Probing disorder in pyrochlore oxides using *in situ* synchrotron diffraction from levitated solids—A thermodynamic perspective

Pardha S. Maram1, Sergey V. Ushakov1, Richard J. K. Weber2,3, Chris J. Benmore2 & Alexandra Navrotsky1

Pyrochlore, an ordered derivative of the defect fluorite structure, shows complex disordering behavior as a function of composition, temperature, pressure, and radiation damage. We propose a thermodynamic model to calculate the disordering enthalpies for several RE2Zr2O7 (RE = Sm, Eu, Gd) pyrochlores from experimental site distribution data obtained by *in situ* high temperature synchrotron X-ray diffraction. Site occupancies show a gradual increase in disorder on both cation and anion sublattices with increasing temperature and even greater disorder is achieved close to the phase transition to defect fluorite. The enthalpy associated with cation disorder depends on the radius of the rare earth ion, while the enthalpy of oxygen disordering is relatively constant for different compositions. The experimental data support trends predicted by *ab initio* calculations, but the obtained enthalpies of disordering are less endothermic than the predicted values. Thermal expansion coefficients are in the range \((8.6 – 10.8) \times 10^{-6} \text{ K}^{-1}\). These new experimental determinations of defect formation energies are important for understanding the stability of pyrochlore oxides and their disordering mechanisms, which are essential in the context of their potential applications in nuclear waste management and other technologies.

Structural disorder of A2B2O7 pyrochlore (PY) is a major factor determining their physical properties and stability. Many undergo an order–disorder transformation at high temperatures, high pressures and under grinding or ion irradiation where the PY superstructure is lost, leaving long-range defect fluorite-type (DF) disorder1–3. Their functional properties are very sensitive to the degree of disorder4–6, which appears to be governed by radius ratio rules6. Despite extensive technological applications as fast ionic conductors, thermal barrier coatings, and ceramics for the immobilization of radioactive waste4,10–13, our understanding of their disordering mechanism and defect formation energies is still incomplete. Recently, Shamblin et al. pointed out that the structure of disordered PY produced by radiation damage is more complex than previously thought and may involve domains of a weberite-like structure with an intermediate degree of order14–16. The order–disorder transition from PY to DF is a rare example of simultaneous disordering in both anion and cation sublattices17. The most important defects that form in PY are the cation antisite (CA) and anion Frenkel pair (AFP), with their formation driving the phase transitions18. Several authors have investigated the relationship between the structural stability of PY oxides and the defect formation energies (DFE) using computational techniques, and the results have been widely used to interpret the experimental findings19.

Sickafus et al. presented contour plots of DFE across a wide variety of PY oxides using force–field atomistic simulations (FFA)3,20,21. Panero et al. applied DFT methods to the DFE in Y2(Ti, Sn, Zr)2O7, and the results indicate that the CA pair has lower energy (0–2 eV) than the AFP (4–11 eV). They also found that the stannates like Y2Sn2O7 have larger DFE than titanates and zirconates because of the greater covalent character of the Sn–O bond compared to Ti–O and Zr–O22,23. Chartier et al. simulated radiation damage cascades in Ti-doped La2Zr2O7 and...
from Table 2 and Fig. 1, TEC increases as the size of the lanthanide ion decreases, and the zirconate series has higher from the linear regression fit, so a temperature independent TEC is supported. Some general trends can be noticed corrections are reasonable. For comparison, the temperature range selected for linear regression analysis was fixed to anomalous lattice constant behavior is detected at high temperature, confirming that the applied temperature cor-

For the first time, we have adopted a high temperature in situ levitation and laser heating. The site occupancies (atomic sublattice disorder), lattice constants and positional PYs samples by thermal treatment close to the melting point using aerodynamic technique to induce equilibrium cation and anion disorder within the PY samples by thermal treatment close to the melting point using aerodynamic levitation and laser heating. The site occupancies (atomic sublattice disorder), lattice constants and positional parameters were refined at a number of temperatures by Rietveld structure analysis, and the obtained site occupancies were then subjected to thermodynamic analysis.

Table 1. Chemical composition, room temperature lattice parameter and melting temperatures for all the studied PY oxides after quenching from the melt. *Error in parenthesis is a standard deviation in the last digit. †N = Number of data points used to calculate the average composition of a respective phase. Room temperature lattice parameter from synchrotron diffraction. No recalcence peak observed for Gd2Zr2O7 in cooling profile. ‡Melt quench phase is defect fluorite and the lattice parameter is doubled for direct comparison. §Melting temperatures corrected with reference to the thermal arrest observed in cooling trace profile of the respective composition.

| Composition by Microprobe analysis | N | *Lattice constant, Å | Melting temp. from cooling traces, T(K) | Melting temp. from in situ diffraction T(K) |
|-----------------------------------|---|----------------------|----------------------------------------|-------------------------------------------|
| La1.97(2)Hf3−xZr4xO7            | 10 | 10.7916(1)          | 2633 ± 10                              | 2673                                      |
| Nd1.99(2)Hf4−xZr4xO7            | 7  | 10.6455(1)          | 2706 ± 20                              | 2773                                      |
| Sm1.98(10)Hf4−xZr4xO7           | 10 | 10.5840(1)          | 2843 ± 10                              | 2873                                      |
| Nd2(10.6±0.0)Zr2O7              | 9  | 10.6607(1)          | 2650 ± 50                              | 2673                                      |
| Sm2(10.5965(2))Zr2O7            | 10 | 10.5965(2)          | 2836 ± 14                              | 2823                                      |
| Eu1.99(10)Zr2O7                 | 10 | 10.5489(1)          | 2343 ± 10                              | —                                         |
| Gd1.99(10)Zr2O7                 | 13 | 10.5258(1)*         | —                                      | —                                         |

found a significant difference in Zr–La and Ti–La CA DFE, supporting the observation that titanate PYs may be unfavorable for radioactive waste immobilization as radiation damage causes amorphization rather than disordering4. All of the reported computational studies support experimental correlations that link observed PY – DF transformations with simple radius ratio (rA/rB) rules2. However, the predicted energies (at least 2–3 eV)20,22,24 appear to be too large for significant disordering to occur prior to melting. On the other hand, recent DFT studies on select PY oxides show that these energies are substantially smaller than those predicted with FFA methods25. It is clear that the computational studies need comparison with experimental determinations of DFE. Our goal is to develop an in situ experimental method for quantitative determination of site distributions from which DFE can be calculated by a thermodynamic model. In situ structural studies are essential because the high temperatures involved in equilibrium disordering make it questionable whether the disordering can be preserved on “quenching” the sample to ambient conditions. Indeed, numerous authors have studied functional properties of PY oxides with different degrees of disorder made by quenching from high temperatures, but they achieved very low percentages of disorder (5–22%) and did not reach the fully disordered state26–28.

