First-Principles Structural, Mechanical, and Thermodynamic Calculations of the Negative Thermal Expansion Compound $\text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2$

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ABSTRACT: The negative thermal expansion (NTE) material $\text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2$ has been investigated for the first time within the framework of the density functional perturbation theory (DFPT). The structural, mechanical, and thermodynamic properties of this material have been predicted using the Perdew, Burke and Ernzerhof for solid (PBEsol) exchange–correlation functional, which showed superior accuracy over standard functionals in previous computational studies of the NTE material $\alpha$-$\text{ZrW}_2\text{O}_8$. The bulk modulus calculated for $\text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2$ using the Vinet equation of state at room temperature is $K_0 = 63.6$ GPa, which is in close agreement with the experimental estimate of 61.3(8) at $T = 296$ K. The computed mean linear coefficient of thermal expansion is $-3.1 \times 10^{-5}$ K$^{-1}$ in the temperature range $\sim 0$–70 K, in line with the X-ray diffraction measurements. The mean Grüneisen parameter controlling the thermal expansion of $\text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2$ is negative below 205 K, with a minimum of $-2.1$ at 10 K. The calculated standard molar heat capacity and entropy are $C_V = 287.6$ and $S^0 = 321.9$ J mol$^{-1}$ K$^{-1}$, respectively. The results reported in this study demonstrate the accuracy of DFPT/PBEsol for assessing or predicting the relationship between structural and thermomechanical properties of NTE materials.

1. INTRODUCTION

Negative thermal expansion (NTE) materials have received considerable experimental and theoretical attention over the past few decades.1–9 In contrast to most materials, which expand on heating due to anharmonic lattice dynamics,10 NTE materials contract as the temperature rises, owing to mechanisms ranging from structural/magnetic phase transitions to anomalous vibrational modes (e.g., transverse vibrational modes or rigid unit modes).3,5,7,8 Well-known examples of NTE materials include silicon, germanium, uranium, $\beta$-quartz, elastomers, as well as some framework-structured ceramics and zeolites.1,3 NTE materials are often used as thermal-expansion compensators in composites designed to have overall zero or tunable thermal expansion.7,8 Precise control of the thermal expansion of materials is critical, for example, in high-precision optical systems, nanoscale semiconductor devices, fuel cells, or high-performance thermoelectric converters.5,7,8

Several phases in the $\text{Zr}/\text{W}/\text{O}$, $\text{Zr}/\text{V}/\text{P}/\text{O}$, and $\text{Zr}/\text{W}/\text{P}/\text{O}$ systems have been identified as low or negative thermal expansion materials.11–28 Among crystalline phases of the $\text{Zr}/\text{W}/\text{P}/\text{O}$ system, $\text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2$ was the first reported structure featuring coexistence of $\text{WO}_4$ and $\text{PO}_4$ coordination.

$\text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2$ was originally synthesized by Martinek and Hummel29 as the ternary compound $2\text{ZrO}_2\cdot\text{WO}_3\cdot\text{P}_2\text{O}_5$ and characterized by Tsvigunov and Sirotinkin.30 Using room-temperature powder X-ray diffraction (XRD) data, Evans et al.31 fully solved the structure of $\text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2$, which crystallizes in the orthorhombic space group $\text{Pnca}$ (IT no. 60, setting no. 3 $\text{Pnca}$ $(c, a, b)$; $a = 9.35451(9)$, $b = 12.31831(9)$, and $c = 9.16711(8)$ $\text{Å}$; $Z = 4$), with corner-sharing $\text{ZrO}_6$ octahedral and $\text{WO}_4$ and $\text{PO}_4$ tetrahedral coordination units. This structure is related to the phases $\text{A}_2(\text{MO}_4)_3$ (with $\text{M} = \text{Mo, A = Al, Sc, Cr, Fe, Y, In, Ho, Er, Tm, Yb, and Lu}$, or with $\text{M} = \text{W, A = Al, Sc, Fe, In, Y, Gd, Tb, Dy, Ho, Yb, Tm, Yb, and Lu}$) which adopt the orthorhombic $\text{Pbnm}$ or monoclinic $\text{P2}_1/\text{a}$ arrangements.

As shown in dilatometer and XRD studies, orthorhombic $\text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2$ exhibits unusual NTE over a broad temperature range from below room-temperature up to $\sim 1373$ K, without phase transition at atmospheric pressure.32–37 As discussed by Evans et al.,32 NTE in both $\text{A}_2(\text{MO}_4)_3$ and...
ZrW$_2$O$_8$_-type structures stems from the transverse thermal motion of bridging O atoms in A–O–M or Zr–O–W linkages. Owing to its remarkable thermal stability, Zr$_2$(WO$_4$)$_3$(PO$_4$)$_2$ is often combined with other NTE materials in the fabrication of a variety of NTE composites (e.g., Zr$_2$(WO$_4$)$_3$(PO$_4$)$_2$/ZrW$_2$O$_8$ or Zr$_2$(WO$_4$)$_3$(PO$_4$)$_2$/ZrV$_0.6$P$_1.4$O$_7$).

