Supplementary Materials

Uncovering the Effects of Non-Hydrostaticity on Pressure-Induced Phase Transformation in Xenotime-Structured $TbPO_4$

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Sample synthesis: Xenotime $TbPO_4$ powder is synthesized via precipitation reaction and two subsequent calcination steps. First, 0.1 mol of $Tb(NO_3)_3 \cdot 5H_2O$ (≥99.9% RE oxide basis, Alfa Aesar) is dissolved in 200 mL of deionized water. Then, an excess of H_3PO_4 (>0.1 mol, 85% w/w aqueous solution, Alfa Aesar) is diluted in 200 mL of deionized water. This excess helps to ensure that all rare earth precursor reacts. These two solutions are then combined under vigorous magnetic stirring because the precipitation of white powder begins immediately. The resultant solution has a pH of ~1, which is then adjusted to ~10 via the addition of ammonium hydroxide (NH_4OH, 30%, Alfa Aesar) to accelerate precipitation. Next, the solution is centrifuged for 10 min at 1500 rpm. The supernatant solution is decanted, and the powder is dried overnight in a vacuum oven (100 °C, ~0.1 atm). The dried powder is then ball milled in ethanol with zirconia media for 24 h. The same centrifuge process is used to separate the milled powder from the ethanol, and vacuum-drying the powder takes a few hours (80 °C, ~0.1 atm). The first calcination profile for $TbPO_4$ is as follows: 5 °C/min ramp to 550 °C, 3 h hold at 550 °C, 5 °C/min ramp to 1600 °C, and 5 h hold at 1600 °C. Next, the powder goes through a second calcination profile: a 5 °C/min ramp to 1200 °C with a 5 h hold at 1200 °C. All cooling is performed at a rate of 5 °C/min.