The disordering in PY oxides may be viewed as an equilibrium reflecting the balance of a positive enthalpy of interchange on cation and on anion sublattices and a positive configurational entropy of disordering. Such gradual disordering in spinels has been described by a simple thermodynamic model, treating cation distribution as a chemical equilibrium at a given temperature29. The cation distribution as a function of temperature can be used to calculate the appropriate interchange enthalpies for both CA and AFP. In this study, a similar thermodynamic model is applied to the disordering in PY oxides, with independent reactions representing CA and AFP disorder. For the first time, we have adopted a high temperature in situ diffraction technique to induce equilibrium cation and anion disorder within the PY samples by thermal treatment close to the melting point using aerodynamic levitation and laser heating. The site occupancies (atomic sublattice disorder), lattice constants and positional parameters were refined at a number of temperatures by Rietveld structure analysis, and the obtained site occupancies were then subjected to thermodynamic analysis.

Results and Discussion

Composition and thermal expansion. Chemical analysis of the melt-quenched spheroids by microprobe showed stoichiometric composition within experimental error, see Table 1. The room temperature synchrotron X-ray diffraction pattern of all the melt-quenched compositions, showed intense and sharp patterns, and no impurity phases could be detected (Figure S1 in SI). All the compositions showed DF-based diffraction peaks, (222), (400), (440) and (622). Also, superlattice reflections, (111), (311), (331) and (511) are seen in La2Hf2O7, Nd2Hf2O7, Sm2Hf2O7, Nd2Zr2O7, and Sm2Zr2O7, indicating the doubling of the cubic unit cell. The cation radius ratio, 1.46 ≤ rA/rB ≤ 1.80 governs the formation, and structural stability of the oxide PYs8. For the rare earth zirconate series, Gd2Zr2O7 (rGd3+ /rZr4+) = 1.46) is considered the boundary between PY and DF structures8. The absence of superlattice reflections in the melt-quenched Eu2Zr2O7 and Gd2Zr2O7 samples indicate the DF structure50. Thus, during quenching from the melt, compositions with rA/rB at and slightly above 1.46 formed DF structures. The calculated room temperature lattice parameters are given in Table 1. A systematic decrease in lattice constant is observed as the ionic radius of the lanthanide decreases.

For all the compositions tested, the unit cell size changes smoothly as a function of temperature till melting. No anomalous lattice constant behavior is detected at high temperature, confirming that the applied temperature corrections are reasonable. For comparison, the temperature range selected for linear regression analysis was fixed to 1123–2373 K. The variation of thermal expansion coefficients (TEC) vs. temperature is within reported uncertainty from the linear regression fit, so a temperature independent TEC is supported. Some general trends can be noticed from Table 2 and Fig. 1, TEC increases as the size of the lanthanide ion decreases, and the zirconate series has higher TEC than the hafnate series. TEC of studied compositions varies from (8.6 to 10.8) × 10−6 K−1, the lowest TEC being observed for La2Hf2O7. The highest TEC is seen for Sm2Zr2O7 and Gd2Zr2O7 = (10.8 ± 0.5) × 10−6 K−1 and (10.6 ± 0.3) × 10−6 K−1. The TEC values within the studied temperature range, 1123–2373 K, measured by the levitation method, agree well with previously reported values of 8–11 × 10−6 K−1 in the 298–1473 K temperature range51.
Pyrochlore structure as a function of temperature. During heating, the *PY* La$_2$Hf$_2$O$_7$ and Nd$_2$Hf$_2$O$_7$ persist to the melting temperatures, 2673 and 2773 K, respectively (Figures S2 & S3 in SI). In Nd$_2$Zr$_2$O$_7$, all the superlattice reflections are present to 2523 K, but with further increase in temperature, the (311) reflection disappears, but (111), (331), and (511) reflections persist to melting at 2623 K (Figure S4 in SI). It is known that Nd$_2$Zr$_2$O$_7$ shows a *PY* to *DF* phase transition, with a reported transition temperature between 2493 and 2573 K$^{1,32}$. In this study, the (311) reflection disappears at 2423 K, within the reported temperature range, confirming the existence of the phase transition. However, the presence of residual superlattice reflections till melting may be due to the presence of small *PY* domains within the *DF* matrix$^{33}$. Also, inhomogeneity in specimen temperature could cause the observed residual superlattice reflections. For Sm$_2$Hf$_2$O$_7$, the reflections of the *PY* structure intensify up to 2123 K, but further increase in temperature weakens the superlattice reflections, that then disappear completely, indicating transformation to *DF* just before melting at 2823 K (Figure S5 in SI).

For Sm$_2$Zr$_2$O$_7$, the superlattice reflections disappear, indicating transformation to *DF* at 2323 K, and melting occurs at 2823 K (Figure S6 in SI). For Eu$_2$Zr$_2$O$_7$, previously we reported a reversible *PY*–*DF* phase transition at 2173 K during heating and 2073 K during cooling (Figure S7 in SI)$^5$. Similarly, Gd$_2$Zr$_2$O$_7$ shows a reversible *PY*–*DF* phase transformation during heating and cooling in the range 1773–1873 K (Figure S8 in SI). Synchrotron diffraction patterns of all the compositions as a function of temperature and the results of profile fitting for La$_2$Hf$_2$O$_7$, Nd$_2$Zr$_2$O$_7$, Nd$_2$Hf$_2$O$_7$, and Sm$_2$Hf$_2$O$_7$ are given in Figures (S2–S8) and Table S1 in the SI. Figure 2(a–d) shows the 2D synchrotron diffraction images tracking the structure change as a function of temperature and the corresponding Rietveld refinement plots. Since the sample is initially in the metastable *DF* phase (beads made by melt quench), during heating superlattice reflections (111) start to appear around 1473 K and become significant at 1673 K (Fig. 2a). Further increase in temperature to 1873 K shows minor superlattice reflections (Fig. 2b), while...
above this temperature no (111) reflection is visible (Fig. 2C), confirming the phase transition to DF. Similar behavior is also observed during cooling; from 2573 to 1773 K there is a (111) superlattice reflection indicative of PY structure (Fig. 2d). Thus, a stepwise first-order (with some hysteresis) reversible phase transformation from ordered (PY) to disordered (DF) is captured for Gd$_2$Zr$_2$O$_7$.

We conducted high-temperature differential thermal analysis (DTA) on Sm$_2$Zr$_2$O$_7$, Eu$_2$Zr$_2$O$_7$, and Gd$_2$Zr$_2$O$_7$. Distinct endothermic (heating) and exothermic (cooling) peaks are observed for Sm$_2$Zr$_2$O$_7$, and Eu$_2$Zr$_2$O$_7$, but no peaks are observed in Gd$_2$Zr$_2$O$_7$. For example, Fig. 3 shows the heating/cooling traces observed for Sm$_2$Zr$_2$O$_7$. The DTA traces indicate a phase transformation at 2282 ± 10 K for Sm$_2$Zr$_2$O$_7$ and 2100 ± 18 K for Eu$_2$Zr$_2$O$_7$. The transition enthalpies for Sm$_2$Zr$_2$O$_7$ and Eu$_2$Zr$_2$O$_7$ were obtained by integrating the high-temperature DTA signal using the melting enthalpy of corundum as a calibration. The measured phase transition enthalpies are 11 ± 2 kJ mol$^{-1}$ on heating and −14 ± 2 kJ mol$^{-1}$ on cooling for Sm$_2$Zr$_2$O$_7$ and 7.4 ± 0.4 kJ mol$^{-1}$ on heating and −8.3 ± 1.0 kJ mol$^{-1}$ on cooling for Eu$_2$Zr$_2$O$_7$. The newly measured transition temperatures from in situ synchrotron diffraction are 2323 K for Sm$_2$Zr$_2$O$_7$ and 2123 K for Eu$_2$Zr$_2$O$_7$, corroborating the DTA studies.