However, synthesis of Zr$_2$(WO$_4$)$_3$(PO$_4$)$_2$ with consistent and well-controlled NTE properties has revealed to be challenging. Evans et al.\textsuperscript{32} reported mean linear coefficients of thermal expansion (CTE) of $-6 \times 10^{-6}$ and $-3 \times 10^{-6} \text{K}^{-1}$ using dilatometer and XRD measurements, respectively, in the temperature range $\sim$50–450 K. Cetinkol and Wilkinson\textsuperscript{34} obtained a value of $-5 \times 10^{-6} \text{K}^{-1}$ from neutron diffraction data between 60 and 300 K and Isobe et al. measured a value of $-3.4 \times 10^{-6} \text{K}^{-1}$ in the range $\sim$300–875 K. Recently, values of $-2.36 \times 10^{-6}$ and $-2.61 \times 10^{-6} \text{K}^{-1}$ were estimated by Liu et al. in the temperature range $\sim$300–1000 K for Zr$_2$(WO$_4$)$_3$(PO$_4$)$_2$ samples sintered at 1573 and 1673 K, respectively. Such differences in CTE can be ascribed to the different porosities or average grain sizes resulting from sintering conditions and synthesis reactions\textsuperscript{35–37} as well as to possible pressure-induced phase transformations\textsuperscript{41} during sample fabrication. Apart from these CTE experimental estimates, very limited information is available on the mechanical and thermodynamic properties of Zr$_2$(WO$_4$)$_3$(PO$_4$)$_2$, and no computational studies of this NTE material have been conducted, to the best of our knowledge.

In this work, the orthorhombic phase of Zr$_2$(WO$_4$)$_3$(PO$_4$)$_2$ has been investigated for the first time within the framework of the density functional perturbation theory (DFPT). Specifically, the structural, mechanical, and thermodynamic properties of this material have been predicted using the exchange–correlation (XC) functional parameterized by Perdew, Burke, and Ernzerhof for solids (PBEsol),\textsuperscript{42} which showed superior accuracy over standard functionals in recent density functional studies of the NTE material $\alpha$-ZrW$_2$O$_8$.\textsuperscript{45,44} As demonstrated in previous studies, lattice dynamics simulations using density functional theory (DFT) approaches can provide invaluable information on the structure–properties relationship of NTE materials.\textsuperscript{43–46} As limited experimental data exist on the mechanical and thermodynamic properties of Zr$_2$(WO$_4$)$_3$(PO$_4$)$_2$, results predicted in this study have also been systematically compared to measured and calculated properties of $\alpha$-ZrW$_2$O$_8$.

Analysis and discussion of our results are given in Section 2, followed by a summary of our findings and conclusions in Section 3. Details of our computational approach are provided in Section 4.

2. RESULTS AND DISCUSSION

2.1. Crystal Structure. Figure 1 shows the XRD pattern simulated from the relaxed crystal structure optimized with DFT in this study, along with the room-temperature powder XRD pattern of the orthorhombic Zr$_2$(WO$_4$)$_3$(PO$_4$)$_2$ structure (space group Pbcm) characterized by Evans et al.\textsuperscript{31} (Cu Kα radiation, $\lambda = 1.5406$ Å). Excellent overall agreement is achieved between the simulated and measured XRD patterns, without noticeable peak shift of 2θ values.

The orthorhombic Zr$_2$(WO$_4$)$_3$(PO$_4$)$_2$ structure optimized with generalized gradient approximation (GGA)/PBEsol at $T = 0$ K possesses crystal unit-cell parameters of $a = 9.432$, $b = 12.432$, and $c = 9.250$ Å ($b/a = 1.318$, $c/a = 0.981$; $V = 1084.59$ Å$^3$). Owing to NTE and to the fact that GGA functionals typically overestimate bond distances, the unit-cell volume predicted in the athermal limit is $\sim$2.3% larger than the estimate of $V = 1059.34(4)$ Å$^3$ ($a = 9.3640(3)$, $b = 12.3243(4)$, and $c = 9.1793(3)$ Å; $b/a = 1.3161$, $c/a = 0.9803$) obtained at $T = 60$ K by Cetinkol and Wilkinson\textsuperscript{34} using neutron diffraction data. As reported in Table 1, these predicted lattice constants remain close to neutron data\textsuperscript{44} at $T = 296$ K [$a = 9.3462(3)$, $b = 12.3313(4)$, and $c = 9.1606(3)$ Å; $b/a = 1.3194$, $c/a = 0.9801$; $V = 1055.77(4)$ Å$^3$], and the powder XRD data measured by Evans et al.\textsuperscript{31} at $T = 300$ K [$a = 9.35451(9)$, $b = 12.31831(9)$, and $c = 9.16711(8)$ Å; $b/a = 1.3168$, $c/a = 0.9800$; $V = 1056.34$ Å$^3$].

Ball-and-stick representations of the optimized orthorhombic Zr$_2$(WO$_4$)$_3$(PO$_4$)$_2$ structure down the [001], [010], and [100] axes are shown in Figure 2 and selected bond distances and angles calculated with DFT and measured by Evans et al.\textsuperscript{31} using room temperature powder XRD are summarized in Table 2.

