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High-pressure optical study of HfW_2O_8

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Abstract

A high-pressure optical absorption study and Raman and infrared spectroscopy are carried out on hafnium tungstate (HfW_2O_8) at room temperature. The band gap decreases rapidly with pressure until ~ 9 GPa is reached, increases between 9 and 16 GPa, and slowly decreases with pressure from 16 to 47 GPa. The changes under pressure of the vibrational modes have been studied, and an estimate of the thermal expansion coefficient has been calculated, and found to be in reasonable agreement with the measured value. The α - γ phase transition can be observed via Raman and infrared spectroscopy. Around 2 GPa, HfW_2O_8 undergoes an irreversible transition from the γ -phase to an amorphous structure.

1. Introduction

Negative thermal expansion (NTE) materials can be used to achieve engineered thermal expansion, and have attracted scientific and technological interest. Among these materials, mainly due to the isotropic NTE over a wide temperature range, the MX_2O_8 family ($M = \text{Zr}, \text{Hf}$ and $X = \text{W}, \text{Mo}$) has been extensively studied [1, 2].

The α -phase HfW_2O_8 , which is cubic, consists of HfO_6 octahedra each of whose corners shares an oxygen atom with a WO_4 tetrahedron. Each of the WO_4 tetrahedra has an oxygen atom bonded only to the W atom, while the other three oxygen atoms are also part of HfO_6 octahedra. With increasing temperature, the amplitudes of the transverse vibrations of the bridging O atoms of the Hf–O–W linkage decrease the distance between W and Hf and give rise to NTE.

Previous studies have shown that HfW_2O_8 undergoes temperature- and pressure-induced phase transitions [1, 3]. It has been reported that an irreversible phase transition from the α -phase to an orthorhombic (γ -) phase occurs at 0.6 GPa [3].

High pressures may be necessary for the synthesis of composites exhibiting NTE. Consequently, it is important to understand their high-pressure behaviour. For example, the high-pressure phase (γ) of ZrW_2O_8 has been found to show weaker NTE over a narrower

temperature range compared with its cubic counterpart. Thus, pressure-induced phase transitions could degrade the performance of these materials.

2. Experimental details

Powder samples of α -HfW₂O₈ were loaded in a Mao–Bell-type diamond anvil cell. Less than 5% ruby powder was included and used to calibrate the pressure. In the Raman experiments, a mixture of 4:1 methanol:ethanol was also loaded into the sample compartment to reduce the nonhydrostatic stresses. For the mid-infrared measurements the sample was diluted with KBr powder, while for the far-infrared measurements, petroleum jelly was used as the pressure-transmitting medium to avoid saturation. Due to the reflection, the light leaking via the pressure-transmitting medium seriously degrades the absorption measurement, so no pressure-transmitting medium was used in the optical absorption measurements.

Raman measurements with a resolution of 4 cm⁻¹ were carried out using an OMARS 89 Raman spectrometer equipped with a liquid-nitrogen-cooled CCD. The 514.5 nm line of an argon-ion laser was used as the excitation source and the scattered light from the sample was collected in backscattering geometry. A purged Nicolet Nexus 670 FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT-A detector was used for mid-infrared spectroscopy, and the spectra were collected with a resolution of 4 cm⁻¹. Far-infrared measurements were collected with 4 cm⁻¹ resolution at beamline U2A at the National Synchrotron Light Source, using a Bruker IFS-66V FTIR, and a liquid-helium-cooled bolometer as the detector. High-pressure optical absorption measurements in the range 1–4 eV were carried out in transmission geometry using a monochromator with liquid-nitrogen-cooled photomultiplier tubes, and a tungsten–halogen lamp as the source.

3. Results and discussion

Figure 1 shows the Raman spectra of HfW₂O₈ between 100 and 1200 cm⁻¹ at ambient conditions and under high pressure. Thirteen modes are observed at 0 GPa. By comparison with the spectra of other tungstates [1] the modes centred at 1040, 977, 937, 912 and 875 cm⁻¹ are assigned to the symmetric stretching of WO₄ tetrahedra, the 809 and 761 cm⁻¹ modes to the asymmetric stretching, the one at 391 cm⁻¹ to the WO₄ asymmetric bending, the two at 340 and 314 cm⁻¹ to symmetric bending, and those at 215, 144 and 119 cm⁻¹ to lattice modes.

There are a number of discontinuities which develop in the spectra at ~0.9 GPa. A strong mode at 937 cm⁻¹ disappears, three new strong modes at 1031, 868 and 797 cm⁻¹ appear and there is a discontinuity in the position of the modes at 977 and 875 cm⁻¹ (figures 1, 2). A very weak mode at 423 cm⁻¹ comes into existence. The changes in the Raman spectra occur near the transformation pressure found in the neutron diffraction study, and we therefore associate them with the α – γ phase transition [3].

