The Structural Response of Gadolinium Phosphate to Pressure

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Abstract

Accurate elastic constants for gadolinium phosphate (GdPO_4) have been measured by single-crystal high-pressure diffraction methods. The bulk modulus of GdPO_4 determined under hydrostatic conditions, 128.1(8) GPa ($K' = 5.8(2)$), is markedly different from that obtained with GdPO_4 under non-hydrostatic conditions (160(2) GPa), which indicates the importance of shear stresses on the elastic response of this phosphate. High pressure Raman and diffraction analysis indicate that the PO_4 tetrahedra behave as rigid units in response to pressure and that contraction of the GdPO_4 structure is facilitated by bending/twisting of the Gd–O–P links that result in increased distortion in the GdO_9 polyhedra.

Introduction

Rare-earth minerals with the general formula, MPO_4 (M = trivalent lanthanide cation) are widespread accessory minerals that are frequently doped with uranium and/or thorium. Phosphates of this class that incorporate the larger rare-earth cations (M = Ce, Pr, Nd, Pm, Sm, Eu, and Gd) adopt a monoclinic structure and are isostructural with the cerium phosphate mineral monazite, whereas phosphates with smaller cations (M = Tb, Dy, Ho, Er, Tm, Yb and Lu) are isostructural with xenotime (tetragonal, $I4_1/amd$). The doping of these phosphates with radioactive elements, which have half-lives on the order of billions of years, has led to their use as geochronometers for the dating of geological formations.¹ There has also been a developing interest in utilising simple phosphates as possible solid state repositories for nuclear waste,² and due to its high neutron absorption capabilities, GdPO_4 has been proposed as an inclusion compound for the construction of spent nuclear fuel canisters.³ The development of simple phosphate compounds for addressing this important socio-political problem has been driven by their excellent resistance to temperature and pressure fluctuations and low solubility and ion leaching. Although there has been considerable focus on determining the elastic properties of MPO_4 compounds,⁴ the actual *structural response* of these materials to pressure remains underexplored. This important oversight must be addressed if these materials are to find practical application as safe and effective repository materials. In this contribution, we report the elastic constants of GdPO_4 and correlate these with the underlying changes in the crystal structure in response to hydrostatic pressure. Structural studies of this kind will lead to a greater understanding of the origins of the stability of MPO_4 compounds and facilitate progress in their development for nuclear waste storage applications.

GdPO_4 crystallises in the monoclinic space group $P2_1/n$. The asymmetric unit comprises a single Gd^{3+} ion and one PO_4^{3-} anion. The phosphate anion has the expected tetrahedral coordination with no significant distortion. The coordination geometry of the nine-coordinate

Gd^{3+} ion is best described as a severely distorted mono-capped square antiprism (MCSAP). The packing arrangement of the polyhedra is complex (Fig. 1a) but can be described as chains of alternating PO_4 and GdO_9 polyhedra that, in the standard $P2_1/n$ setting, lie parallel to the $[100]$ direction. These chains are then cross-linked via bridging oxygen atoms between the Gd^{3+} ions. This packing arrangement results in each Gd^{3+} being coordinated to seven PO_4 tetrahedra, five of which are vertex sharing, while the remaining two are edge sharing. Furthermore, each Gd^{3+} ion shares common edges with six neighbouring Gd^{3+} cations (Fig. 1b).

Figure 1. (a) The crystal structure of GdPO_4 as viewed along the $[010]$ direction; (b) the secondary coordination sphere of the Gd^{3+} ion in GdPO_4 . Each ion is coordinated to seven PO_4 tetrahedra and has six edge-sharing interactions with neighboring Gd^{3+} ions. Green: Gd; red: O; light grey: P. Green struts represent the bond between Gd^{3+} ions and the capping oxygen atoms of the MCSAP, all other covalent bonds are shown in grey. Symmetry codes: (i) $-x+1/2, y+1/2, -z+3/2$; (ii) $-x+1/2, y-1/2, -z+3/2$; (iii) $x-1/2, -y+3/2, z-1/2$; (vii) $x+1/2, -y+3/2, z+1/2$; (xi) $-x, 1-y, 1-z$; (xii) $-x, 1-y, 2-z$.