As described by Evans and coworkers\textsuperscript{31} the orthorhombic Zr$_2$(WO$_4$)$_3$(PO$_4$)$_2$ phase is made up of corner-sharing ZrO$_6$ octahedral and WO$_4$ and PO$_4$ tetrahedral coordination units. Each ZrO$_6$ octahedron is connected to four PO$_4$ and two WO$_4$ units. Unlike $\alpha$-ZrW$_2$O$_8$ which features two distinct WO$_4$ tetrahedral coordination units, all WO$_4$ units in Zr$_2$(WO$_4$)$_3$(PO$_4$)$_2$ are crystallographically equivalent. W atoms occupy 4c Wyckoff sites (0.2 symmetry), whereas Zr, P, and O atoms are all positioned on 8d Wyckoff sites (1 symmetry). The average O–Zr, O–W, and O–P bond distances are predicted to be 2.085, 1.783, and 1.537 Å, respectively, which are in good agreement with the XRD estimates of 2.087, 1.767, and 1.500 Å (see Table 2). These values are also in line with the average O–Zr, O–W, and O–W2 bond distances of 2.084, 1.799, and 1.787 Å, respectively, calculated for $\alpha$-ZrW$_2$O$_8$ using PBEsol.\textsuperscript{31} The large difference between coordination distances at the W and P sites directly reflects the difference in cation

Figure 1. (a) Observed room-temperature powder XRD pattern of Zr$_2$(WO$_4$)$_3$(PO$_4$)$_2$ (Cu Kα radiation, $\lambda = 1.5406$ Å) (ref 31) and (b) XRD pattern simulated from the relaxed crystal structure optimized with DFT at the GGA/PBEsol level of theory. Major observed reflections are indexed in the $\text{hk}l$ representation.
Table 1. Lattice Parameters and Volume of Orthorhombic Zr$_2$(WO$_4$)(PO$_4$)$_2$ Unit Cell (Space Group Pbcn, IT No. 60; Z = 4) Calculated with DFT and Determined from Powder X-ray and Neutron Diffraction Data

| method | T (K) | a (Å)  | b (Å)  | c (Å)  | V (Å$^3$) |
|--------|-------|--------|--------|--------|-----------|
| DFT$^a$ | 0     | 9.432  | 12.432 | 9.250  | 1084.59   |
| expt$^a$ | 300   | 9.35451(9) | 12.31831(9) | 9.16711(8) | 1056.34   |
| expt$^c$ | 60    | 9.3640(3)  | 12.3243(4) | 9.1793(3) | 1059.34(4) |
| expt$^c$ | 296   | 9.3462(3)  | 12.3313(4) | 9.1606(3) | 1055.77(4) |

$^a$This study. $^b$Evans et al.; ref 31: powder XRD. $^c$Cetinkol and Wilkinson; ref 34; neutron diffraction.

Figure 2. Orthorhombic crystal unit cell of Zr$_2$(WO$_4$)(PO$_4$)$_2$ [space group Pbcn, IT No. 60, setting no. 3 Pnca (c, a, b); Z = 4], with corner-sharing ZrO$_6$ (green) octahedral and WO$_4$ (grey) and PO$_4$ (blue) tetrahedral coordination units, optimized using DFT with GGA/PBEsol. Views along the (a) [001], (b) [010], and (c) [100] directions. Color legend: O, red; P, blue; W, grey; Zr, green.

Table 2. Selected Bond Distances (Å) and Angles (°) of Zr$_2$(WO$_4$)(PO$_4$)$_2$ (Space Group Pbcn, IT No. 60; Z = 4) Calculated with DFT and Measured Using Room Temperature Powder XRD

|      | O1       | O2       | O3       | O4       | O5       | O6       |
|------|----------|----------|----------|----------|----------|----------|
| Zr1$^a$ | 2.141    | 2.038    | 2.063    | 2.051    | 2.167    | 2.049    |
| Zr1$^b$ | 2.186(13) | 2.039(12) | 2.045(12) | 2.042(10) | 2.149(13) | 2.060(16) |
| W1$^a$ | 1.784    | 1.784    | 1.806(12) | 1.783    | 1.806(12) | 1.783    |
| W1$^b$ | 1.728(13) | 1.728(13) | 1.537    | 1.531    | 1.537    | 1.534    |
| P1$^a$ | 1.491(12) | 1.541(12) | 1.514(12) | 1.456(16) |
| P1$^b$ | 1.109(12) | 1.104(12) | 1.109(12) | 1.105(5)  |
| O−W−O$^a$ | 109.1    | 110.4    | 109.0    |          |          |          |
| O−W−O$^b$ | 110.8(9) | 111.8(6) | 105.7(5) |          |          |          |
| O−P−O$^a$ | 110.4    | 108.9    | 108.7    | 109.2    | 109.6    | 109.9    |
| O−P−O$^b$ | 109.3(7) | 109.9(8) | 109.9(7) | 107.8(7) | 107.2(7) | 112.5(8) |
| W−O−Zr$^a$ | 169.8    |          |          |          |          |          |
| W−O−Zr$^b$ | 164.6(7) |          |          |          |          |          |
| Zr−O−P$^a$ | 155.9    | 175.0    |          |          |          |          |
| Zr−O−P$^b$ | 155.7(8) | 175.6(7) |          |          |          |          |

$^a$This study. $^b$Evans et al.; ref 31; powder XRD.
\[ F_{\text{phonon}}(T) = \frac{1}{2} \sum_{qv} \hbar \omega_{qv} + k_B T \sum_{qv} \ln[1 - e^{-\hbar \omega_{qv}}] \]  

where \( v \) and \( q \) are the band index and wave vector, respectively, \( \hbar \) is the reduced Planck constant, \( \omega_{qv} \) is the energy of a single phonon with angular frequency \( \omega_{qv} \), \( T \) is the temperature of the system, \( k_B \) is the Boltzmann constant, and \( \beta = (k_B T)^{-1} \).