As the γ -phase is compressed further, there is broadening of the high-energy (> 600 cm⁻¹) modes and also a loss of the low-energy modes (figure 1). With compression beyond 2 GPa, there are two strong broad bands observed at around 817 and 1031 cm⁻¹, and a weak band centred at 380 cm⁻¹. The strong modes shift to lower energy with increasing pressure, while the weak one at 380 cm⁻¹ disappears beyond 8 GPa. Broadening of the modes suggests that pressure-induced amorphization occurs, as observed for ZrW₂O₈ [4]. The spectrum from the decompressed sample implies that the amorphous structure is quenchable.

We follow the procedure of Ravindran *et al* to get the molar specific heat, C_v , and average Grüneisen parameter, γ_{AV} , as 214 J mol⁻¹ K⁻¹ and –0.88, respectively [5]. The calculated

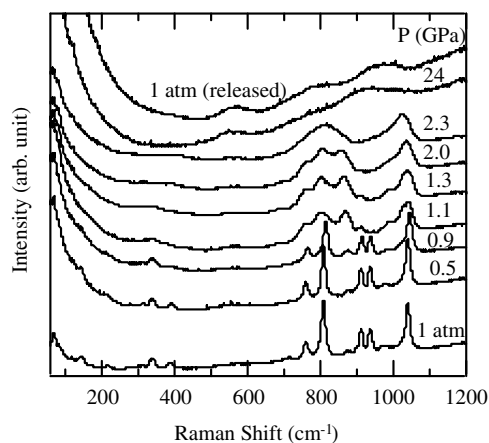


Figure 1. Representative Raman spectra.

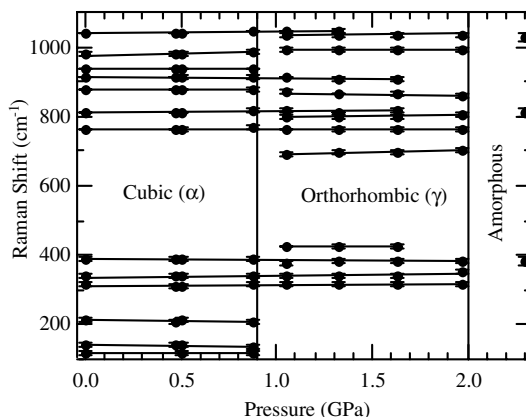


Figure 2. The pressure dependence of the Raman modes.

value of the thermal expansion coefficient, α , is $-1.01 \times 10^{-5} \text{ K}^{-1}$, which is in good agreement with the measured value of $-1.10 \times 10^{-5} \text{ K}^{-1}$ [1, 3, 5].

The observed infrared-active modes of HfW₂O₈ at different pressures are shown in figure 3. Under ambient conditions, 15 modes are observed. Like the Raman-active modes, the infrared-active vibrations centred at 939, 914, 883 and 854 cm^{-1} are assigned to the symmetric stretching of WO₄ tetrahedra, the 815, 780 and 761 cm^{-1} modes to the asymmetric stretching, the ones at 391, 372 and 362 cm^{-1} to WO₄ asymmetric bending, those at 333, 322 and 295 cm^{-1} to symmetric bending, and the two at 241 and 179 cm^{-1} to lattice modes.

When the pressure is increased to ~ 0.6 GPa, six new modes at 199, 212, 261, 416, 437 and 685 cm^{-1} are detected and the original modes at 372, 815 and 939 cm^{-1} disappear. In figure 4, the shifts with pressure of the infrared modes are presented. On the basis of the discontinuities in the infrared spectra which occur at ~ 0.6 GPa, we deduce that the α - γ phase transition occurs at this pressure. The reduced transition pressure, in comparison with what was found from the Raman spectra, is most probably due to the differences in shear stress of the two experiments.

When the pressure is raised to 1.7 GPa, peaks begin to broaden and merge. Upon further compression to 2.6 GPa and above, only three broad modes centred at 200, 350 and 830 cm^{-1}

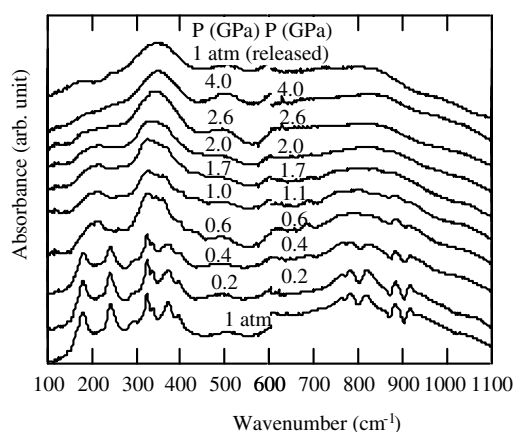


Figure 3. Representative infrared spectra.