Experimental Methods

Synthesis: Single crystals of GdPO_4 were grown by a high-temperature solution (flux) growth method that has been described in detail previously.⁵ For the growth of single crystals of GdPO_4 , high-purity Gd_2O_3 was combined with lead hydrogen phosphate in a 50 ml platinum crucible that was then heated to 1360°C for several days. At 1360°C , lead pyrophosphate, $\text{Pb}_2\text{P}_2\text{O}_7$, forms via the decomposition of the lead hydrogen phosphate that then reacts with Gd_2O_3 to form GdPO_4 dissolved in a solution of molten $\text{Pb}_2\text{P}_2\text{O}_7$. Single crystals of GdPO_4 grow from the flux as the system is cooled to $\sim 900^\circ\text{C}$. At this temperature, the growth furnace is rapidly cooled to room temperature, and the crystals are removed from the solidified flux by boiling the Pt crucible and growth charge in nitric acid for several weeks. The entire growth process requires a total period of over two months.

High-pressure diffraction (HP-XRD): A single crystal of GdPO_4 ($81 \times 153 \times 248 \mu\text{m}^3$) was loaded into a sample chamber approx. $290 \times 100 \mu\text{m}^2$ in size that was drilled into a steel gasket that was fitted into a standard ETH diamond anvil cell (DAC).⁶ A quartz crystal was loaded into the cell with the sample crystal to act as a pressure calibrant.⁷ Diffraction data were first collected under ambient conditions before a 4:1 MeOH:EtOH mixture was added to the DAC. This mixture acts as a pressure-transmitting medium and is known to remain hydrostatic up to 9.8 GPa.⁸

Precise unit cell parameters for both the sample and quartz crystal were obtained from data collected on a Huber diffractometer equipped with a Eulerian cradle and point detector. The method is based on the 8-position centering of 10-25 intense diffraction maxima within the $9^\circ < 2\theta < 33^\circ$ range.⁹ Data for structural analysis were collected at select pressures with an XCalibur-1 (Rigaku Oxford Diffraction) diffractometer equipped with a CCD detector and operating with monochromatic Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The data were processed with standard instrument software. Sample and DAC absorption effects were corrected for with ABSORB-7.¹⁰ Diamond dips and statistical corrections were performed with AVERAGE (R. J. Angel, 2003-2011). High-pressure structural models for GdPO_4 were determined from the refinement, against the pressure data, of a structural model determined with the crystal in air and under ambient conditions (see SI for details). This was possible because the sample underwent no phase transitions over the pressure range investigated. Refinement was against F^2 by full-matrix least-squares refinement techniques. Due to restricted access to reciprocal space due to spatial restrictions imposed by the DAC all atoms in the high-pressure structural models were refined isotropically. Key data and refinement parameter for the HP-XRD analysis are listed in Table 1.

Table 1. Data and refinement parameters for GdPO_4 as a function of pressure.

	~1 bar	2.903(4) GPa	5.372(6) GPa	7.062(6) GPa
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
<i>a</i> (Å)	6.33571(12)	6.29790(12)	6.26830(11)	6.24937(12)
<i>b</i> (Å)	6.84840(17)	6.80019(19)	6.7632(2)	6.7397(2)
<i>c</i> (Å)	6.6516(3)	6.5923(2)	6.5466(2)	6.5189(2)
β (°)	104.023(2)	103.833(2)	103.672(2)	103.563(2)
<i>V</i> (Å³)	280.008(14)	274.139(13)	269.674(13)	266.912(14)
ρ (g/cm³)	5.983	6.111	6.212	6.277
Collected reflns	1022	1948	1915	1821
<i>R</i>_{int}	0.059	0.070	0.071	0.067
Data/parameters	357/26	460/26	449 / 26	438 / 26
<i>S</i>	1.073	1.026	1.030	0.999
<i>R</i>1 (<i>I</i> > 2σ<i>I</i>)	0.0451	0.0433	0.0442	0.0418
<i>wR</i>2 (<i>I</i> > 2σ<i>I</i>)	0.1016	0.0958	0.1079	0.0945

High-pressure Raman spectroscopy: A second GdPO_4 crystal was loaded into a Brillouin-Raman (BR-series) DAC (High-Pressure Diamond Optics, Inc., U.S.A) fitted with two type-IIa diamonds, both 600 μm in diameter. These diamonds, along with others in their class, have very low levels of impurities and therefore display negligible photoluminescence. The sample chamber (~ 300 μm in diameter) was drilled in a steel gasket that was fitted between the diamonds of the DAC. A ruby ball was also loaded into the DAC for pressure calibration measurements.¹¹ A 4:1 MeOH:EtOH mixture was added to the chamber to act as the pressure medium. High-pressure Raman spectra were recorded on a JY Horiba LabRam HR spectrometer fitted with a 40 x objective and equipped with a red laser ($\lambda = 632.817$ nm). The spectral slits were 150 μm in size, and the confocal hole was set to 400 μm . The spectrograph grating had 1200 grooves/mm. Each data collection comprised two scans, each 40 s in duration. The photoluminescence signals (at ca. 694 nm) of the ruby were measured under the same experimental conditions as the sample data collections - except that the scans lengths were varied to adjust the signal intensity when required.

