

High Pressure Behavior of ZrW_2O_8 : Grüneisen Parameter and Thermal Properties

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High pressure Raman spectroscopic studies are carried out on negative thermal expansion material ZrW_2O_8 . The system exhibits amorphization at 2.2 ± 0.3 GPa via an intermediate orthorhombic phase. In the cubic phase most modes below 50 meV are found to have negative Grüneisen parameter. Using the reported phonon density of states thermal properties are calculated and compared with the reported results. In contrast to the earlier belief, the present results show that modes of energies much higher than 10 meV also contribute substantially to the negative thermal expansion.

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Negative thermal expansion (NTE) has been known for some time in several compounds such as perovskite ferroelectrics [1], tetrahedral semiconductors [2], ice [3], quartz [4], and zeolites [5]. In most of the systems, NTE occurs over a limited temperature range and is often anisotropic. Recent report of large isotropic NTE over a wide temperature range (0.3 to 1050 K) in zirconium tungstate ZrW_2O_8 [6] has generated considerable current interest [7] although NTE had been discovered long ago in this system [8]. In view of these remarkable properties, ZrW_2O_8 is considered as a potential material for synthesizing composites with an engineered thermal expansion coefficient α .

At ambient temperature and pressure, the structure of ZrW_2O_8 is a framework of corner-sharing ZrO_6 octahedra and WO_4 tetrahedra. The octahedra share all their six corners with different WO_4 tetrahedra while WO_4 tetrahedra share only three of their four oxygens with the neighboring ZrO_6 octahedra. The fourth oxygen is bonded only to W. The compound undergoes an isostructural order-disorder transition at 428 K, the disordered phase having higher oxygen mobility. High pressure neutron diffraction studies have suggested an irreversible structural transition from cubic to an orthorhombic (γ) phase between 0.2 and 0.4 GPa resulting in cell tripling along the orthorhombic b -axis [9]. In the γ phase, one third of the WO_4 units are inverted [10]. Subsequent energy dispersive x-ray diffraction and Raman spectroscopic measurements at high pressure have revealed gradual amorphization between 1.5 and 3.5 GPa [11]. However, the low frequency rigid unit modes, which have been proposed [12] to contribute significantly to the large value of low temperature specific heat [13] and also to NTE [14], have not been studied yet. Based on the fitting of the specific heat data, a 5 meV weakly dispersive optical phonon has been argued [13] to influence the low temperature NTE. Recently, phonon density of states has been reported [14] from neutron scattering measurements which show several pronounced peaks below 50 meV. Negative α could be reproduced by fitting the data to a model which assumes [14] the Grüneisen parameter to have a value -14 between 1.5 and 8.5 meV; however, there are no reports on the measurement of the Grüneisen parameter for vari-

ous modes. In the present work we report a high pressure Raman spectroscopic study of optical phonons in ZrW_2O_8 in the complete range of energies from 5 to 140 meV also covering the rigid unit modes. The Grüneisen parameters are obtained for all the modes in the cubic and the orthorhombic phases. From these and the reported phonon density of states, we have calculated the thermal properties such as specific heat C_V , average Grüneisen parameter γ_{AV} , and α , and discussed these in the light of prevailing models. The origin of the two persisting low frequency modes in the amorphous phase is also discussed.

Samples of ZrW_2O_8 were synthesized from appropriate quantities of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and H_2WO_4 using the procedure reported earlier [6]. Raman measurements were carried out on unoriented single crystal pieces in a gasketed diamond anvil cell (DAC) in the back scattering geometry using a setup described [15] elsewhere. A 488 nm line of the argon ion laser was used to excite the Raman spectra. A 4:1 mixture of methanol and ethanol was used as pressure transmitting medium. Pressure inside the DAC was estimated using a standard ruby fluorescence technique. Scattered light was analyzed using a Spex double monochromator and detected using a cooled photomultiplier tube operated in the photon counting mode.

At ambient temperature and pressure the cubic phase $P2_13$ (T^4) of zirconium tungstate (α - ZrW_2O_8) has four formula units per unit cell. Factor group analysis gives the optical phonons to be distributed among different irreducible representations as $11A + 11E + 32F$. All the modes are Raman active. On the other hand, the unit cell of the high pressure orthorhombic phase (γ - ZrW_2O_8) $P2_12_12_1$ (D_2^4) contains 12 formula units. This results in a larger number of modes. Further, the doubly and triply degenerate modes of the cubic phase are split due to lowering of symmetry to orthorhombic. Factor group analysis yields $99A + 98B_1 + 98B_2 + 98B_3$ optical phonons, all of which are Raman active.