The thermal variation of the \( U(V) + F_{\text{phonon}}(T;V) \) energy as a function of the orthorhombic \( \text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2 \) unit-cell volume calculated with DFPT at the GGA/PBSol level from \( T = 0 \) to \( 950 \) K is displayed in Figure 3. The variation of the locus of points corresponding to the local free energy curve (represented by red circles at 10 K intervals in Figure 3) shows a slight initial contraction in unit-cell volume as the temperature increases, followed by typical thermal expansion at higher temperature.

A volume dependence of the thermodynamic functions needs to be introduced through a transformation to determine the thermal properties of \( \text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2 \) at constant pressure. This is achieved by defining the Gibbs free energy at constant pressure as follows:

\[ G(T, P) = \min_{V} [U(V) + F_{\text{phonon}}(T;V) + PV] \]

where \( \min_{V} \) [function of \( V \)] corresponds to a unique minimum of the expression between brackets with respect to the volume \( V \), and \( U \) and \( P \) are the total energy and pressure of the system. \( F_{\text{phonon}}(T;V) \) and \( U(V) \) were computed with DFPT/DFT, and the thermodynamic functions of the right-hand side of eq 2 were fitted to the integral form of the universal Vinet equation of state (EoS). The Vinet EoS is defined as:

\[ P(V) = 3K_0 \left(1 - \frac{V}{V_0}\right) \frac{3}{2} (K_0' - 1)(1 - \frac{V}{V_0}) \]

where \( P \) corresponds to the uniform hydrostatic pressure, \( V_0 \) and \( V \) are the reference and deformed cell volumes, respectively, and where \( K_0 \) and \( K_0' \) are the bulk modulus and its first derivative with respect to the pressure, expressed as:

\[ K_0(T) = -V \left( \frac{dP}{dV} \right)_{P=0} \quad \text{and} \quad K_0'(T) = \left( \frac{dK}{dP} \right)_{P=0} \]

with

\[ x = \left( \frac{V}{V_0} \right)^{1/3} \]

The bulk modulus values for single-crystal \( \text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2 \) calculated using the Vinet EoS [eqs 3–5] at \( T = 0 \) and 300 K are \( K_0 = 62.9 \) and 63.6 GPa, respectively, close to the experimental estimate of 61.3(8) at \( T = 296 \) K, reported by Cetinkol and Wilkinson using a 3rd order Birch–Murnaghan (BM) EoS to fit measured unit-cell volumes. However, these predicted values appear significantly larger than the other experimental value of 49(2) GPa estimated by Cetinkol et al. using a BM EoS (Figure 4).

For the sake of comparison, the bulk modulus for polycrystalline \( \text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2 \) was estimated to be 75.0 GPa within the Voigt–Reuss–Hill (VRH) approximations. As described in Supporting Information, this value was obtained from the elastic constants calculated at \( T = 0 \) K with DFPT as the second derivative of the energy with respect to the strain. The nine independent elastic constants in the stiffness matrix calculated with DFPT/PBSol for the orthorhombic \( \text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2 \) structure are: \( C_{11} = 150.0 \) GPa, \( C_{12} = 109.9 \) GPa, \( C_{33} = 139.4 \) GPa, \( C_{44} = 31.4 \) GPa, \( C_{55} = 51.6 \) GPa, \( C_{66} = 29.8 \) GPa, \( C_{12} = 39.4 \) GPa, \( C_{13} = 76.6 \) GPa, and \( C_{23} = 39.0 \) GPa. The orthorhombic \( \text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2 \) structure appears to be mechanically stable because the Born stability conditions are satisfied (cf. Supporting Information). As shown in Table 3, these values are relatively close to the elastic constants predicted for cubic \( \alpha-\text{ZrW}_2\text{O}_8 \) at \( T = 0 \) K with DFPT/PBSol. Let us note that, although the VRH polycrystalline bulk modulus is slightly larger than its corresponding single-crystal value for \( \text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2 \), it remains appreciably smaller than the VRH value of 105.7 GPa obtained at the same level of theory for polycrystalline \( \alpha-\text{ZrW}_2\text{O}_8 \).

In addition, the VRH shear \( (G) \) and Young’s \( (E) \) moduli, Poisson’s ratio \( (\nu) \), Vickers microhardness \( (H_v) \), and Debye temperature \( (\theta_D) \) for polycrystalline \( \text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2 \) were computed from elastic constants (see Table 3 and Supporting Information). The predicted shear modulus of \( G = 37.2 \) GPa is close to the value of 34.4 GPa obtained for \( \alpha-\text{ZrW}_2\text{O}_8 \) with DFPT/PBSol. The calculated Young’s modulus—representing the ratio of stress to strain—of \( E = 95.7 \) GPa is also close to the computed values of 93.2 and 98.8 GPa.

![Figure 3](image-url)  
**Figure 3.** Variation of the total energy with phonon contribution, \( U(V) + F_{\text{phonon}}(T;V) \), of orthorhombic \( \text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2 \) as a function of the unit-cell volume calculated with DFPT at the GGA/PBSol level from \( T = 0 \) to \( 950 \) K, at 50 K intervals. Local free energy minima are indicated by red circles, at 10 K intervals.