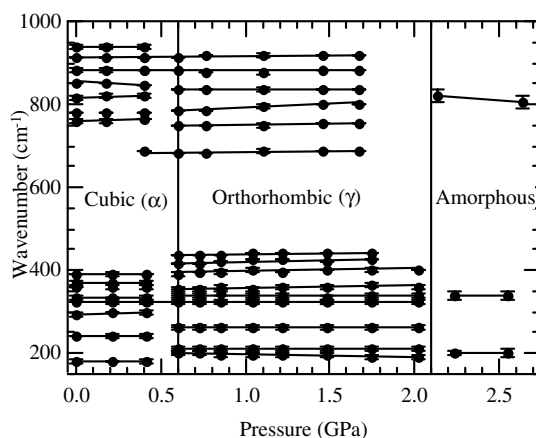


Figure 4. The pressure dependence of the infrared modes.

remain, which we interpret as meaning that HfW_2O_8 is completely amorphous. As with the Raman spectra, the three modes remain broad upon quenching of the sample, implying that the γ -amorphous transition is irreversible.

In our optical absorption experiments, we have collected transmission data versus incident energy at different pressures. Figure 5 shows a representative plot of $(\alpha t E)^{1/2}$ versus the incident energy E at various pressures, where α denotes the absorption coefficient and t the sample thickness. By linearly fitting the edge at the higher-energy region and extrapolating to zero, an estimate of the direct band gap value can be obtained [6]. In the pressure range plotted in figure 5, the increase in the incident energy of the absorption edge with increasing pressure is presented.

Figure 6 is the pressure dependence of the band gap of HfW_2O_8 . The band gap decreases sharply by 0.85 eV with pressure increasing from 4 to 9 GPa. From 9 to 16 GPa, the band gap widens, and from 16 to at least 47 GPa, the band gap decreases. Visually, we track the colour change with pressure. HfW_2O_8 becomes completely transparent around 6 GPa, yellowish at 9 GPa and red at 28 GPa. It becomes deep red beyond that.

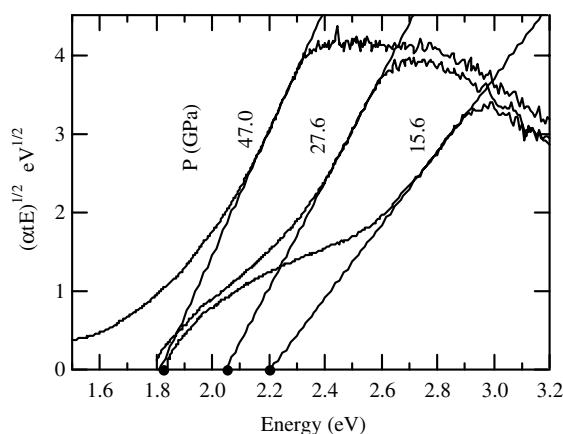


Figure 5. $(\alpha E)^{1/2}$ versus incident energy.

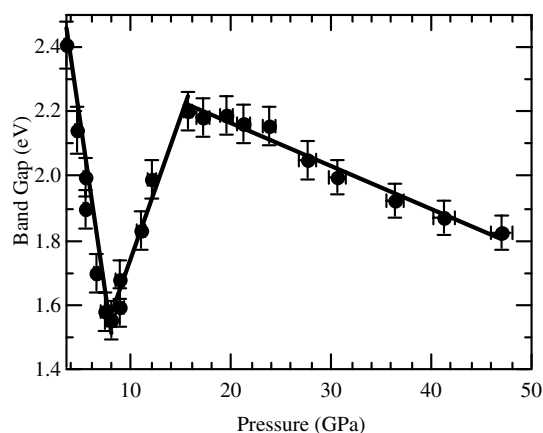


Figure 6. The pressure dependence of the band gap.

Although data were also collected for pressures less than 4 GPa, concerns about the effects of scattering from the relatively loose grain boundaries, and the limited spectral range of the study, prevented extraction of band gaps from the data. The band gap measurements shown here are for the sample of amorphous phase. It is believed that the application of pressure shortens the bond length and compresses the band gap. The mechanism for the increase of the band gap with increasing pressure in the range of pressure 9–16 GPa is still unclear. It is probably related to the transformation of amorphous phases. Unfortunately, our Raman and infrared measurements cannot effectively detect this kind of phase change.

4. Conclusions

We report the optical absorption and the Raman and infrared spectra of HfW_2O_8 under pressure. The average Grüneisen parameter was determined, from which an estimate of the thermal expansion coefficient was made. Discontinuities in the pressure dependences of some modes, loss of modes and the appearance of new modes mark the α - γ phase transition. This transformation is found to occur at 0.6–0.9 GPa. The spectra also indicate that HfW_2O_8

becomes amorphous above 2 GPa and that the amorphous structure is quenchable to ambient conditions. The pressure dependence of the band gap of HfW₂O₈ has been determined, and a linear extrapolation indicates that HfW₂O₈ will become a metal at around 180 GPa.

Acknowledgments

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