Figure 1 shows the Raman spectra of zirconium tungstate at several pressures for Raman shifts lower than 450 cm^{-1} . This region corresponds to those of lattice modes, translational and librational or rigid unit modes

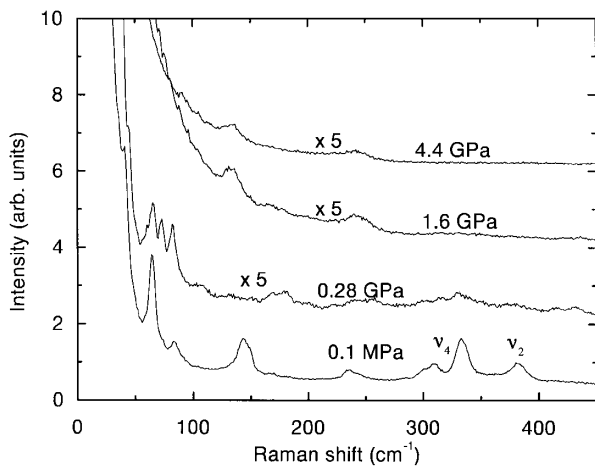


FIG. 1. Raman spectrum of ZrW_2O_8 in the low frequency region at various pressures. The ν_2 and ν_4 internal modes of the WO_4 tetrahedra also appear in this range.

of tungstate (WO_4) tetrahedra, and $\nu_2(E)$ and $\nu_4(F)$ internal bending modes [16] of WO_4 . In the cubic phase ten modes are found in this region. As the pressure is increased above 0.24 GPa, new modes are observed while the old ones continue to exist, confirming the coexistence of cubic and orthorhombic phases reported from neutron diffraction measurements [9]. The $\nu_1(A)$ and $\nu_3(F)$ internal modes in the $650\text{--}1100\text{ cm}^{-1}$ region also exhibit similar behavior as shown in Fig. 2. No modes were found between 450 and 650 cm^{-1} . Note the dramatic splitting of $\nu_3(F)$ modes into several components across the phase transition. Between 1.9 and 2.5 GPa, the internal modes exhibit excessive broadening resulting in broad bands at 780 and 995 cm^{-1} , while most of the lattice and external modes are found to disappear except those at 138 and 244 cm^{-1} . The origin of these modes will be discussed later. Broadening of internal modes by a factor more than 4 [17] and disappearance of lattice and external modes [18] is often taken as signature of amorphization

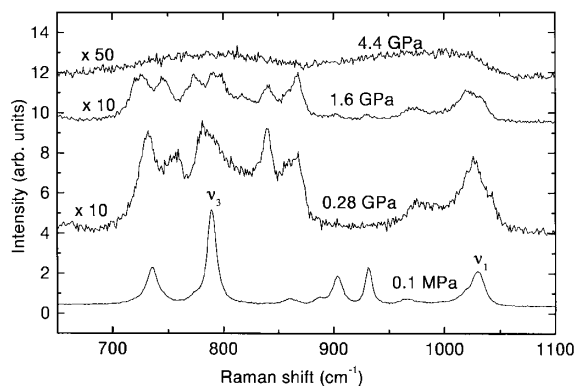


FIG. 2. Raman spectrum of ZrW_2O_8 in the ν_1 and ν_3 internal mode region of WO_4 tetrahedra at various pressures. These modes exhibit splitting in the orthorhombic phase and broaden in the amorphous phase.

[19]. In view of this, one can treat $2.2 \pm 0.3\text{ GPa}$ as the amorphization pressure.

Figure 3 shows the pressure dependence of mode frequencies corresponding to the Raman spectra displayed in Figs. 1 and 2. A total number of 21 modes could be identified in the cubic phase while in the orthorhombic phase 24 modes were observed. Although group theory predicts a much larger number of modes for both these phases, observation of a lesser number of modes could either be due to accidental degeneracy or due to insufficient intensity or both. It is important to point out that among the ten low frequency modes below 400 cm^{-1} in $\alpha\text{-ZrW}_2\text{O}_8$ eight modes exhibit softening. Soft phonons imply lattice instability [20] and consequent structural phase transitions [21]. Cell tripling along the b -axis across $\alpha \rightarrow \gamma$ transition suggests that softening of a phonon at $(2/3)q_B$, where q_B is the wave vector corresponding to the Brillouin zone boundary, could be responsible for the $\alpha \rightarrow \gamma$ phase transition at high pressure. Mode softening also implies a negative mode Grüneisen parameter, which is a key parameter for determining thermal properties such as the thermal expansion coefficient. The mode Grüneisen parameter γ_i is defined as [20] $\gamma_i = -(\partial \ln \omega_i / \partial \ln V) = (\omega_i \chi_T)^{-1} (\partial \omega_i / \partial P)$, where ω_i is the frequency of the i th mode, V is the volume, P is the pressure, and $\chi_T = -V^{-1} (\partial V / \partial P)$ is the isothermal compressibility. In order to obtain reliable values of γ_i , measurements are made at close intervals of pressure in the cubic phase. Table I lists the values of γ_i s for all the modes in both the phases. Note that in the orthorhombic phase also several modes exhibit negative Grüneisen parameter suggesting instability of this structure as well.