A few reports exist on the high-temperature PY–DF transformations and the existing data show discrepancies. The first report was by Michel et al. on Ln$_2$Zr$_2$O$_7$ (Ln = La, Nd, Sm, Gd) 1. The reported phase transformation temperatures are 2573 K for Nd$_2$Zr$_2$O$_7$, 2273 K for Sm$_2$Zr$_2$O$_7$, 1803 K for Gd$_2$Zr$_2$O$_7$ and 2673 K for Gd$_2$Hf$_2$O$_7$. Zoz et al. reported the transformation at 1993–2053 K in Eu$_2$Zr$_2$O$_7$ 34. Fabrichnaya et al. corrected the PY–DF transition in Eu$_2$Zr$_2$O$_7$ to 2128 K 35. The phase transition temperatures obtained by in situ diffraction and DTA generally show good agreement with literature reports (see Table 3). These observations confirm that aerodynamic levitation combined with in situ diffraction is a very reliable technique to study the phase equilibria of high-temperature ceramics.

Figure 4(a,b) presents the temperature dependence of antisite cationic and oxygen Frenkel occupancies of Sm$_2$Zr$_2$O$_7$ (heating), Eu$_2$Zr$_2$O$_7$ (cooling), and Gd$_2$Zr$_2$O$_7$ (cooling). At lower temperature, the antisite occupancies change smoothly till 2023 K, 1873 K and 1573 K for Sm$_2$Zr$_2$O$_7$, Eu$_2$Zr$_2$O$_7$, and Gd$_2$Zr$_2$O$_7$, respectively. Further increase in temperature shows an abrupt change in antisite occupancies indicating the phase transition to DF. In Eu$_2$Zr$_2$O$_7$ (cooling), and Gd$_2$Zr$_2$O$_7$ (cooling), as temperature decreases, disordering decreases and the structure becomes closer to the ideal PY. Disordering in both cation/ and anion sublattices is inevitable, and intrinsic to PY oxides. For example, it was reported that the as made stoichiometric PYs show disorder in the range of 5 to 10% at room temperature 36,38. Shlyakhitina et al. observed cation antisite disorder of approximately 8, 5, and 22% for Sm$_2$Zr$_2$O$_7$, Eu$_2$Zr$_2$O$_7$, and Gd$_2$Zr$_2$O$_7$, respectively 36. Zhang et al. attempted to synthesize Gd$_2$Zr$_2$O$_7$ samples with different degrees of the disorder by isothermal annealing at 1100–1500 °C. However, a perfectly ordered Gd$_2$Zr$_2$O$_7$ PY structure was never attained even for extended periods of heat treatment. In Gd$_2$Zr$_2$O$_7$, cation disorder of 36.3% was reported in a sample annealed at 1550 °C for 24 hours 37.

From the current study, the percentages of cationic and anionic disorder as a function of temperature are given in Fig. 4(c). Gd$_2$Zr$_2$O$_7$ shows the greatest cationic and anionic disorder, 34.3 ± 1.9% and 16.8 ± 1.6%, respectively. It is well-known that heavier lanthanides do not form ordered zirconates with PY structure and Gd is considered...
the borderline lanthanide between PY and DF structures, so its greater disordering is not surprising. Direct comparison of refinements is not fully appropriate since our study includes Rietveld refinement of both cation and anion disorder whereas the majority of published results refined only cation antisite disorder. However, quenching PY samples such that they would retain different equilibrium degrees of disorder may be difficult or even impossible, particularly for lighter lanthanides which strongly prefer ordered structures. In contrast, aerodynamic levitation and laser heating in combination with in situ synchrotron diffraction is a versatile technique to obtain the actual degree of disorder under high temperature conditions. Previously, we have shown the systematic behavior of cation and anion disorder in Eu$_2$Zr$_2$O$_7$ during heating and cooling using this methodology.

Change of ‘x’ (48f) as a function of temperature. Disordering as a function of temperature can also be observed by monitoring the changes in the 48f oxygen ‘x’ positional parameter. In a large number of PYs, the ‘x’ parameter lies well below 0.375. In the present study, 48f oxygen ‘x’ parameters for Sm$_2$Zr$_2$O$_7$, Eu$_2$Zr$_2$O$_7$ and Gd$_2$Zr$_2$O$_7$ are 0.346 (1), 0.339(2) and 0.345(2), respectively at room temperature. For Eu$_2$Zr$_2$O$_7$ and Gd$_2$Zr$_2$O$_7$, since the initial melt-quench phases are DF, the given ‘x’ values are after quenching from the melt. As the 48f oxygen positional ‘x’ parameter changes smoothly with temperature, until reaching the PY–DF phase boundary, further increase in temperature abruptly raises the value toward 0.375 (see Fig. 4d). In Sm$_2$Zr$_2$O$_7$, ‘x’ is 0.355(3) at 1123 K, showing slightly higher values as it has more disorder due to melt quench, and ‘x’ is lowered to 0.345(2) at 2273 K, indicating the change toward the ideal PY structure. Increasing the temperature to 2373 K raises ‘x’ to 0.352(2), and ‘x’ reaches a maximum of 0.361(5) at 2523 K close to the value for DF (0.375). In Gd$_2$Zr$_2$O$_7$, during...

---

**Table 3.** The PY–DF phase transition temperature and entropy change at Tc (critical transition temp). The given phase transformation temperature from in situ are average during heating and cooling. For Gd$_2$Zr$_2$O$_7$ no heat signal observed in DTA experiment. The $\Delta S_{\text{conf}}$ are calculated right below the transition temperature to that of completely disordered DF.

|                  | Sm$_2$Zr$_2$O$_7$ | Eu$_2$Zr$_2$O$_7$ | Gd$_2$Zr$_2$O$_7$ |
|------------------|-------------------|-------------------|-------------------|
| Tc, K (Literature) | 2273$^3$          | 2128$^3$          | 1803$^3$          |
| Tc, K (in situ)  | 2323              | 2073              | 1773              |
| Tc, K (DTA)      | —                 | —                 | —                 |
| Heating          | 2285 ± 10         | 2113 ± 18         |                   |
| Cooling          | 2278 ± 10         | 2087 ± 12         |                   |
| $\Delta H_{\text{trans}}$, kJ mol$^{-1}$ (DTA) | —                 | —                 | —                 |
| Heating          | 11.0 ± 2.0        | 7.4 ± 0.4         |                   |
| Cooling          | −14.0 ± 2.0       | −8.3 ± 1.0        |                   |
| $\Delta S$, J mol$^{-1}$ K$^{-1}$ (DTA) | 4.8 ± 0.9         | 3.5 ± 0.2         |                   |
| Heating          | −6.2 ± 0.9        | −4.0 ± 0.5        |                   |
| Cooling          | −6.1 ± 0.4        | −5.9 ± 0.7        |                   |
| $\Delta S_{\text{conf}}$, J mol$^{-1}$ K$^{-1}$ (site distribution) | 6.9 ± 0.8         | 7.4 ± 0.5         | —                 |
| Heating          | —                 | —                 | −6.1 ± 0.4        |
| Cooling          | —                 | —                 | −5.9 ± 0.7        |

---

**Figure 3.** Ultra-high-temperature differential thermal analysis performed on Sm$_2$Zr$_2$O$_7$. The given heating and cooling curves are shown after correcting the sample temperature using Al$_2$O$_3$ melting. Heating rate = 20 degrees/min.