![Figure 4](image-url)  
**Figure 4.** Thermal evolution of the bulk modulus, \( K_0 \), for \( \text{Zr}_2(\text{WO}_4)(\text{PO}_4)_2 \), calculated using the Vinet EoS with DFPT/PBSol. The experimental estimate from Cetinkol and Wilkinson (ref 34) at \( T = 296 \) K is also depicted.
for $\alpha$-ZrW$_2$O$_8$, although it is $\sim 29\%$ larger than the experimental estimate of 74 GPa determined by Isobe et al.\textsuperscript{33} Such a large discrepancy might stem in part from the density ($95\%$ of the theoretical density) and the presence of MgO additive contained in the Zr$_2$(WO$_4$)(PO$_4$)$_2$ samples characterized experimentally by Isobe et al.\textsuperscript{33} Nevertheless, the calculated Poisson's ratio of $\nu = 0.287$ and Vickers microhardness (i.e., the material's ability to resist plastic deformation) of $H_v = 4.3$ GPa are in good agreement with the experimental values of 0.25 and 4.4 GPa, respectively, reported by Isobe et al.\textsuperscript{33} Poisson's ratio provides a measure of the malleability of crystalline compounds,\textsuperscript{51} the Poisson's ratio is close to $1/3$ for ductile materials, whereas for brittle materials, it is generally much less than $1/3$. Therefore, Zr$_2$(WO$_4$)(PO$_4$)$_2$ can be considered ductile, although slightly less ductile than $\alpha$-ZrW$_2$O$_8$, which features larger computed and measured Poisson's ratios of 0.353 and 0.342, respectively. The Debye temperature for polycrystalline Zr$_2$(WO$_4$)(PO$_4$)$_2$ is predicted to be $\theta_D = 413$ K, suggesting a higher microhardness than $\alpha$-ZrW$_2$O$_8$, which exhibits lower calculated\textsuperscript{33} and measured\textsuperscript{24} Debye temperatures of 337 and 333 K, respectively.

Figure 5 shows the variation with temperature of the linear CTE of orthorhombic Zr$_2$(WO$_4$)(PO$_4$)$_2$ computed with DFPT/PBEsol within the QHA, along with the mean linear CTE values for Zr$_2$(WO$_4$)(PO$_4$)$_2$ from the dilatometer and XRD measurements in the range 50–450 K (ref 32) and from neutron diffraction data in the range 60–300 K (ref 34) are displayed as horizontal lines. DFPT results for single crystal $\alpha$-ZrW$_2$O$_8$ (ref 43) and linear CTE estimates (circles) from high-resolution neutron diffraction data for polycrystalline ZrW$_2$O$_8$ (ref 18) are also represented for comparison.

Table 3. Elastic Constants ($C_{ij}$ in GPa) of polycrystalline Zr$_2$(WO$_4$)(PO$_4$)$_2$. Calculated at $T = 0$ K at the GGA/PBEsol level and Bulk ($K$ in GPa), Shear ($G$ in GPa), and Young's ($E$ in GPa) Moduli, Poisson's Ratio ($\nu$), Vickers Microhardness ($H_v$ in GPa), and Debye Temperature ($\theta_D$ in K) Derived within the VRH Approximation\textsuperscript{42}

| $C_{ij}$ | $\alpha$-ZrW$_2$O$_8$ |
|---------|-------------------|
| $C_{11}$ | 150.0             |
| $C_{12}$ | 100.9             |
| $C_{13}$ | 139.4             |
| $C_{44}$ | 31.4              |
| $C_{55}$ | 51.6              |
| $C_{66}$ | 29.8              |
| $C_{12}$ | 39.4              |
| $C_{13}$ | 76.6              |
| $K$     | 75.0 (61.3(8) 49(2)) | 105.7 (104.3) |
| $G$     | 37.2              |
| $E$     | 95.7 (74)         |
| $\nu$   | 0.287 (0.25)      |
| $H_v$   | 4.3 (4.4)         |
| $\theta_D$ | 413 (337)         |

$^a$GGA/PBEsol calculations and experimental estimates for $\alpha$-ZrW$_2$O$_8$ are reported for comparison. $^b$This study. $^c$Isobe et al., 2009; ref 33; $^d$T ≈ 300 K. $^e$Cetinkol and Wilkinson, 2009; ref 34; $^f$T = 296 K. $^g$Cetinkol et al., 2009; ref 41; $^h$T = 300 K. $^i$Weck et al., 2018; ref 43. $^j$Drymiotis et al., 2004; ref 24; resonant-ultrasound spectroscopy at $T$ ≈ 0 K.