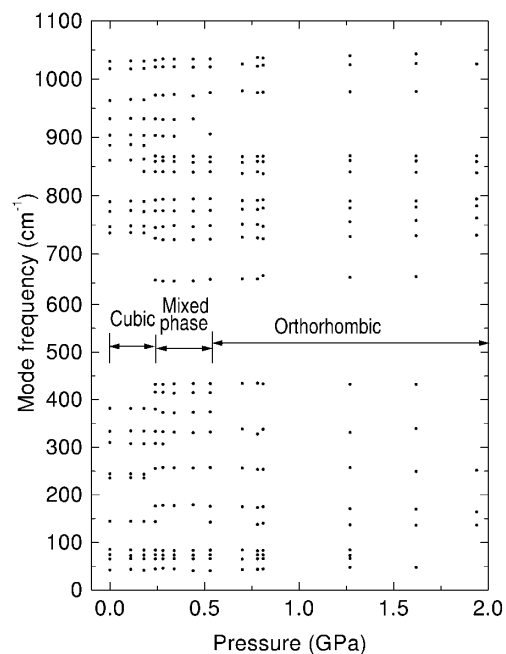


FIG. 3. Pressure dependence of frequencies of the Raman modes presented in Figs. 1 and 2.

TABLE I. Mode Grüneisen parameters of the various mode frequencies of α -ZrW₂O₈ and γ -ZrW₂O₈. Reported values of $\chi_T = 1.38 \times 10^{-2} \text{ GPa}^{-1}$ and $1.53 \times 10^{-2} \text{ GPa}^{-1}$, respectively, in the two phases [10] are used in the calculation.

α -ZrW ₂ O ₈		γ -ZrW ₂ O ₈	
Mode freq. (cm ⁻¹)	γ_i	Mode freq. (cm ⁻¹)	γ_i
41	-1.29	42	4.92
65	2.51	65	0.69
74	-2.25	73	-0.29
84	-4.66	83	0.89
144	-2.21	142	-1.81
...	...	176	-2.68
235	0.12
244	-1.60	255	-0.86
310	-2.24
333	-0.17	332	0.72
382	-1.12	373	1.08
...	...	416	-0.41
...	...	432	-0.04
...	...	653	0.58
736	0.08	727	0.41
746	0.82	745	0.77
773	-0.1	774	0.43
790	0.28	792	-0.06
...	...	841	-0.08
861	0.87	859	0.04
...	...	868	0.06
886	-0.05
904	0.32	903	-1.1
932	0.13	931	0.02
967	-0.6	973	0.33
1019	0.23	1021	0.22
1030	2.2	1032	0.44

In order to calculate the α , one needs to evaluate the average Grüneisen parameter γ_{AV} . These are related as

$$\alpha = \frac{\gamma_{AV} C_V}{3V_m B}, \quad (1)$$

where B is the bulk modulus, V_m is the molar volume, and C_V is the molar specific heat at constant volume defined as the sum of contributions over all the modes,

$$C_V = \frac{1}{4} \sum p_i C_i, \quad (2)$$

where p_i is the number of phonons/branches of frequency ω_i and C_i is the specific heat contribution from a single mode of frequency ω_i . The factor 1/4 in Eq. (2) takes into account the fact that the cubic unit cell contains four formula units of ZrW₂O₈. $C_i = R[x_i^2 \exp(x_i)]/[\exp(x_i) - 1]^2$, where $x_i = \hbar\omega_i/k_B T$ is the dimensionless phonon energy and R the gas constant, k_B is the Boltzmann constant, and T is the temperature. The average Grüneisen parameter is defined as

$$\gamma_{AV} = \left(\frac{1}{4} \sum p_i C_i \gamma_i \right) / C_V. \quad (3)$$