Results & Discussion

Elastic Properties

Figure 2 shows the pressure dependence of the unit cell volume of GdPO_4 , as well as the normalized pressure (F_e) versus the Eulerian strain (f_e) curves, and Figure 3 shows the changes in the unit cell parameters of GdPO_4 as a function of pressure. The F_e vs. f_e plot emphasizes small structural changes that may occur in response to pressure. All these plots show that GdPO_4 undergoes no phase transitions over the investigated pressure range (0–7 GPa) and that the compression mechanisms operating in this material are fully reversible.

Figure 2. (a) Volume ratio vs. pressure for GdPO_4 . Error bars are smaller than the data points; (b) F_e vs. f_e plot. The black curves represent the 3rd BM-EoS fits to the data. Data recorded during both pressure increase and decrease are shown as solid black and red circles, respectively.

Figure 3. Unit cell parameters vs. pressure for GdPO₄. Red: *a*-axis; green: *b*-axis; blue: *c*-axis. The black curves represent the 3rd BM-EoS fits to the data. Error bars are smaller than the symbols.

Each of these curves was fit with a 3rd-order Birch-Murnaghan equation of state (BM-EoS)¹² from which the elastic constants were derived (Table 2). GdPO₄ is reasonably incompressible with a unit cell volume decrease of only 4.68% over the 0–7.062(6) GPa pressure range, and has a bulk modulus (K_0) of 128.1(8) GPa ($K' = 5.8(2)$). A previously documented high-pressure powder diffraction study on synthetic GdPO₄, conducted up to 30 GPa, reported a significantly higher bulk modulus of 160(2) GPa.¹³ However, these authors used neon as their pressure transmitting medium, which solidifies at ~5 GPa. Above this pressure their GdPO₄ sample is likely to have experienced deviatoric stresses that are known to significantly influence the high-pressure behavior of rare-earth orthophosphates and other crystalline materials.¹⁴ It is therefore not unreasonable that our bulk modulus value, which was determined from data collected under hydrostatic conditions, varies significantly from theirs. This result highlights the critical need to understand the sample stress state (applied and internal) when determining the elastic properties of MPO₄ compounds of this class. Consistent with the high bulk modulus for GdPO₄ the axial moduli (M_0) are also large, however the values of M_0 show a trend of decreasing axial compression in the order: [001] > [010] > [100]. This suggests that the chains of alternating polyhedra that lie parallel to [100] are more rigid than the directions perpendicular to them. This is consistent with the cross-linking of the chains through edge-sharing GdO₉ polyhedra resulting in flexibility in the [001] and [010] directions.

Table 2. Elastic constants for GdPO₄ derived from 3rd-order BM-EoS fits to the variable pressure unit cell parameters.

			<i>a</i> -axis	<i>b</i> -axis	<i>c</i> -axis
V_0 (Å ³)	280.017(18)	X_0 (Å)	6.33584(11)	6.84839(18)	6.6519(2)
K_0 (GPa)	128.1(8)	M_0 (GPa)	463(3)	389(3)	297(2)
K'	5.8(2)	M'	15.2(9)	15.8(11)	16.2(8)
K'' (GPa ⁻¹)	-0.06991	M'' (GPa ⁻¹)	-0.11929	-0.15689	-0.21983

Compression Mechanism:

Due to the relatively high bulk modulus of GdPO_4 only small structural changes occur over the pressure range investigated here. Indeed, the subtlety of the pressure-induced changes can be seen visually in Figure 4. This figure shows an overlay of the gadolinium coordination sphere at room-pressure and at 7.062(6) GPa, and it is immediately clear that there are no significant alterations to the structure between these two pressure points. Therefore, to analyze how the structure changes, it is necessary to consider the effect of pressure on the larger features of the GdPO_4 structure rather than the small changes to individual angles/bonds, the magnitudes of which are within the estimated standard deviation for these parameters. To achieve this objective, we will consider the pressure-induced alterations to three components of the structure in turn: (i) the phosphate tetrahedra, (ii) the gadolinium polyhedra, and (iii) the inter-polyhedral distances.