---

The change of 'x' parameter is a function of temperature, showing a smooth transition from the PY to DF structure. The transition temperature, Tc, and the corresponding heat and entropy changes are summarized in Table 3. The in situ measurements provide a more accurate representation of the phase transition, while the DTA data give an overview of the transition behavior.

---

The behavior of 'x' parameter as a function of temperature is shown in Figure 3, where the heating and cooling curves are plotted after correcting the sample temperature using Al$_2$O$_3$ melting. The heating rate is 20 degrees/min.

---

The table below summarizes the transition temperature (Tc) and the corresponding heat and entropy changes for Sm$_2$Zr$_2$O$_7$, Eu$_2$Zr$_2$O$_7$, and Gd$_2$Zr$_2$O$_7$. The in situ measurements provide a more accurate representation of the phase transition, while the DTA data give an overview of the transition behavior.

---

The change of 'x' parameter is a function of temperature, showing a smooth transition from the PY to DF structure. The transition temperature, Tc, and the corresponding heat and entropy changes are summarized in Table 3. The in situ measurements provide a more accurate representation of the phase transition, while the DTA data give an overview of the transition behavior.

---

The behavior of 'x' parameter as a function of temperature is shown in Figure 3, where the heating and cooling curves are plotted after correcting the sample temperature using Al$_2$O$_3$ melting. The heating rate is 20 degrees/min.

---

The table below summarizes the transition temperature (Tc) and the corresponding heat and entropy changes for Sm$_2$Zr$_2$O$_7$, Eu$_2$Zr$_2$O$_7$, and Gd$_2$Zr$_2$O$_7$. The in situ measurements provide a more accurate representation of the phase transition, while the DTA data give an overview of the transition behavior.

---

The change of 'x' parameter is a function of temperature, showing a smooth transition from the PY to DF structure. The transition temperature, Tc, and the corresponding heat and entropy changes are summarized in Table 3. The in situ measurements provide a more accurate representation of the phase transition, while the DTA data give an overview of the transition behavior.

---

The behavior of 'x' parameter as a function of temperature is shown in Figure 3, where the heating and cooling curves are plotted after correcting the sample temperature using Al$_2$O$_3$ melting. The heating rate is 20 degrees/min.

---

The table below summarizes the transition temperature (Tc) and the corresponding heat and entropy changes for Sm$_2$Zr$_2$O$_7$, Eu$_2$Zr$_2$O$_7$, and Gd$_2$Zr$_2$O$_7$. The in situ measurements provide a more accurate representation of the phase transition, while the DTA data give an overview of the transition behavior.
cooling from 2373 K to room temperature, the PY phase appears at 1873 K, and \( \alpha \) decreases from 0.367(5) to 0.345(2), indicating change toward the ideal PY structure. Previously, we have reported the changes in \( \alpha \) vs. temperature for Eu2Zr2O7, and the trend correlates well with the current study. The change in lattice constant, refined occupancies, 48f oxygen \( \alpha \) positional parameter, % disorder (both cation and anion), and agreement factors (R-factors namely Bragg R, Rf-factor, and Chi2) during heating and cooling as a function of temperature are documented in Tables S2, S3 and S4 in SI.

**Thermodynamic Model of Disordering**

Any high temperature equilibrium phase transactions involving order–disorder reflects a balance between the enthalpy of disordering and the configurational entropy created by disorder on crystallographic sites on the available sublattices. The equilibrium disordering can occur gradually with temperature, representing a second order or more complex transition, or it can occur sharply at one temperature (sometimes with hysteresis), representing a first order transition. In real systems, a transition can show complex behavior, with gradual disordering over a temperature range culminating in a first order transition, or with some short-range order persisting in the high temperature nominally disordered phase. A first-order transformation is accompanied by an abrupt change in enthalpy and entropy. The Gibbs free energy difference between the two phases is

\[
\Delta G = \Delta H - T \Delta S
\]

and since \( \Delta G = 0 \) at the equilibrium temperature,

\[
\Delta H = T \Delta S
\]

In pyrochlore oxides, the disordering proceeds gradually as a function of temperature via the formation of cation antisite (CA) and anion Frenkel pair (AFB) defects. For the general formula, \([(A_{1-x}B_x)_{16d} \{B_{1-x}A_x\}_{16c} (O_{6-y}\square_y)_{48f} (\square_{1-y}O_y)_{8a} O'_{8b}]\), the cation/anion distribution is described by the following site interchange reactions. For cation antisite disorder:

\[
A_{16d}^{3+} + B_{16c}^{4+} \leftrightarrow A_{16c}^{3+} + B_{16d}^{4+} \quad (1-x) \quad (1-x) \quad x \quad x
\]

**Figure 4.** Change in (a) antisite cation occupancies, (b) anion Frenkel occupancy, (c) percentage of cation and anion disorder and (d) change in 48f oxygen \( \alpha \) positional parameter as a function of temperature for Sm2Zr2O7, Eu2Zr2O7 and Gd2Zr2O7. In the case of Sm2Zr2O7, the temperatures are corrected to diffracted volume (\( T_v \)). The \( T_v \) was calculated based on the observed difference in melting temperature from cooling trace and in situ diffraction.
For anion Frenkel disorder:

$$O_{4y'} + \square_{8a} \rightarrow O_{8a}^2 + \square_{4g}$$

(6-\(y\)) \(y\) \(y\) \(y\) (4)

Eq. (3) represents the cation exchange equilibrium reaction involving one mole of ‘A’ and one of ‘B’. The equilibrium constant at a given temperature is written as:

$$K_{cat} = \ln \left[ \frac{x^2}{(1-x)^y} \right]$$

$$\ln K_{cat} = 2 \ln \left[ \frac{x}{1-x} \right] \text{ (for two moles of cations)}$$

$$\ln K_{cat} = 4 \ln \left[ \frac{x}{1-x} \right] \text{ (for four moles of cations per A}_2\text{B}_2\text{O}_7 \text{ formula)}$$

(5)

Eq. (4) represents the anion exchange equilibrium reaction involving six moles of oxide ions and one mole of vacant anionic sites per A2B2O7 formula. The equilibrium constant at a given temperature is:

$$\ln K_{anion} = \ln \left[ \frac{y^2}{(6-y)(1-y)} \right]$$

(6)

