in zirconate pyrochlores have been studied by both experimental [56, 57, 58, 59] and theoretical [60, 61] studies. These studies explored the possibility of these materials as radionuclide hosts in ceramic waste forms and the likelihood of their formation caused by the reaction between the zircalloy cladding and the fission products of severe nuclear reactor accident scenarios [56]. $\text{Gd}_2\text{Zr}_2\text{O}_7$ undergoes an order-disorder structural transformation at 1550 °C. This disordered defect fluorite structure shows strong resistance to radiation damage, even at extremely high doses. Upon irradiation, $\text{La}_2\text{Zr}_2\text{O}_7$ first undergoes initial disordering of the oxygen sublattice with random occupation of the oxygen vacancies and then random distributions of **the** cations and anions, leading to **the** formation of disordered fluorite phase [57, 62]. However, this ion-irradiation-induced disordered state is transient and amorphization takes place on further irradiation [63, 57]. Fluorite is also observed to form on crystallization of amorphous lanthanum zirconate in a wide range of compositions [64]. However, the fluorite phase has never been quenched from high temperature, and it is not clear whether it is stable in bulk at any temperature.

Disordering has a strong impact on thermal performance of TBC materials.

The disordering of TBC leads to volume change and hence mismatch between
 195 body coat and topcoat, which results in cracking in TBC, a common mode
 of materials failure. Also, oxygen sublattice disorder determines whether a
 material is oxygen-transparent. If oxygen atoms can diffuse readily in TBC, the
 underlying body coat is exposed to the oxygen environment in the heat flux,
 which rapidly oxidizes the body coat and forms thermally grown oxide (TGO).
 200 Irregularly grown TGO exaggerates the strain in the coating, which is a major
 mechanism of thermal failure.

In our simulations, we find strong evidence that the system undergoes a sub-
 lattice disordering transition (on the oxygen sublattice) just before melting. Our
 results also indicate that disordering of the cation sublattice is unlikely. Syn-
 205 chrotron X-ray diffraction confirms cation ordering in pyrochlore up to complete
 melting.

The energy scale of the oxygen-sublattice disordering transition is found
 to be very small, hence the precise nature of the ordering in the solid phase
 turns out to have little impact on the calculated melting point. We find that
 210 disordering on the oxygen sublattice fortunately occurs only close to the melting
 point, so it will not affect the prospective use of $\text{La}_2\text{Zr}_2\text{O}_7$ as thermal barrier
 coating since service temperatures normally do not exceed 2/3 of the melting
 temperature of the material.

3.3.1. Oxygen sublattice

215 We observe oxygen diffusion in MD simulation of pyrochlore lanthanum zir-
 conate, as shown in Fig. 5(a), which implies disordering on the oxygen sublat-
 tice. Transition state analysis also supports this finding. For oxygen moving
 to a nearby vacancy, the transition barrier is 0.5 eV (48 kJ), and the energy
 penalty for the final state after diffusion is only 0.4 eV (39 kJ), as shown in
 220 Fig. 5(b). At 2500 K, this corresponds to a Boltzmann distribution factor of
 0.16, which is further increased to ~ 1 since each vacancy has six degenerate
 neighboring oxygen atoms. These two observations strongly suggest disordering
 on the oxygen sublattice.

Figure 5: (a) Distance to ideal pyrochlore position during MD simulation of the solid phase at 2500 K. (blue: O; green: Zr; yellow: La.) Distance is normalized so that the nearest neighbor distance between two oxygen atoms is 1. Diffusion is observed on two oxygen atoms near 35 ps. (b) Potential energy diagram based on nudged elastic band (NEB) method [65, 66]. For an oxygen atom moving to its neighboring vacancy, the activation energy is 0.5 eV (48 kJ). The energy of the final state is 0.4 eV (39 kJ) higher than pyrochlore.