Figure 4. An overlay of the Gd atom's coordination sphere at ~1 bar and 7.062(6) GPa. The ~1 bar structure is shown in dark purple and red, while the 7.062(6) GPa structure is shown in light pink and blue.

To discern whether there are any changes to the phosphate tetrahedra in response to pressure, it is useful to first calculate distortion parameters for these polyhedra. The distortion parameters of interest are the elongation parameter ($\langle\lambda_{\text{tet}}\rangle$) that quantifies the distortion to the tetrahedra due to variation in the bond lengths, and the bond angle variance ($\sigma_{(\text{tet})}^2$) that quantifies the distortion due to variation in the bond angles within the tetrahedra.¹⁵ For an ideal tetrahedron ($\langle\lambda_{\text{tet}}\rangle = 1$ and $\sigma_{(\text{tet})}^2 = 0$). Table 3 reports the values of these distortion parameters at various pressures. The PO_4 tetrahedra contain a fair amount of distortion. This is primarily due to deviations in the bond angles, as evident from the variance parameter that ranges from 22(3) to 29(4); while the elongation parameter remains constant at 1.01, and implies that the bond lengths do not vary greatly within the tetrahedra. However, there is no statistically relevant change in either distortion parameter with increasing pressure. Therefore, the phosphate tetrahedra can be treated as rigid units when analyzing the overall compression mechanisms of GdPO_4 up to 7.062(6) GPa.

Table 3. Distortion parameters for the phosphate tetrahedra at select pressures.

Pressure (GPa)	$V_{\text{tet}} (\text{\AA}^3)$	$l_0 (\text{\AA})$	$\langle \lambda_{\text{tet}} \rangle$	$(\sigma_{\text{tet}})^2$
~1 bar	1.826	1.527	1.01	29(4)
2.903(4)	1.816	1.524	1.01	23(3)
5.372(6)	1.807	1.521	1.01	29(3)
7.062(6)	1.820	1.525	1.01	26(3)

The gadolinium polyhedra were also analyzed for pressure-induced structural changes. However, before any distortion parameters could be calculated the geometry of the polyhedra had to be determined. The central gadolinium ion is coordinated to nine oxygen atoms with bond lengths ranging from 2.326(10)–2.788(13) Å; eight of these nine bonds are ~2.45 Å while one bond is ~2.75 Å. The GdO₉ coordination geometry is similar to that of a heavily distorted mono-capped square antiprism (MCSAP, Fig. 5a). To date, no distortion parameters have been defined for a MCSAP polyhedron, so we will use the following parameters to quantify the distortion of the single symmetry independent GdO₉ MCSAP in GdPO₄: (i) plane centroid⋯centroid distance, pc⋯pc; (ii) the Gd ion offset, Δ(Gd⋯pc), where Δ(Gd⋯pc) = $a - b$ (Fig. 5b); (iii) the elongation parameter, $\langle \lambda_{\text{sap}} \rangle$, which quantifies the distortion of the square antiprism due to variations in the M–O bond lengths (Eq. 1). This is equivalent to $\langle \lambda_{\text{tet}} \rangle$ (*vide supra*); and (iv) the angular variance, $\sigma_{(\text{mcsap})}^2$, which is equivalent to $\sigma_{(\text{tet})}^2$, and is calculated with Equation 2:

$$\langle \lambda_{\text{sap}} \rangle = \frac{1}{8} \sum_{i=1}^4 \left(\frac{{}^t l_i}{{}^t l_0} \right)^2 + \frac{1}{8} \sum_{i=1}^4 \left(\frac{{}^b l_i}{{}^b l_0} \right)^2$$

Equation 1.

$$\sigma_{(\text{mcsap})}^2 = \frac{1}{11} \sum_{i=4}^4 ({}^t \theta_i - 90)^2 + \frac{1}{11} \sum_{i=4}^4 ({}^b \theta_i - 90)^2 + \frac{1}{11} \sum_{i=4}^4 ({}^c \theta_i - 90)^2$$

Equation 2.