The relation between equilibrium constant (\(\ln K\)) and Gibbs free energy is,

$$\Delta G = -RT \ln K$$

By substituting Eq. (6) & (7) in Eq. (1), the equilibrium constant can be written as follows

$$\ln K = -\frac{\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

(8)

The non-configurational entropy change associated with disordering is neglected, and we assumed the distribution of both cations and anions in a given sublattice is random. The configurational entropy (\(S_{conf}\)) for a PY phase involves four moles of cations (2 moles of A-site + 2 moles of B-site), six moles of oxygens (6 moles of 48f) and 1 mole of 8a vacant sites (whereas the 1 mole of 8b oxygens does not participate in Frenkel formation), is

$$S_{conf, cat} = -4R[(1-x)\ln(1-x) + x \ln x]$$

$$S_{conf, ani} = -R \left[ \frac{y}{6} \ln \left( \frac{y}{6} \right) + \frac{6-y}{6} \ln \left( \frac{6-y}{6} \right) \right] + (1-y)\ln(1-y) + y \ln y$$

(9)

$$S_{conf, ani} = -R \left[ \frac{6-y}{6} \ln \left( \frac{6-y}{6} \right) + \frac{y}{6} \ln \left( \frac{y}{6} \right) \right] + (1-y)\ln(1-y) + y \ln y$$

(10)

where ‘x’ is the fraction of 16d-site cations in the 16c-site and ‘y’ is the fraction of 48f oxygens in 8a vacant site. The total configuration entropy for both cation and anion distribution in a disordered PY (DPY) is given by \(S_{conf, DPY} = S_{conf, cat} + S_{conf, ani}\). The configurational entropy of the fully disordered DF (i.e. A1_0.5B1_0.5O_2-x) is 0.5 is fully disordered state) equivalent to PY stoichiometry including the disordering of 8b oxygens is constructed as follows:

$$S_{conf, DF} = -4R[(1-x)\ln(1-x) + x \ln x] + \frac{x}{2} \ln \frac{x}{4} + \frac{2-x}{2} \ln \left[ \frac{1-x}{4} \right]$$

(11)

The configurational entropy for an ideal fully ordered PY phase is zero, and that of the completely disordered DF phase is 48.11 J K^{-1} mol^{-1}. The detailed configurational entropy calculations are provided in the supporting information.

The \(S_{conf}\) for Sm2Zr2O7, Eu2Zr2O7, and Gd2Zr2O7, based on site distribution at each temperature increment is given in the supporting information, Table S5. The entropy change for the phase transition from PY to DF is also calculated from the enthalpies obtained by DTA using Eq. (8). The calculated entropy change during cooling from DTA are 4.8 ± 0.9/−6.2 ± 0.9 and 3.5 ± 0.2/−4.0 ± 0.5 J mol^{-1} K^{-1} for Sm2Zr2O7 and Eu2Zr2O7, respectively (see, Table 3). The Table 3 shows that the entropy change calculated from the enthalpies obtained by DTA using Eq. (2) is indeed similar to the \(\Delta S_{conf}\) from site distribution. For example, for Eu2Zr2O7, the entropy change for ordering during cooling is −4.0 ± 0.5 J mol^{-1} K^{-1} from the site distribution. Previously we reported the PY–DF phase transformation enthalpy for Eu2Zr2O7 to be 37.8 ± 3.1 kJ mol^{-1} by measuring the enthalpy of the solution in a molten oxide solvent of PY and a laser-melt-quenched DF phase of the same composition. However, the structural state of the samples was not characterized in detail, so the results cannot be compared directly to those from the in situ high temperature DTA and site distributions in the present work.

Shamblin et al. and others suggest substantial short-range order at the nanoscale, as described as a weberite-type structure that is derivitive of fluorite structure bearing a higher degree of order than DF, in radiation-damaged PY. However, at present, there is no evidence, pro or con, of weberite-like ordering in situ at high temperatures, in either the partially disordered PY or DF phases. In situ, high-temperature neutron studies would be desirable to investigate this further, as X-ray diffraction gives little information about the short-range order on the oxygen sublattice. Without further information about range order, we proceed below to apply a thermodynamic model that assumes random distributions of the ions on each sublattice constrained by the measured site occupancies.
In the gradual disordering of PY with temperature, the favorable configurational entropy and the unfavorable energy (enthalpy) of disordering balance each other, resulting in greater disorder with increasing temperature. This balance can be described by an equilibrium constant analogous to that for spinel disordering\(^{22}\) to calculate the disordering enthalpy from the site distribution. Using this approach, the cation and anion disorder follow simple interchange reactions.

The following assumptions are made based on Navrotsky and Kleppa’s work on spinel disordering\(^{22}\):

\[
\Delta H = x \Delta H_{\text{int}}; \tag{12}
\]
\[
\Delta H = y \Delta H_{\text{int}}; \tag{13}
\]

(‘\(x\)’ and ‘\(y\)’ are fractions of cation and anion interchange)

\[
\Delta S = S_{\text{conf cat}}. \tag{14}
\]

or

\[
S_{\text{conf ani}}. \tag{15}
\]

These equations imply that (a) the exchange of both cations and anions on each sublattice is ideal, i.e. there is negligible short-range order on each sublattice and no correlation between cation and anion distributions, (b) the enthalpy depends only on the interchange parameter and not on the extent of exchange, and (c) the entropy of disordering is configurational only. Substituting Eq. (11), (13) in (8) for cation antisite disorder and Eq. (12), (14) in (8) for anion Frenkel disorder and minimizing the free energy at a given temperature leads to the following relation for cation and anion interchange or disordering enthalpy:

\[
\text{For cation interchange, } \Delta H_{\text{int, cat}} = -4RT \ln \left( \frac{x}{1-x} \right) \tag{16}
\]

\[
\text{For anion interchange } \Delta H_{\text{int, ani}} = -RT \ln \left( \frac{y^2}{(6-y)(1-y)} \right) \tag{17}
\]

The molar enthalpies of interchange as a function of temperature using equations (15) and (16) are calculated for both CA and AFP disorder. Table 4 provides the calculated interchange enthalpy (enthalpy of disordering) values for RE\(_2\)Zr\(_2\)O\(_7\) [RE = Sm, Eu, and Gd]; the disordering appears to reach equilibrium (similar site occupancies on heating and cooling and consistent calculated interchange enthalpies over the range of temperatures marked in bold and italic). The calculations of equilibrium constant also left out the highest temperature points in the region of the transition from PY to DF since that transition appears to have a first order component and represents changes distinct from the equilibrium disordering within the PY phase. The average interchange enthalpies for cation disorder (CA) are 114.9 ± 9.6, 109.1 ± 13.6 and 90.9 ± 5.4 kJ·mol\(^{-1}\), and for anion Frenkel pair (AFP) disorder 29.9 ± 3.7, 35.6 ± 3.5 and 35.9 ± 2.8 kJ·mol\(^{-1}\) for Sm, Eu, and Gd zirconates, respectively. The AFP interchange enthalpies show similar values for all three compositions and apparently do not depend on the size of the cation. The CA interchange enthalpy decrease with decreasing A-cation radius suggests greater disorder for smaller A-site cations at a given temperature. At any given temperature greater anion disorder exists than cation disorder.