A rigorous evaluation of the phase stability requires a cluster expansion
 [67, 68] in order to capture all important configurational states that contribute
 to the disordered phase. This would be very difficult to carry out for a complex
 ionic substance such as $\text{La}_2\text{Zr}_2\text{O}_7$, especially given that the anharmonic
 effects are likely to be large. Instead, we employ the special quasirandom structure
 (SQS) approach [69] implemented in the “mcsqs” [70] code in ATAT [71]
 to estimate the phase stability. At first, a completely random oxygen-vacancy
 sublattice is studied. But we find most SQS’s are unstable. Upon structural
 optimization, some oxygen atoms move to other lattice sites, which changes the
 original configuration. In particular, the tetrahedron center of 4 Zr atoms (called
 8a-site) is highly unfavored for the oxygen atom, and the high oxygen concentration
 at these 8a-sites is the major reason for the instability. Indeed, these
 sites are vacant in the pyrochlore structure. In response to this phenomenon, we
 limit the oxygen concentration on these 8a-sites and study a disordered phase
 as described below.

1. The cations are ordered as in pyrochlore.
2. Oxygen is randomly distributed on 8a-sites, with a concentration of 1/4.
3. Oxygen is randomly distributed on the rest sublattice, with a concentration of 27/28 (so that the chemical composition is $\text{La}_2\text{Zr}_2\text{O}_7$).

We generate a SQS representation of this disordered phase. The SQS is stable. With respect to pyrochlore, its energy is 33 meV/atom (35 kJ/mol $\text{La}_2\text{Zr}_2\text{O}_7$). The entropic free energy at 2500 K is

$$-TS_{\text{fluorite}} = kT \sum n_i \ln x_i / \sum n_i = -32 \text{ meV/atom.}$$

Combining energy and entropy, this disordered phase is of comparable stability as the pyrochlore phase.

245 The actual disordered phase in reality will populate configurational states according to a Boltzmann distribution, rather than the uniform distribution we assume in the random structure. A Boltzmann distribution will result in the lowest free energy compared to any other distribution, therefore the free energy we calculate above is the upper limit for the disordered phase. The actual
250 disordered phase in reality will be more stable than the randomly disordered one, which makes it very likely to replace the pyrochlore phase at high temperatures. The fact that energetic and entropic effects are so close suggests the transition temperature will be close to 2500 K, very near the melting point.

Experimental X-ray diffraction cannot capture signals from oxygen atoms
255 clearly, as they are overwhelmed by signals from heavy La and Zr atoms. However, neutron diffraction will clearly capture oxygen atoms, and we plan to work on this aspect in the near future.

3.3.2. Cation sublattice

During MD simulation of solid-liquid coexistence, we observe a cation-disordered
260 solid phase when the liquid portion of the supercell solidifies. Although this may serve as evidence for cation disordering, we cannot rule out the possibility that this disordered solid is metastable. When solidifying, the random chaotic liquid portion may not fully optimize and arrange itself to the thermodynamically most favored solid structure, due to the limited length of time (only on the order
265 of 10 picoseconds). It requires a thermodynamic study on this disordered phase to assess its relative phase stability.

The energy of this phase is first extracted from coexistence MD simulations.

Table 4: Pair correlation as an order parameter to quantify the randomness of newly formed solid from MD. The values for ordered pyrochlore and completely disordered random fluorite are listed for comparison.

	Zr-Zr	La-La	Zr-La
2300 K	0.36 ± 0.01	0.36 ± 0.01	0.27 ± 0.02
2400 K	0.31 ± 0.02	0.32 ± 0.02	0.37 ± 0.02
2500 K	0.32 ± 0.02	0.32 ± 0.02	0.35 ± 0.04
pyrochlore	0.5	0.5	0
random fluorite	0.25	0.25	0.5