where ${}^t l_i$ and ${}^b l_i$ are the measured lengths of the Gd–O bonds that define the sides of the top and bottom square pyramids, respectively. ${}^t l_0$ and ${}^b l_0$ are the ideal Gd–O distances for a perfect square pyramid with a volume equal to that of the top and bottom pyramid, respectively. Parameters ${}^t \theta_i$ and ${}^b \theta_i$ are the for O–pc–O angles within the bases of the top and bottom square pyramids, respectively; ${}^c \theta_i$ are the four O–pc–O angles between the oxygen atoms comprising the base of the top pyramid and the capping oxygen atom. These distortion parameters are shown in Table 4. For an ideal MCSAP, these parameters are $\langle \lambda_{\text{sap}} \rangle = 1$ and $\sigma_{(\text{mcsap})}^2 = 0$. Under ambient pressure these parameters indicate that the MCSAP environment of the Gd³⁺ ion is heavily distorted, and this is primarily due to considerable deviation of the O–pc–O angles from 90° rather than because of variation in the Gd–O bond lengths.

Figure 5. (a) Schematic representation of an ideal MCSAP; (b) Distorted MCSAP geometry of the Gd^{3+} ions in GdPO_4 under ambient pressure. The Gd–O bond involving the capping oxygen atom is shown in green.

Table 4. Distortion parameters for the gadolinium polyhedra at select pressures.

Pressure (GPa)	$\text{pc} \cdots \text{pc}$ (Å)	$\Delta(\text{Gd} \cdots \text{pc})$ (Å)	l_0^a / l_0^b (Å)	$\langle \lambda_{\text{sap}} \rangle$	$(\sigma_{\text{mcsap}})^2$
~1 bar	2.332(8)	0.669(10)	2.455/2.434	1.00	631(6)
2.903(4)	2.308(7)	0.688(9)	2.509/2.423	0.97	644(5)
5.372(6)	2.288(8)	0.708(7)	2.543/2.468	0.93	631(5)
7.062(6)	2.271(6)	0.722(9)	2.399/2.414	1.00	637(5)

Figure 6. Pictorial representation of changes to the distances between neighbouring Gd^{3+} ions. Green struts represent a 0.104(1) Å decrease, black a 0.088(3) Å decrease, blue a 0.058(1) Å decrease, and the red struts represent no change in these distances between ambient and 7.062(6) GPa: (a) view along [100]; (b) view along [010]; (c) view along [001]. The unit cell is shown in grey.

There are no statistically relevant changes to the parameters $\langle \lambda_{\text{sap}} \rangle$ and $\sigma_{(\text{mcsap})}^2$ with pressure. However, there are statistically relevant changes to both the pc...pc distance and the $\Delta(\text{Gd}\cdots\text{pc})$ parameter with increasing pressure. As the pressure increases, the distance between the centroids of the square pyramid bases of the MCSAP decrease. Yet, the increase in the $\Delta(\text{Gd}\cdots\text{pc})$ parameter with pressure indicates that this is an asymmetrical compression (*i.e.* $\Delta a \neq \Delta b$). In fact, $\Delta b > \Delta a$ indicating that the Gd^{3+} ion is displaced towards the top plane of the MCSAP with increasing pressure. As shown in Figure 1, the Gd–O bond involving the capping oxygen atoms of the MCSAP polyhedra are orientated approximately parallel to the [100] direction. Therefore, these alterations to the MCSAP polyhedra can be envisaged as facilitating compression in this direction.

To evaluate the overall pressure-induced changes to the GdPO_4 structure it is beneficial to assess the secondary coordination sphere of the Gd^{3+} ions by considering the $\text{Gd}\cdots\text{Gd}$ distances between neighboring ions as these can be determined reliably from our high-pressure XRD data (Table 5). Figure 6 is a pictorial representation of how these pressure-induced decreases in the $\text{Gd}\cdots\text{Gd}$ distances relate to the overall compression of the structure. The largest decrease occurs between $\text{Gd}1\cdots^{\text{edge}}\text{Gd}^{\text{i}}$ and $\text{Gd}1\cdots^{\text{edge}}\text{Gd}^{\text{ii}}$ (see Fig. 1b for atom labeling scheme) is 0.104(1) Å and these interactions are aligned approximately parallel to the [100] and [010] directions. The two intermediate decreases of 0.058(1) Å (between $\text{Gd}1\cdots^{\text{edge}}\text{Gd}^{\text{iii}}$ and $\text{Gd}1\cdots^{\text{edge}}\text{Gd}^{\text{vii}}$) and 0.088(3) Å (between $\text{Gd}1\cdots^{\text{edge}}\text{Gd}^{\text{xi}}$) are aligned closest to the [010] and [001] directions. Lastly, there is no statistical change in the $\text{Gd}\cdots\text{Gd}$ distances that would contribute to a reduction in the *c*-axis ($\text{Gd}1\cdots^{\text{edge}}\text{Gd}^{\text{xii}}$). This analysis indicates that the combination of these structural changes corresponds well with the measured elastic constants for GdPO_4 (Table 2) that shows a decrease in compression in the order: [001] > [010] > [100].