Since numerous computational studies report somewhat different defect energies in various PY oxides by applying force field (FF) and density functional theory (DFT) calculations, we will not compare our experimental values individually, but discuss general trends. The energies obtained by FFA calculations for RE\(_2\)Zr\(_2\)O\(_7\) [RE = Sm, Eu, and Gd] range between 360 and 400 kJ·mol\(^{-1}\) for cation disorder and 480 and 560 kJ·mol\(^{-1}\) for anion Frenkel disorder\(^{22,23}\). The FF modeling studies consider a single defect formation energies at 0 K, whereas in the current study the defect energy values are obtained on a structure that already contains a significant amount of disorder at room temperature (5–10%) and even more in the range of the measurements. So, the direct quantitative comparison may not be appropriate. The recent DFT calculations show lower values ranging between 160 and 200 kJ·mol\(^{-1}\) for cation disorder and negative values for anion Frenkel disorder, especially for compositions that lie near the PY–DF phase boundary\(^{24}\).

The current experimentally derived values range between 90 and 140 kJ·mol\(^{-1}\) for CA, and 30–36 kJ·mol\(^{-1}\) for AFP disorder, reasonably similar to the DFT calculations\(^{24}\). Both computational and experimental trends follow radius ratio \(r_A/r_{Zr}\) rules; i.e. the phase transition to DF shifts to lower temperatures as the radius of the A-site cation decreases and the lowest interchange enthalpy is associated with Gd\(_2\)Zr\(_2\)O\(_7\), which shows the greatest tendency to disorder.

**Conclusions**

We investigated the temperature-induced order–disorder phase transition in zirconate pyrochlores using a combination of in situ synchrotron X-ray diffraction and aerodynamic levitation with laser heating up to the melting points. The obtained diffraction pattern at each temperature was subjected to Rietveld analysis to extract the change in lattice constant, antisite cation/anion occupancies and phase transition temperatures. The lattice constant changed smoothly as a function of temperature, and the calculated thermal expansion coefficients fall in the range of 8.6 to 10.8 \(\times\) 10\(^{-5}\) K\(^{-1}\). For the first time, we have experimentally determined the cation and anion disorder enthalpies based on a simple thermodynamic model and antisite cation and anion Frenkel occupancies. The anion Frenkel disorder enthalpies are lower than those for cation antisite disorder. This thermodynamic
### Table 4. The calculated Interchange enthalpies based on site distribution for Sm$_2$Zr$_2$O$_7$, Eu$_2$Zr$_2$O$_7$ and Gd$_2$Zr$_2$O$_7$ as a function of temperature. Sm$_2$Zr$_2$O$_7$ (heating) whereas Eu$_2$Zr$_2$O$_7$ and Gd$_2$Zr$_2$O$_7$ (cooling), the bold & italic face numbers show the state of equilibrium. The temperature of diffraeted volume, $T_v$ was calculated based on the observed differences in melting temperature obtained from cooling traces and in situ diffraction.

| $T_v$, K | $\Delta H_{\text{int}}$, kJ.mol$^{-1}$ Sm$_2$Zr$_2$O$_7$ | $\Delta H_{\text{int}}$, kJ.mol$^{-1}$ Eu$_2$Zr$_2$O$_7$ | $\Delta H_{\text{int}}$, kJ.mol$^{-1}$ Gd$_2$Zr$_2$O$_7$
|---|---|---|---|
| Cation | Anion | Cation | Anion | Cation | Anion |
| 2423 | 80.3 ± 8.9 | 2073 | 119.7 ± 6.6 | 2423 | 23.7 ± 5.9 |
| 2223 | 93.3 ± 5.2 | 1873 | 6.2 ± 3.5 | 2123 | 23.2 ± 3.9 |
| 1223 | 120.0 ± 5.3 | 1673 | 121.8 ± 3.7 | 2023 | 6.8 ± 3.3 |
| 1923 | 128.3 ± 5.1 | 1573 | 112.5 ± 3.4 | 1823 | 5.0 ± 3.2 |
| 1723 | 115.9 ± 9.3 | 1373 | 120.6 ± 2.6 | 1623 | 4.0 ± 3.0 |
| 1523 | 104.4 ± 5.4 | 1173 | 89.6 ± 2.8 | 1423 | 3.2 ± 3.0 |
| 1323 | 97.4 ± 4.3 | 973 | 107.0 ± 2.1 | 1223 | 2.6 ± 2.2 |
| 1123 | 75.0 ± 3.7 | 873 | 54.5 ± 1.5 | 1023 | 1.7 ± 1.5 |
| 298 | 15.0 ± 0.4 | 5.50 ± 0.7 | 298 | 2.6 ± 2.2 |

**Model**: The model can easily be extended to a variety of PY compounds to understand the disordering energetics, thereby tuning their functional properties. Diffraction on laser-heated aerodynamically levitated samples allows precise structural characterization and enables determination of disordering enthalpies and thermal expansion close to the melting point.

**Methods**

**Sample preparation and characterization.** A series of stoichiometric rare earth pyrochlores (PY) with the general formula $\text{A}_2\text{B}_2\text{O}_7$, where $\text{A} =$ Rare earth (RE), $\text{B} =$ Zr, Hf was synthesized by laser hearth melting. The starting materials used were high purity ZrO$_2$ (Aldrich; 99.99%), HfO$_2$ (Alfa Aesar; 99.9%), and RE$_2$O$_3$ (Alfa Chino, Tokyo, Japan) with emissivity set to 0.93. An unconditioned beam from a Synrad CO$_2$ laser was used for high-sensitivity fast-readout large-area flat panel detector based on amorphous silicon was used to collect the measurements, 0.139397 Å in beamline 6-ID-D, and 0.10798 Å in beamline 11-ID-C. A Perkin Elmer XRD 1621 structural characterization and enables determination of disordering enthalpies and thermal expansion close to the melting point.

**Thermal Analysis.** Ultra-high-temperature differential thermal analysis (DTA) was carried out on Sm$_2$Zr$_2$O$_7$, Eu$_2$Zr$_2$O$_7$ and Gd$_2$Zr$_2$O$_7$ using a Setaram Setsys 2400 (Caluire, France). Tungsten crucibles with lids were finely ground and melted in a copper hearth into oblate spheroids 1.5–2.5 mm in diameter with a CO$_2$ laser using an experimental setup described in detail elsewhere.