DFPT/PBEsol within the QHA depart significantly from the experimental data above $\sim 70$ K, therefore the calculated linear CTE results for Zr$_2$(WO$_4$)(PO$_4$)$_2$ are shown for only up to room temperature (see ref 43 for details). The linear CTE was calculated using the expression $\alpha_T = V_0 \frac{\Delta V}{\Delta T} / V_0$, where $V_0$ corresponds to the temperature $T = 0$ K and $\Delta V / \Delta T$ is the variation of the cell volume with temperature. As discussed above (see Figure 3), the volume dependence of the phonon free energy varies with temperature, resulting in a temperature-dependent equilibrium volume of Zr$_2$(WO$_4$)(PO$_4$)$_2$, which can be assimilated into thermal expansion within the QHA approach. As depicted in Figure 5, the computed linear CTE for Zr$_2$(WO$_4$)(PO$_4$)$_2$ reaches an extremum of $-5.6 \times 10^{-6}$ K$^{-1}$ at $\sim 70$ K, and NTE persists below 207 K. Similar behavior was predicted with DFPT/PBEsol for single-crystal $\alpha$-ZrW$_2$O$_8$, reaching an extremum of $-7.7 \times 10^{-6}$ K$^{-1}$ near $\sim 70$ K and exhibiting NTE below 242 K.\textsuperscript{43} In previous studies of $\alpha$-ZrW$_2$O$_8$, discrepancies were found above $\sim 60$–70 K between experimental NTE data for polycrystalline samples\textsuperscript{18} and DFT/B3LYP or DFPT/PBEsol calculations of ideal single-crystal $\alpha$-ZrW$_2$O$_8$ models\textsuperscript{35,40} (see Figure 5). Such differences were attributed in part to the creation of thermally induced defects in real samples and might also be ascribed to inherent limitations of the QHA approach, which fails to accurately account for explicit/true anharmonicity. The mean linear CTE calculated here for orthorhombic single-crystal Zr$_2$(WO$_4$)(PO$_4$)$_2$ is $-3.1 \times 10^{-6}$ K$^{-1}$ in the temperature range $\sim 0$–70 K. This value is in good agreement with the mean linear CTE of $-3 \times 10^{-6}$ K$^{-1}$ measured by Evans et al.\textsuperscript{32} using XRD measurements in the temperature range $\sim 50$–450 K, although only half of the value of $-6 \times 10^{-6}$ K$^{-1}$ reported by these authors using dilatometer data was over the same temperature range and smaller than the estimate of $-5 \times 10^{-6}$ K$^{-1}$ as reported by Cetinkol and Wilkinson\textsuperscript{34} from neutron diffraction data between 60 and 300 K. Other recent experimental mean
linear CTE estimates above room temperature are consistent with the value calculated in this study at low temperature. For example, Isobe and coworkers\textsuperscript{33} measured a value of $-3.4 \times 10^{-6}$ K\textsuperscript{-1} in the range $\sim 300$–$875$ K, and Liu et al.\textsuperscript{36} reported values of $-2.36 \times 10^{-6}$ and $-2.61 \times 10^{-6}$ K\textsuperscript{-1} in the temperature range $\sim 300$–$1000$ K for Zr\textsubscript{2}(WO\textsubscript{4})(PO\textsubscript{4})\textsubscript{2} samples sintered at 1573 and 1673 K, respectively. It is important to note that, as mentioned in the Introduction section, differences in the CTE for Zr\textsubscript{2}(WO\textsubscript{4})(PO\textsubscript{4})\textsubscript{2} can be attributed to different porosities or average grain sizes resulting from sintering conditions and/or synthesis reactions and to possible pressure-induced phase transformations during sample fabrication.

The vibrational theory of thermal expansion formulated by Grüneisen\textsuperscript{53,54} was utilized to calculate the thermal evolution of the mean Grüneisen parameter $\gamma$ of Zr\textsubscript{2}(WO\textsubscript{4})(PO\textsubscript{4})\textsubscript{2} as well as the mode Grüneisen parameters as functions of frequency, represented in Figure 6. Within this theoretical framework, the thermal expansion of materials is given by $\alpha = \sum_i \alpha_i = \gamma C_v / 3K$, where $C_v$ is the specific heat capacity, $K$ is the bulk modulus, and $\gamma$ is the mean Grüneisen parameter expressed as $\gamma = \sum_i \gamma_i c_i / \sum c_i$, where the mode Grüneisen parameters given by $\gamma_i = -\partial \ln \omega_i / \partial \ln V$ represent the relative change of mode frequencies, $\omega_i$ with crystal cell volume $V$ and $c_i$ are the contributions of these vibrational modes to the total specific heat $C_v$.

In the expression of the thermal expansion $\alpha = \gamma C_v / 3K$, both the bulk modulus and the specific heat are positive, therefore, the mean Grüneisen parameter, $\gamma$, is the parameter controlling the positive or negative thermal expansion, with the NTE originating from vibrational modes with $\gamma < 0$. As shown in Figure 6, the mean Grüneisen parameter of Zr\textsubscript{2}(WO\textsubscript{4})(PO\textsubscript{4})\textsubscript{2} calculated using DFT/PBEsol is negative below 205 K, with a minimum of $-2.1$ at 10 K. At the same level of theory, $\gamma$ was predicted to be negative below 245 K for $\alpha$: Zr\textsubscript{2}W\textsubscript{2}O\textsubscript{8}, with a minimum of $-6.56$ at 10 K. Despite being positive above 205 K, $\gamma$ for Zr\textsubscript{2}(WO\textsubscript{4})(PO\textsubscript{4})\textsubscript{2} remains close to zero up to its Debye temperature of 413 K, which is the temperature above which most vibrational modes of the crystal are fully excited. Therefore, phonon modes have little to no net effect on the lattice expansion between $\sim 205$ and 413 K. Similarly, David et al.\textsuperscript{18} observed that phonon modes play a very limited role in the lattice expansion of $\alpha$: Zr\textsubscript{2}W\textsubscript{2}O\textsubscript{8} in the temperature range of $\sim 300$–$550$ K. A closer examination of the computed mode Grüneisen parameters of Zr\textsubscript{2}(WO\textsubscript{4})(PO\textsubscript{4})\textsubscript{2} (see inset in Figure 6) reveals that the two lowest-frequency optical phonons at 24 cm$^{-1} (\gamma_1 = -17.7)$ and 38 cm$^{-1} (\gamma_2 = -6.8)$ contribute mainly to NTE, along with numerous phonon modes with $\gamma_i < 0$ below $\sim 300$ K. Although a full analysis of the phonon modes is beyond the scope of the present study and will be the focus of a forthcoming investigation, preliminary analysis suggests that both the lowest-temperature modes are characterized by variations of intrapolyhedral bond angles $O$–$M$–$O$ ($M = W$, Zr), with relatively limited $M$–$O$ bond distance variation. These results are consistent with the findings for $\alpha$: Zr\textsubscript{2}W\textsubscript{2}O\textsubscript{8}, showing that both the lowest-frequency optical phonons, predicted at 36 cm$^{-1} (T_{\text{trip}})$ and 37 cm$^{-1} (E_{\text{trip}})$ with PBEsol,\textsuperscript{43} are responsible for most of the low temperature NTE, that is, up to $\sim 70\%$ of the CTE in the vicinity of 30 K according to the Debye–Einstein QHA calculations.\textsuperscript{46} Intrapolyhedral bond angle $O$–$M$–$O$ variations for these lowest-frequency vibrational modes of $\alpha$: Zr\textsubscript{2}W\textsubscript{2}O\textsubscript{8} were achieved through libration/translation of $WO_4$ building blocks.