Table 5. Distances between Gd atom positions at select pressures.

Distance	~1 bar	2.903(4)GPa	5.372(6) GPa	7.062(6) GPa	$\Delta(\text{P}_{\text{min}}/\text{P}_{\text{max}})$
$\text{Gd}1\cdots^{\text{edge}}\text{Gd}^{\text{i}}$	4.0075(7)	3.9614(6)	3.9268(7)	3.9033(6)	0.104(1)
$\text{Gd}1\cdots^{\text{edge}}\text{Gd}^{\text{ii}}$	4.0075(7)	3.9614(6)	3.9268(7)	3.9033(6)	0.104(1)
$\text{Gd}1\cdots^{\text{edge}}\text{Gd}^{\text{iii}}$	4.2036(4)	4.1771(4)	4.1569(4)	4.1454(4)	0.058(1)
$\text{Gd}1\cdots^{\text{edge}}\text{Gd}^{\text{vii}}$	4.2036(4)	4.1771(4)	4.1569(4)	4.1454(4)	0.058(1)
$\text{Gd}1\cdots^{\text{edge}}\text{Gd}^{\text{xi}}$	4.2212(18)	4.1793(14)	4.1509(13)	4.1328(13)	0.088(3)
$\text{Gd}1\cdots^{\text{edge}}\text{Gd}^{\text{xii}}$	4.0277(14)	4.0277(12)	4.0251(14)	4.0240(12)	0.00(4)

Symmetry codes: (i) $-x+1/2, y+1/2, -z+3/2$; (ii) $-x+1/2, y-1/2, -z+3/2$; (iii) $x-1/2, -y+3/2, z-1/2$; (vii) $x+1/2, -y+3/2, z+1/2$; (xi) $-x, 1-y, 1-z$; (xii) $-x, 1-y, 2-z$.

Raman Spectroscopy:

The Raman spectrum of GdPO_4 recorded in air under ambient conditions is shown in Figure 7. The peak assignments have been made based on polarized Raman data reported by Silva *et al.*¹⁶ Peaks below 450 cm^{-1} are associated with the lattice modes of the crystal structure and the low-frequency stretching vibrations of the Gd–O bonds ($300\text{--}350\text{ cm}^{-1}$). The ν_1 , ν_2 , ν_3 and ν_4 peaks are affiliated with internal modes of the PO_4 tetrahedra. According to group theory, several of these modes are multiply degenerate: $1\nu_1$, $2\nu_2$, $3\nu_3$ and $3\nu_4$.

Figure 7. Raman spectrum of GdPO₄ recorded in air under ambient conditions. Peak assignments are based on the polarized Raman results reported by Silva *et al.*¹⁶

Also present in the spectrum are unexpected peaks that are not predicted by theory. The origin of peaks that are in the regions of the ν_3 and ν_4 peaks has been a matter of contention. Several theories have been proposed for their occurrence including that they arise from splitting of the ν_3 and ν_4 fundamentals due to coupling between the PO₄ tetrahedra - or that they are overtone modes. It has also been suggested that they arise due to the activation of the transverse and longitudinal optical components of the IR modes.¹⁶