**High-temperature in situ diffraction on levitated samples.** To gain insight into the essential structural features associated with temperature change, and to capture the gradual disordering in complex PY oxides, all the compositions were subjected to incremental heating using aerodynamic levitation and laser heating followed by in situ synchrotron diffraction at each temperature. The high-temperature in situ synchrotron X-ray diffraction experiments were performed at the Advanced Photon Source, Argonne National Laboratory, Illinois (USA) at beamlines 11-ID-C and 6-ID-D. Two different wavelengths were used for the high-energy X-ray measurements, 0.139397 Å in beamline 6-ID-D, and 0.10798 Å in beamline 11-ID-C. A Perkin Elmer XRD 1621 high-sensitivity fast-readout large-area flat panel detector based on amorphous silicon was used to collect the scattered high-energy X-rays. The sample–detector distance and tilt angle were set to the maximum distance (~1 m) to increase resolution. The sample temperature was measured by a single-band pyrometer (IR-CAS5CS; Chino, Tokyo, Japan) with emissivity set to 0.93. An unconditioned beam from a Synrad CO$_2$ laser was used for sample heating. The experimental arrangement, including the aerodynamic levitator, was described in detail by...
Rietveld structure refinement. The high-temperature in situ synchrotron diffraction data was grouped into two sets based on the quality of data obtained and beamline used. A complete Rietveld structure refinement was performed for high-temperature diffraction data on Sm₂Zr₂O₇, Eu₂Zr₂O₇, and Gd₂Zr₂O₇ using the FULLPROF program. All the refinements were performed in the following manner. The background was selected manually, and a pseudo-Voigt function was used to model the peak shape. After successful refinement of the scale factor, lattice constant, peak shape, the antisite cation distribution (between 16d/16c crystallographic sites) and anion Frenkel (vacancy on a 48f site and oxygen on 8a site) was refined under the constraint of stoichiometric composition. Finally, the 48f ‘x’ positional and isothermal parameters were refined. For the high-temperature diffraction data from the LaₓHfₓO₇, NdₓZrₓO₇, NdₓHfₓO₃ and SmₓHfₓO₇ phases, pattern matching was performed using the Le Bail method for unit cell refinement.