When solid-liquid coexistence evolves to pure solid phase, we find, in most cases, half of the supercell is in the cation-disordered phase, while the other half is in the original pyrochlore phase. The energy of this disordered phase is calculated to be 114 meV/atom (121 kJ/mol $\text{La}_2\text{Zr}_2\text{O}_7$), compared to fully ordered pyrochlore. This energy is much higher than the oxygen-sublattice disordered phase (33 meV/atom, 35 kJ/mol $\text{La}_2\text{Zr}_2\text{O}_7$). Indeed, this penalty is so large that we find only the maximal configuration entropy could counteract it. At 2500 K, the maximal configurational entropy is achieved if both cation and anion sublattices are completely random. Its contribution to free energy is

$$-TS_{\text{fluorite}} = kT \sum n_i \ln x_i / \sum n_i = -113 \text{ meV/atom.}$$

Therefore, unless this cation-disordered phase is highly random (i.e., with virtually no short-range order) in reality, it would be thermodynamically disfavored with respect to the pyrochlore phase.

270 We use two approaches to determine the randomness of this disordered phase. Our analysis shows this phase is only partially disordered, so it is thermodynamically unstable. In order to quantify the extent of disordering, we introduce a specific pair correlation as an order parameter. We select a pair cluster twice the distance between nearest neighbor La-La, and we calculate the pair correlation of cations, as shown in Table 4. Two benchmarks, ordered pyrochlore
275 and completely disordered random fluorite, are listed for comparison. These

Figure 6: Synchrotron ($\lambda = 0.10798 \text{ \AA}$) X-ray diffraction of $\text{La}_2\text{Zr}_2\text{O}_7$ at $\sim 2000 - 2450 \text{ }^\circ\text{C}$. Pyrochlore (111) reflection is evident until complete melting. Theoretical X-ray diffraction from MD snapshots (generated by AFLOW/ACONVASP[73]) is plotted for comparison.

data suggest the newly formed solid is partially disordered. SQS analysis also shows the disordering is limited. We generate SQS assuming complete disordering on both sublattices, i.e., the (La, Zr) and the (O, vacancy) sublattices. After structural optimization, we find some oxygen atoms moving to neighboring lattice sites, suggesting the SQS is unstable before configurational change. Such behavior means this disordered phase is constrained in a limited portion of configuration space, i.e., it is partially disordered.

Our theoretical result is confirmed by both X-ray diffraction and quenching experiments. Synchrotron X-ray diffraction experiments were performed on laser heated sample levitated in oxygen flow. Pyrochlore (111) reflections were observed up to complete melting (Fig. 6). The ratio of (111)/(222) reflections was previously used for evaluation of radiation induced antisite disorder in pyrochlores [72]. Our diffraction data indicate no significant variation (from 0.020 to 0.018) in (111)/(222) ratio with temperature. Experiments on containerless quenching and splat quenching of $\text{La}_2\text{Zr}_2\text{O}_7$ melt were performed using a split-table nozzle aerodynamic levitator. The pyrochlore phase was observed in all experiments with $\text{La}_2\text{Zr}_2\text{O}_7$, even though fluorite phase has been obtained by this method for $\text{Eu}_2\text{Zr}_2\text{O}_7$ [74].

Differential thermal analysis also clearly indicates the absence of metastable phase. Heat effects on melting and solidifying are quantified by differential ther-

mal analysis. As shown in Fig. 2, the values from integration of peaks in heat flow on melting and crystallization are consistent within experimental uncertainty, indicating no formation of a metastable phase of significantly different energy upon crystallization.

Although we have strong evidences from both computation and experiment, we note that we still cannot completely rule out the possibility of a cation-disordered phase. The fact that this phase is present in MD simulation indicates either the transition to pyrochlore phase is kinetically hindered or this phase is slightly unstable relative to the pyrochlore phase so MD simulation does not reflect the stability difference. X-ray diffraction results do not completely exclude the possibility of disordering either. As a thermal gradient is present in the diffracted volume [48], the disordered phase could occur ~ 100 °C below melting. Even if this is the case, the possibility of transient defect fluorite phase occurrence in $\text{La}_2\text{Zr}_2\text{O}_7$ right before melting can be treated more as a peculiarity of solid to liquid transition rather than solid state phase transition and of little significance for $\text{La}_2\text{Zr}_2\text{O}_7$ application as a thermal barrier coating. Reported occurrences of lanthanum zirconate in disordered fluorite phase at low temperature in precipitates and in small particles from vapor deposition are likely to be induced by a surface energy term. This may play an important role in design of thermal barrier coating microstructures and choice of the method of their manufacturing and warrant separate investigation. However, analysis of these effects is beyond the scope of this paper.