Lattice vibration contributions from phonon calculations were used to derive thermodynamic functions fitted to the Vinet EoS. The electronic contribution to the thermodynamic properties is negligible because the band gap computed with PBEsol for orthorhombic Zr\textsubscript{2}(WO\textsubscript{4})(PO\textsubscript{4})\textsubscript{2} is 3.20 eV, that is, comparable to the value of 3.45 eV obtained for $\alpha$: Zr\textsubscript{2}W\textsubscript{2}O\textsubscript{8} at the same level of theory.\textsuperscript{45} Within the QHA, the molar isobaric heat capacity, $C_p$, was calculated as a function of temperature and pressure according to

$$C_p(T, P) = -T \frac{dG(T, P)}{dT^2} = T \frac{dV(T, P)}{dT} \frac{\partial S(T, V)}{\partial V} \bigg|_{V=V(T, P)} + C_V(T, V(T, P))$$

where $V(T, P)$ is the equilibrium volume at $T$ and $P$, and the pressure is set to the reference ambient pressure for the standard state adopted in calorimetric data, that is, $P = 1$ bar and where the molar entropy, $S$, is expressed as

$$S = -k_B \sum_{q, v} \ln [1 - e^{-\beta \omega_{qv}}] - \frac{1}{T} \sum_{q, v} \frac{\hbar \omega_{qv}}{e^{\beta \omega_{qv}} - 1}$$

with the molar isochoric heat capacity, $C_V$, given by

$$C_V = k_B \sum_{q, v} (\beta \omega_{qv})^2 \left[ e^{\beta \omega_{qv}} - 1 \right]$$

where the remaining variables in eqs 6–8 have been defined in eqs 1 and 2. The molar isochoric and isobaric heat capacity calculated at constant atmospheric pressure for Zr\textsubscript{2}(WO\textsubscript{4})(PO\textsubscript{4})\textsubscript{2} are displayed in Figure 7, along with $C_p$, lattice dynamics results for $\alpha$: Zr\textsubscript{2}W\textsubscript{2}O\textsubscript{8} calculated up to $\sim 431$ K (i.e., the temperature corresponding to the $\alpha \rightarrow \beta$ structural phase transition in Zr\textsubscript{2}W\textsubscript{2}O\textsubscript{8} using DFT/PBEsol within the QHA.\textsuperscript{43} The computed standard molar heat capacity of Zr\textsubscript{2}(WO\textsubscript{4})(PO\textsubscript{4})\textsubscript{2} at $T = 298.15$ K is $C_p = 287.6$ J mol$^{-1}$ K$^{-1}$, which is significantly larger than the corresponding value of $C_p = 192.2$ J mol$^{-1}$ K$^{-1}$ calculated for $\alpha$: Zr\textsubscript{2}W\textsubscript{2}O\textsubscript{8}. At 960 K, the
highest temperature considered in this study for $C_P$, the difference between the calculated $C_P$ and $C_V$ remains small, that is, only $\sim 4$ J mol$^{-1}$K$^{-1}$. At this temperature, $C_P$ is only $\sim 6\%$ below its theoretical Dulong–Petit asymptotic value of $C_P = 3nR = 424.0$ J mol$^{-1}$K$^{-1}$, where $n$ is the number of atoms per formula unit and $R$ (8.314 J mol$^{-1}$K$^{-1}$) is the universal gas constant.

Figure 8 shows the thermal evolution of the molar entropy of $Zr_2(WO_4)(PO_4)_2$ calculated at equilibrium volume with $\alpha$-ZrW$_2$O$_8$ calculated at the same level of theory. The calculated standard molar heat capacity and entropy are $C_P = 287.6$ and $S^0 = 321.9$ J mol$^{-1}$K$^{-1}$, respectively.

Results reported in this study show that the DFPT/PBEsol computational approach is sufficiently accurate for assessing or predicting the relationship between structural and thermomechanical properties of NTE materials.

4. METHODS

4.1. Computational Methods. First-principles calculations were performed using DFT/DFPT implemented in the Vienna Ab initio Simulation package (VASP). The XC energy was computed using the GGA with the Perdew, Burke, and Ernzerhof parameterization revised for solids (PBEsol). The PBEsol XC functional showed superior accuracy over standard functionals, such as PBE, in previous computational studies of the NTE material $\alpha$-ZrW$_2$O$_8$. The accuracy of our DFT/DFPT computational approach was extensively tested in previous lattice dynamics studies.