References
1. Michel, D., Perez, Y. J. M. & Collongues, R. Order-disorder transformation of the fluorite structure to the pyrochlore structure for the phases (1-x)zirconium oxide-x lanthanum oxide. Mater. Res. Bull. 9, 1457–68 (1974).
2. Turner, K. M. et al. Pressure-induced structural modifications of rare-earth hafnate pyrochlore. J. Phys. Condens. Matter Inst. Phys. J. 29, 255401 (2017).
3. Sickafus, K. E. et al. Radiation-induced amorphization resistance and radiation tolerance in structurally related oxides. Nat. Mater. 6, 217–23 (2007).
4. Li, Y. H. et al. Role of antisite disorder on preamorphization swelling in titinate pyrochlores. Phys. Rev. Lett. 108, 195504 (2012).
5. Maram, P. S., Ushakov, S. V., Weber, R. J. K., Benmore, C. J. & Navrotsky, A. In Situ Diffraction from Levitated Solids Under Extreme Conditions—Structure and Thermal Expansion in the EuO₂-ZrO₂ System. J. Am. Ceram. Soc. 98, 1299–1309 (2015).
6. Moon, P. K. & Fuller, H. L. Ionic conduction in the gadolinium titane-gadolinium zirconate (Gd₂Ti₂O₇-Gd₂Zr₂O₇) system. Solid State Ion. 28–30, 470–4 (1988).
7. Wuensch, B. J. et al. Connection between oxygen-ionic conductivity of pyrochlore fuel-cell materials and structural composition with temperature and solid state. Solid State Ion. 129, 111–133 (2000).
8. Oh, S. H., Black, R., Pomerantseva, E., Lee, J.-H. & Nazer, L. F. Synthesis of a metallic mesoporous pyrochlore as a catalyst for lithium- O₂ batteries. Nat Chem 4, 1004–1010 (2012).
9. Subramanian, M. A., Aravamudan, G. & Rao, G. V. S. Oxide pyrochlores - a review. Prog. Solid State Chem. 15, 55–143 (1983).
10. Lehmann, H., Pitzen, D., Pracht, G., Vassen, R. & Stoever, D. Thermal conductivity and thermal expansion coefficients of the lanthanum rare-earth-element zirconate system. J. Am. Ceram. Soc. 86, 1338–1344 (2003).
11. Ewing, R. C., Weber, W. J. & Lian, J. Nuclear waste disposal-pyrochlore (A₂B₂O₇): Nuclear waste form for the immobilization of plutonium and 'minor' actinides. J. Appl. Phys. 95, 5949–5971 (2004).
12. Fischer, C., Finkeldei, S., Brandt, F., Boobach, D. & Luttge, A. Direct Measurement of Surface Dissolution Rates in Potential Nuclear Waste Forms: The Example of Pyrochlore. ACS Appl. Mater. Interfaces 7, 17857–17865 (2015).
13. Shlyakhtina, A. V. et al. Ionic Conductivity of Ln₂₋₀.₅Zr₂₋₀.₅O₇ (Ln = Sm-Gd) Solid Solutions. Inorg. Mater. 41, 854–863 (2005).
14. Shamblin, J. et al. Probing disorder in isometric pyrochlore and related complex oxides. Nat. Mater. 15, 507–511 (2016).
15. Shamblin, J. et al. Similar local order in disordered fluorite and aperiodic pyrochlore structures (2017).
16. Uberuaga, B. P. Complex oxides Intricate disorder. Mater. Res. Bull. 49, 496–497 (2014).
17. Simeone, D. et al. Intricate disorder in defect fluorite/pyrochlore: a concord of chemistry and crystallography. Sci. Rep. 7, 3727 (2017).
18. Solomon, J. M., Sharbini, J., Lang, M., Navrotsky, A. & Asta, M. Chemical ordering in substituted fluorate oxides: a computational investigation of Ho₂ZrO₄ and RE₂ThO₃ (RE = Ho, Y, Gd, Nd, La). Scr. Mater. 86, 3872–3877 (2016).
19. Chriseos, A., Rushton, M. J. D., Jiang, C. & Iosukalas, L. H. Nuclear wasteform materials: Atomic simulation case studies. J. Nucl. Mater. 441, 29–39 (2013).
20. Sickafus, K. E. et al. Radiation tolerance of complex oxides. Science 299, 748–751 (2000).
21. Minervini, L., Grimes, R. W. & Sickafus, K. E. Disorder in pyrochlore oxides. J. Am. Ceram. Soc. 83, 1873–1878 (2000).
22. Panero, W. R., Stixrude, L. & Ewing, R. C. First-principles calculation of defect-formation energies in the Y₂(Sn, Zr)₂O₇ pyrochlore. Phys Rev B 70, 054110 (2004).
23. Chen, Z., Xiao, H. Y., Zu, X. T. & Gao, F. First-principles calculation of defect formation energies and electronic properties in stannate pyrochlores. J. Appl. Phys. 104, 093702 (2008).
24. Chartier, A., Meis, C., Weber, W. I. & Corrales, L. R. Theoretical study of disorder in Ti-substituted LaₓZrₓO₇. Phys Rev B 65, 134116 (2002).
25. Li, Y. V. et al. Defect formation energies in A₂B₂O₇ pyrochlores. Scr. Mater. 107, 18–21 (2015).
26. Shlyakhtina, A. V. et al. Effects of the synthesis procedure, doping and non-stoichiometry on the order-disorder transformation in Ln₂Ti₂O₇ (Ln = Tm-Lu) oxygen-ion conductors. Solid State Ion. 176, 2297–2304 (2005).
27. Shlyakhtina, A. V., Karyagina, O. K. & Scherbakova, L. G. Order-Disorder Transformations in Ln₂Ti₂O₇ (Ln = Lu, Yb, Tm, Gd). Inorg. Mater. Trans. Neorganicheskie Mater. 40, 59–63 (2004).
28. Wilde, P. J. & Catlow, C. R. A. Defects and diffusion in pyrochlore structured oxides. Solid State Ion. 112, 173–183 (1998).
29. Navrotsky, A. & Kleppa, O. J. Thermodynamics of cation distributions in simple spinels. Inorg. Nucl. Chem. 29, 2701–14 (1967).
30. Saradhi, M. P., Ushakov, S. V. & Navrotsky, A. Fluorite-pyrochlore transformation in Eu₂Zr₂O₇-direct calorimetric measurement of phase transition, formation and surface enthalpies. RSC Adv. 2, 3328–3334 (2012).
31. Korty, G. K. V., Rajagopalan, S., Mathews, C. K. & Varadaraju, U. V. Thermal expansion behavior of some rare earth oxide pyrochlores. Mater. Res. Bull. 29, 759–66 (1994).
32. Zoz, E. I., Alekhin, A. I., Nikolaichuk, I. K. & Belyaev, S. L. High-temperature x-ray diffraction study of the structure and properties of solid solutions from zirconium and hafnium dioxides. Ogneupory 26–8 (1986).
33. Van Dijk, T., Helmholdt, R. B. & Burggraaf, A. J. Neutron Powder Diffraction Studies of Fluorite and Pyrochlore Nd₆Zr₁₋ₓO₄₋ₓ/2 Solid Solutions with 0.25. *Phys. Status Solidi B* 101, 765–774 (1980).
34. Zoz, E. I., Fomichev, E. N., Kalashnik, A. A. & Eliseeva, G. G. Structure and properties of zirconates and hafnates of rare-earth elements. *Russ. J. Inorg. Chem.* 27, 54–56 (1982).
35. Fabrichnaya, O. et al. Heat capacity for the Eu₆Zr₂O₉ and phase relations in the ZrO₂-EuO₁₋ₓ system: Experimental studies and calculations. *Thermochim. Acta* 558, 74–82 (2013).
36. Shlyakhtina, A. V. et al. Effect of non-stoichiometry and synthesis temperature on the structure and conductivity of Laₓ₋₀.₅Mₓ₋₀.₅Oₓ₋₁₋₀.₂ (Ln = Sm-Gd; M = Zr, Hf; x = 0–0.286). *Solid State Ion.* 178, 59–66 (2007).
37. Zhang, F. X., Lang, M. & Ewing, R. C. Atomic disorder in Gd₂Zr₂O₇ pyrochlore. *Appl. Phys. Lett.* 106, 191902 (2015).
38. Finkeldi, S. et al. Composition dependent order-disorder transition in Ndₓ₋₀.₅Mₓ₋₀.₅Oₓ₋₁₋₀.₂ pyrochlores: A combined structural, calorimetric and ab initio modeling study. *Acta Mater.* 125, 166–176 (2017).
39. Ushakov, S. V., Shvarev, A., Alexeev, T., Kapush, D. & Navrotsky, A. Drop-and-Catch (DnC) Calorimetry Using Aerodynamic Levitation and Laser Heating. *J. Am. Ceram. Soc.* 100, 754–760 (2017).
40. Pavlik, A. III., Ushakov, S. V., Navrotsky, A., Benmore, C. J. & Weber, R. J. K. Structure and thermal expansion of Lu₂O₃ and Yb₂O₃ up to the melting points. *J. Nucl. Mater.* 495, 385–391 (2017).
41. Radha, A. V., Ushakov, S. V. & Navrotsky, A. Thermochemistry of lanthanum zirconate pyrochlore. *J. Mater. Res.* 24, 3350–3357 (2009).
42. Benmore, C. J. & Weber, R. J. K. Aerodynamic levitation, supercooled liquids and glass formation. *Adv. Phys. X* 2, 717–736 (2017).
43. Chupas, P. J., Chapman, K. W. & Lee, P. L. Applications of an amorphous silicon-based area detector for high-resolution, high-sensitivity and fast time-resolved pair distribution function measurements. *J. Appl. Crystallogr.* 40, 463–470 (2007).
44. Weber, J. K. R., Benmore, C. J., Jennings, G., Wilding, M. C. & Parise, J. B. Instrumentation for fast in situ X-ray structure measurements on non-equilibrium liquids. *Nucl. Instrum. Methods Phys. Res. Sect. Accel. Spectrometers Detect. Assoc. Equip.* 624, 728–730 (2010).
45. Weber, J. K. R. et al. Aerodynamic levitator for in situ X-ray structure measurements on high temperature and molten nuclear fuel materials. *Rev. Sci. Instrum.* 87, 073902/1–073902/9 (2016).
46. Krishnan, S. et al. Levitation apparatus for structural studies of high temperature liquids using synchrotron radiation. *Rev. Sci. Instrum.* 68, 3512–3518 (1997).
47. Weber, R. J. K. et al. AERO-acoustic levitation: a method for containerless liquid–phase processing at high temperatures. *Rev. Sci. Instrum.* 65, 456–65 (1994).
48. Hammersley, A. P., Svensson, S. O., Hanfland, M., Fitch, A. N. & Hausermann, D. Two-dimensional detector software: From real detector to idealised image or two-theta scan. *High Press. Res.* 14, 235–248 (1996).
49. Hammersley, A. P. FIT2L: a multi-purpose data reduction, analysis and visualization program. *J. Appl. Crystallogr.* 49, 646–652 (2016).
50. Ushakov, S. V., Navrotsky, A., Weber, R. J. K. & Neuefeind, J. C. Structure and Thermal Expansion of YSZ and La₂Zr₂O₇ Above 1500 °C from Neutron Diffraction on Levitated Samples. *J. Am. Ceram. Soc.* 98, 3381–3388 (2015).
51. Rietveld, H. M. Profile refinement method for nuclear and magnetic structures. *J. Appl. Crystallogr.* 2, 65–71 (1969).
52. Le Bail, A. Whole powder pattern decompositon methods and applications: A retrospective. *Powder Diffr.* 20, 316–326 (2005).

Acknowledgements
This work was supported by the US Department of Energy, Office of Basic Energy Science, grant DE-FG02-03ER46053. Use of the Advanced Photon Source (APS), an Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory, which is funded under U.S. DOE, BES contract number DE-AC02-06CH11357. The author RJKW was supported by grant number DE-SC0015241. The authors are indebted to Lawrie Skinner for help with data collection at APS.

Author Contributions
P.S.M., S.V.U. and A.N. conceived and designed the experiments. P.S.M., S.U.V., R.J.K.W. and C.J.B. collected experimental data. P.S.M. analyzed the synchrotron X-ray diffraction patterns. P.S.M. and A.N. worked out the thermodynamic model. All the authors contributed to the manuscript preparation.

Additional Information
Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-018-28877-x.

Competing Interests: The authors declare no competing interests.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.