From Eqs. (1) and (3) it is clear that a negative average Grüneisen parameter implies a negative thermal expansion for the material. In order to proceed with the calculation of γ_{AV} , C_V , and α , the values of p_i are required. These are estimated from the recently published literature on the absolute phonon density of states on this material [14] using the following procedure. In the cubic unit cell of α -ZrW₂O₈ out of the total 132 vibrational degrees of freedom 129 contribute to 54 (11A + 11E + 32F) optical phonons and three to acoustic phonons. Thus the phonon spectrum is dominated by the optical phonons. As evident from the present Raman spectra the optical phonons can be divided into two groups, one group with energies below 450 cm⁻¹ (56 meV) and the second with energies above 700 cm⁻¹ (85 meV). The reported density of states also exhibits [14] a corresponding gap in the phonon density of states between 65 and 85 meV. Only the degrees of freedom corresponding to the $\nu_1(A)$ and $\nu_3(F)$ modes of WO₄ tetrahedra contribute to the high energy group. These amount to a total of 32 (4A + 2E + 8F) degrees of freedom. The remaining 100 degrees of freedom belong to the low energy group. These are 3 (F) acoustic, 9 (A + E + 2F) lattice, 24 (2A + 2E + 6F) translational, 24 (2A + 2E + 6F) librational, and 40 internal (2A + 4E + 10F) degrees of freedom distributed among ν_2 and ν_4 modes. In view of this the p_i for the modes observed in the present experiments are taken to be proportional to the reported density of states such that the sum over p_i in the low and high energy phonon groups has values 100 and 32, respectively. Twenty-one distinct phonon energies are considered in the calculation. The molar volume is obtained from the unit cell dimensions [7] as $1.15 \times 10^{-4} \text{ m}^3 \text{ mole}^{-1}$ and the value of the bulk modulus is taken [14] as $4.8 \times 10^{10} \text{ Nm}^{-2}$. The calculated values of γ_{AV} , C_V , and α turn out to be -1.2 , $200 \text{ J mole}^{-1} \text{ K}^{-1}$, and $-15 \times 10^{-6} \text{ K}^{-1}$, respectively. The calculated C_V agrees well with the reported value of $220 \text{ J mole}^{-1} \text{ K}^{-1}$ [13]. In order to compare the values of α and γ_{AV} with those reported earlier, we obtain from the data of Ref. [7] the value of α at ambient temperature as $-(11 \pm 2) \times 10^{-6} \text{ K}^{-1}$ which is significantly higher than its average value. Following [14] one gets from Eq. (1) $\gamma_{AV} = -0.83 \pm 0.16$. Thus γ_{AV} and α agree within 30% with those found in the present work. The difference in the values of α and, consequently, in those of γ_{AV} could possibly be due to the experimental errors in the mode Grüneisen parameters and the bulk modulus. Another source of disagreement could be the omission of phonons with energies less than 5 meV in the present calculation.

It is important to point out that several of the prominent peaks below 50 meV in the reported phonon density of states, e.g., those at 5, 11, 16, 30, 37, 41, and 47 meV have close correspondences with the Raman peaks which exhibit large negative Grüneisen parameters (Table I) and account for nearly all of the NTE at ambient temperature. On the

other hand, in order to explain the observed temperature dependences of α it has been argued in an earlier model [14] that only the phonons of energies less than 10 meV are relevant to NTE in ZrW_2O_8 . Similarly, the temperature dependence of C_V was fitted by assuming that a 5 meV optical phonon contributes substantially to the specific heat [13]. The large oscillator strength of this low frequency phonon was argued to be arising from librational or rigid unit modes. The role of rigid unit modes in determining the negative thermal expansion has also been examined from geometrical considerations [22] and simulation studies [12], whereas recent lattice dynamics calculations seem to suggest [23] that two transverse acoustic branches contribute about 40% of the NTE at 300 K. However, in contrast to these models and calculations, the present results clearly show that several phonons of energies much higher than 10 meV also contribute substantially to the NTE.

As mentioned earlier, zirconium tungstate also undergoes pressure induced amorphization (PIA) at a rather moderate pressure of 2.2 ± 0.3 GPa. Several systems which exhibit PIA [24] have also been found to have NTE over a certain range of temperatures [25]. In view of this the two phenomena have been argued to be correlated [11] and the present system also supports this hypothesis. In most cases the lattice and the external modes are found to disappear across amorphization [18]; however, the present system exhibits persistence of modes at 17 and 30 meV. Although amorphization in ZrW_2O_8 has been examined earlier [11] using Raman spectroscopy, the studies were restricted to energies above 75 meV. The low values of the frequencies of the new modes observed in the amorphous phase suggest that these could possibly belong to the vibrations of units larger than single WO_4 tetrahedron similar to that found in SnI_4 across amorphization [26]. Existence of such larger molecular units in the amorphous phase would also imply persistence of medium range order in the amorphous phase.

In conclusion, high pressure Raman spectroscopic studies on zirconium tungstate have shown that several phonons of energies less than 50 meV have negative Grüneisen parameter. Reasonable agreement of the calculated thermal properties such as average Grüneisen parameter, molar specific heat, and thermal expansion coefficient with those reported experimentally suggests, in contrast to earlier belief, that phonons with energies much larger than 10 meV also contribute substantially to the negative thermal expansion. The new modes found in the amorphous phase at 17 and 30 meV possibly represent persistence of medium range order.

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