The projector augmented wave (PAW) method was utilized to describe the interaction between valence electrons and ionic cores. The O(2$s^2$,2$p^4$), P(3$s^2$,3$p^3$), W(6$s^2$,5$d^4$), and Zr(4$p^6$,5$s^2$,4$d^2$) electrons were treated explicitly as valence electrons of the system.

3. CONCLUSIONS

Using DFPT with the PBEsol XC functional, the crystal structure, phonon, and thermomechanical properties of the orthorhombic NTE material $Zr_2(WO_4)(PO_4)_2$ have been investigated computationally for the first time. The results obtained for $Zr_2(WO_4)(PO_4)_2$ with this approach have been systematically and extensively compared with the available experimental data for this material, as well as with previous results for the notorious $\alpha$-ZrW$_2$O$_8$ NTE compound.

The $Zr_2(WO_4)(PO_4)_2$ structure optimized with GGA/PBEsol at $T = 0$ K possesses crystal unit-cell parameters of $a = 9.432$, $b = 12.432$, and $c = 9.250$ Å, with a unit-cell volume $\sim 2.3\%$ larger than the estimate of $V = 1059.34(4)$ Å$^3$ obtained at $T = 60$ K by Cetinkol and Wilkinson using neutron diffraction data.

The bulk modulus predicted for $Zr_2(WO_4)(PO_4)_2$ using the Vinet EoS is $K_B = 63.6$ GPa at room temperature, which is in close agreement with the experimental estimate of 61.3(8) at $T = 296$ K. At $T = 0$ K, the nine independent elastic constants in the stiffness matrix calculated with DFPT/PBEsol for the orthorhombic $Zr_2(WO_4)(PO_4)_2$ structure are: $C_{11} = 150.0$ GPa, $C_{22} = 100.9$ GPa, $C_{33} = 139.4$ GPa, $C_{44} = 31.4$ GPa, $C_{55} = 51.6$ GPa, $C_{66} = 29.8$ GPa, $C_{12} = 39.4$ GPa, $C_{13} = 76.6$ GPa, and $C_{13} = 39.0$ GPa. The VRH shear and Young’s moduli, Poisson’s ratio, Vickers microhardness, and Debeye temperature for polycrystalline $Zr_2(WO_4)(PO_4)_2$ were computed from elastic constants, that is, $G = 37.2$ GPa, $E = 95.7$ GPa, $\nu = 0.287$, $H_v = 4.3$ GPa, and $\theta_0 = 413$ K, respectively.

The computed mean linear CTE is $-3.1 \times 10^{-6}$ K$^{-1}$ in the temperature range $\sim 0$ to 70 K, in line with the mean linear CTE of $-3 \times 10^{-6}$ K$^{-1}$ measured by Evans et al. using XRD measurements in the temperature range $\sim 50$ to 450 K. The mean Grüneisen parameter controlling the thermal expansion of $Zr_2(WO_4)(PO_4)_2$ is negative below 205 K, with a minimum of $-2.1$ at 10 K. The calculated standard molar heat capacity and entropy are $C_P = 287.6$ and $S^0 = 321.9$ J mol$^{-1}$K$^{-1}$, respectively.

Figure 7. Molar isochoric ($C_V$) and isobaric ($C_P$) heat capacities of $Zr_2(WO_4)(PO_4)_2$ calculated at constant atmospheric pressure using DFPT at the GGA/PBEsol level within the QHA. $C_P$ results for $\alpha$-ZrW$_2$O$_8$ calculated with GGA/PBEsol (ref 43) are also displayed for comparison.

Figure 8. Molar entropy of $Zr_2(WO_4)(PO_4)_2$ calculated at equilibrium volume using DFPT at the GGA/PBEsol level. The molar entropy of $\alpha$-ZrW$_2$O$_8$ calculated at the same level of theory is represented (ref 43).

Figure 7 using DFPT/PBEsol. The calculated molar entropy features the typical logarithmic increase according to the Boltzmann’s entropy formula, $S = k_B \log(W)$, where $W$ is the number of microstates in the system. The standard molar entropy is predicted to be $S^0 = 321.9$ J mol$^{-1}$K$^{-1}$ at $T = 298.15$ K, that is appreciably larger than the corresponding value of 229.2 J mol$^{-1}$K$^{-1}$ predicted for $\alpha$-ZrW$_2$O$_8$ at the same level of theory.
utilized to sample the Brillouin zone using the Monkhorst-Pack k-point scheme. Unit-cell relaxation calculations were initially carried out until the Hellmann–Feynman forces acting on atoms were converged within 0.01 eV/Å, without symmetry constraints imposed. The structure optimized from total-energy minimization was then relaxed with respect to constraints imposed. The structure optimized from total-on atoms were converged within 0.01 eV/Å, without symmetry initially carried out until the Hellmann–Feynman forces acting on atoms were converged within 0.01 eV/Å, and DFPT linear response calculations were carried out with VASP to determine the phonon frequencies and elastic properties. Using the QHA—which introduces a volume dependence of phonon frequencies as a part of the anharmonic effect—the thermal properties of Zr$_2$(WO$_4$)$_2$-PO$_4$ were derived from phonon calculations. This computational approach was validated in previous studies to successfully predict the properties of various Zr-containing compounds and crystalline materials.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02456.

Computational methods utilized to obtain elastic constants, shear and Young’s moduli, Poisson’s ratio, Vickers microhardness, Debye temperature, and Born stability conditions (PDF)

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Notes
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