3.4. Heat capacity

We calculate heat capacity in a temperature region up to the melting point. At each temperature, the heat capacity is calculated as derivative of enthalpy with respect to temperature. We run first-principles MD under the NPT ensemble to obtain the enthalpies at various temperatures. We include quantum corrections to vibrational energies, since they are significant at low tempera-

Figure 7: Heat capacity of pyrochlore $\text{La}_2\text{Zr}_2\text{O}_7$ up to melting temperature. Computational results are shown in red. The last data point at 2375 K may be invalid due to the possible transition to oxygen-sublattice disordered phase near 2500 K. No oxygen diffusion is observed below 2250 K. The black curve is from experiment up to 1550 K. [75]

tures.

$$\Delta H = \frac{1}{N} \sum_{i=1}^{3N} \left(0.5 + \frac{1}{\exp(h\nu_i/k_B T) - 1} \right) \cdot h\nu_i - 3k_B T, \quad (7)$$

where h is Planck constant, N is number of atoms, ν is vibrational frequency. The ATAT package [71] is employed to calculate the phonon frequencies. The calculated heat capacities are shown in red in Fig. 7 and are found in good agreement with available experimental data at lower temperature.

3.5. Thermal expansion

Using the same procedure, thermal expansion coefficients are calculated, as shown in Fig. 8. The calculated thermal expansion coefficient is $11.1 \times 10^{-6} \text{ K}^{-1}$.

Experimental thermal expansion coefficient (Fig. 8) is refined for the range 1400-2100 °C, from X-ray diffraction on a laser heated levitated sample. The difference in the experimental and calculated cell parameters is due to both possible deviation in stoichiometry in laser melted lanthanum zirconate, and the known overestimation from calculations (Table 1). However, the experimental value for thermal expansion coefficient, $11.5 \times 10^{-6} \text{ K}^{-1}$, is in remarkable agreement with MD simulations.

Figure 8: Lattice parameter at various temperatures in MD simulation (+) and X-ray diffraction experiment (o). For theoretical thermal expansion, the coefficient is linearly fitted in temperature region [1000, 2250] K. Lattice parameter is subject to quantum effect at low temperature, thus the first two data points are underestimated.

335 4. Conclusions

In summary, we demonstrate how the combination of computations and experiments can accurately determine key material properties in a complementary manner, as illustrated by the example of $\text{La}_2\text{Zr}_2\text{O}_7$. These properties include fusion enthalpy, melting point, heat capacity, thermal expansion coefficients, and sublattice disordering phase transition. We identify the key factors that contribute to the high melting temperature, namely the large fusion enthalpy, the presence of soft phonon modes and sublattice disordering, which provide guidance in the design of novel refractories. The close agreement with experiment in the known but structurally complex compound $\text{La}_2\text{Zr}_2\text{O}_7$ provides good indication that the computation methods described herein can be used within a computational screening framework to identify novel refractory materials. Conversely, the calculation of thermal properties such as heat of fusion and heat capacity provides useful input for the calibration of an experimental apparatus aimed at calorimetry measurements at high temperatures, where calibration standards are currently lacking. This collaborative work also allowed us to identify high impact areas for computational and experimental efforts towards high temperature properties. Novel experimental techniques, such as structural studies at high temperature, provide validation between closely related phases

often not unambiguously resolved computationally. Measurements of fusion en-
thalpies and heat capacities above 2000 °C are very challenging experimentally
and can be greatly leveraged by computational methods.

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