The hypothesis that these extra peaks originate from the breaking of the degeneracy of the ν_3 and ν_4 mode has previously been discredited for two reasons: (i) the lack of evidence of any covalent character of the Gd-O bond, which supports the idea that the (PO₄)³⁻ units should be considered as “free” (*i.e.* non-interacting) in the GdPO₄ crystal structure; (ii) the fact that the doubly degenerate ν_2 mode does not appear split, which would be expected if the other modes were split due to distortion of the PO₄ tetrahedra.^{16,17} However, more recent DFT calculations performed on isostructural CePO₄ and supported by experimental Raman studies have shown that these peaks are fundamental modes that arise from the local distortions in the PO₄ tetrahedra that leads to the lifting of the degeneracies of the P-O asymmetric stretching modes.¹⁸ This implies that the assumption that the (PO₄)³⁻ units can be regarded as “free” non-interacting units is flawed. Indeed, a systematic theoretical study of a broad range of MXO₄ (M = trivalent lanthanide ion; X = P, As) compounds, including GdPO₄, has unequivocally demonstrated that there is significant covalent character within the M-O bonds.¹⁹ These results are entirely consistent with our crystallographic findings that demonstrate that the tetrahedra are strongly distorted in the GdPO₄ structure (Table 3). This would not be expected if such units were truly structurally independent entities. With respect to the second objection, the ν_2 peak is broad, certainly when compared to the sharp singly degenerate ν_1 peak, and any fine splitting could easily be obscured.

Figure 8. Variable-pressure Raman data for GdPO₄: (a) 100–700 cm⁻¹ range; (b) 700–1200 cm⁻¹ range. The peak at ~1160 cm⁻¹ in the spectrum recorded at 0.439 GPa is an electronic spike and is not sample related. These spectra have been smoothed with a Savitzky–Golay function to enable spectral features to be seen clearly.

Variable-pressure Raman spectra of GdPO₄ are presented in Figure 8. Consistent with our HP-XRD data (Figs. 2 and 3), these data show no evidence of any structural phase transitions over the pressure range investigated (0.439–10.426 GPa). Within the hydrostatic regime ($P < 9.8$ GPa), the spectra are similar, however at 10.426 GPa additional peaks appear adjacent to the ν_3 peak (~1080 cm⁻¹) and between the ν_2 and ν_4 peaks (580–640 cm⁻¹). This could suggest that the presence of shear stresses further distorts the PO₄ units and potentially enhances the non-degeneracy of the internal PO₄ stretching modes.

It is immediately apparent from Figure 8 that the ν_3 asymmetric stretching mode of the PO₄ tetrahedra is the only peak to show a statistically significant shift between 0.439 and 8.244 GPa ($\Delta(\nu_3) = 32.7(1)$ cm⁻¹). This peak is not split in these spectra, presumably because of the reduction in data resolution relative to the spectrum collected with the sample in air (Fig. 7). It is also noticeable that the ν_4 peak becomes more pronounced with increasing pressure. This indicates that the pressure-induced distortions that occur within GdPO₄ impacts the asymmetric stretching of the PO₄ tetrahedra. That said, our HP-XRD results (Table 2) and theoretical studies¹⁹ suggest that the PO₄ units behave as rigid units under pressure, and therefore, we conclude that the changes in these modes are most likely a consequence of alterations in the Gd–O–P linkages (twisting or bending). One can envisage that this would result in the distortions to the GdO₉ polyhedra that were evident in the HP-XRD data. It is rather unfortunate that the Gd–O stretching modes that could potentially support or debunk this hypothesis are too poorly resolved in the Raman data to be analyzed.

Conclusion

In this contribution, we have presented a comprehensive high-pressure study of GdPO₄. Our results have shown that the bulk modulus of GdPO₄ measured under hydrostatic conditions (128(8) GPa) is notably different from the previously reported value of 160(2) GPa measured

under non-hydrostatic conditions. This finding suggests that GdPO₄, and possibly other MPO₄ materials are sensitive to shear stresses that could potentially influence not only their elastic properties but also their structural response to applied pressure. Moreover, accurate determination of the elastic constants for GdPO₄ has shown that the axial compressions are anisotropic and increase in the order of: [100] < [010] < [001].

Analysis of complementary high-pressure single-crystal diffraction and Raman data have established that the PO₄ tetrahedra act as rigid entities under pressure, and compression is enabled through adjustments to the O–Gd–P linkages that result in subtle alterations to the GdPO₉ polyhedra.

Importantly, this study has confirmed the resilience of GdPO₄ to pressure, and has confirmed the suitability of GdPO₄ as a candidate for inclusion in solid-state repository materials for high-level nuclear waste storage.

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Table of Contents Caption:

A high-pressure single crystal diffraction study of GdPO_4 with the monazite structure is presented. The elastic behaviour of rare-earth phosphates are believed to be sensitive to shear forces. The bulk modulus of GdPO_4 measured under hydrostatic conditions is 128.1(8) GPa. Compression of the structure is facilitated by bending/twisting of the Gd–O–P links that result in increased distortion in the GdO_9 polyhedra.