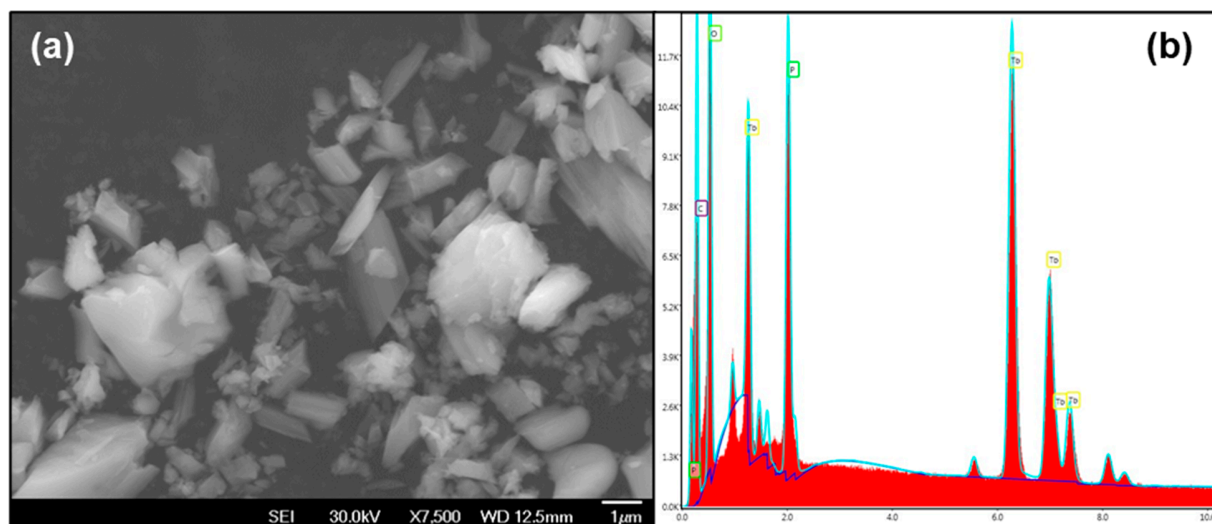
Figure S1. (a) Scanning electron microscope (SEM) image showing the expected tetragonal crystal habit of xenotime $TbPO_4$ grains with sizes ranging from sub-micrometer to several micrometers. (b) Energy-dispersive x-ray (EDX) spectrum of the xenotime $DyPO_4$ sample powder. All peaks in the spectrum can be attributed to the elements Tb, P, O, and C. The C signal comes from a deposited carbon coating (to reduce charging) and carbon tape under the sample. The image and spectrum were obtained using a JEOL 7000F SEM operating at 30.0 kV.
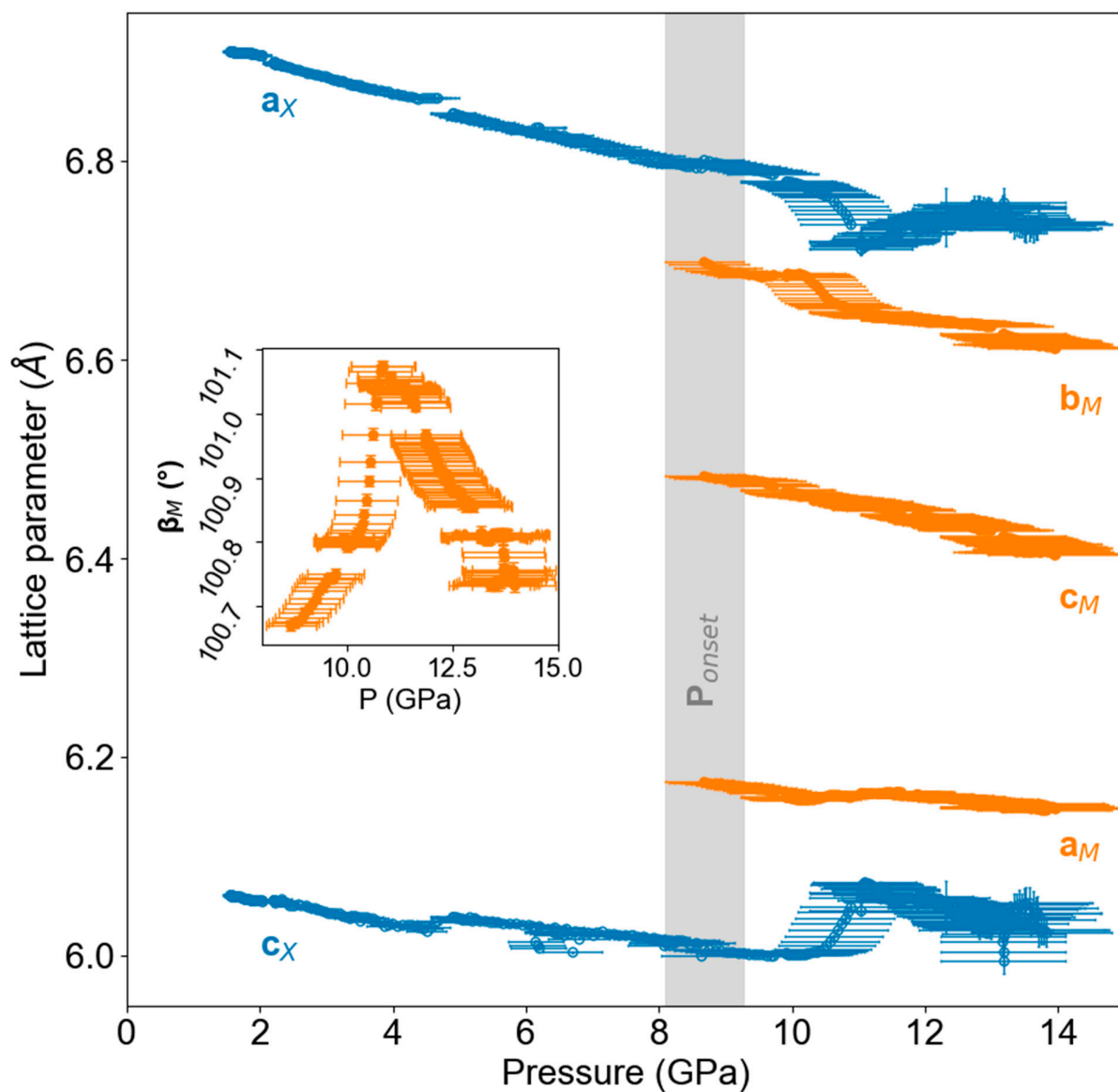
Figure S2. Pressure dependence of xenotime and monazite lattice parameters from the Tb-neon experiment with standard deviation error bars. The grey rectangle indicates P_{onset}. The inset shows the monazite beta angle with standard deviation error bars. Lattice parameters shown in blue and orange belong to the xenotime and monazite phases, respectively.

Figure S3. Pressure dependence of xenotime and monazite lattice parameters from the Tb-KCl experiment with standard deviation error bars. The grey rectangle indicates P_onset. The inset shows the monazite beta angle with standard deviation error bars. Lattice parameters shown in blue and orange belong to the xenotime and monazite phases, respectively.
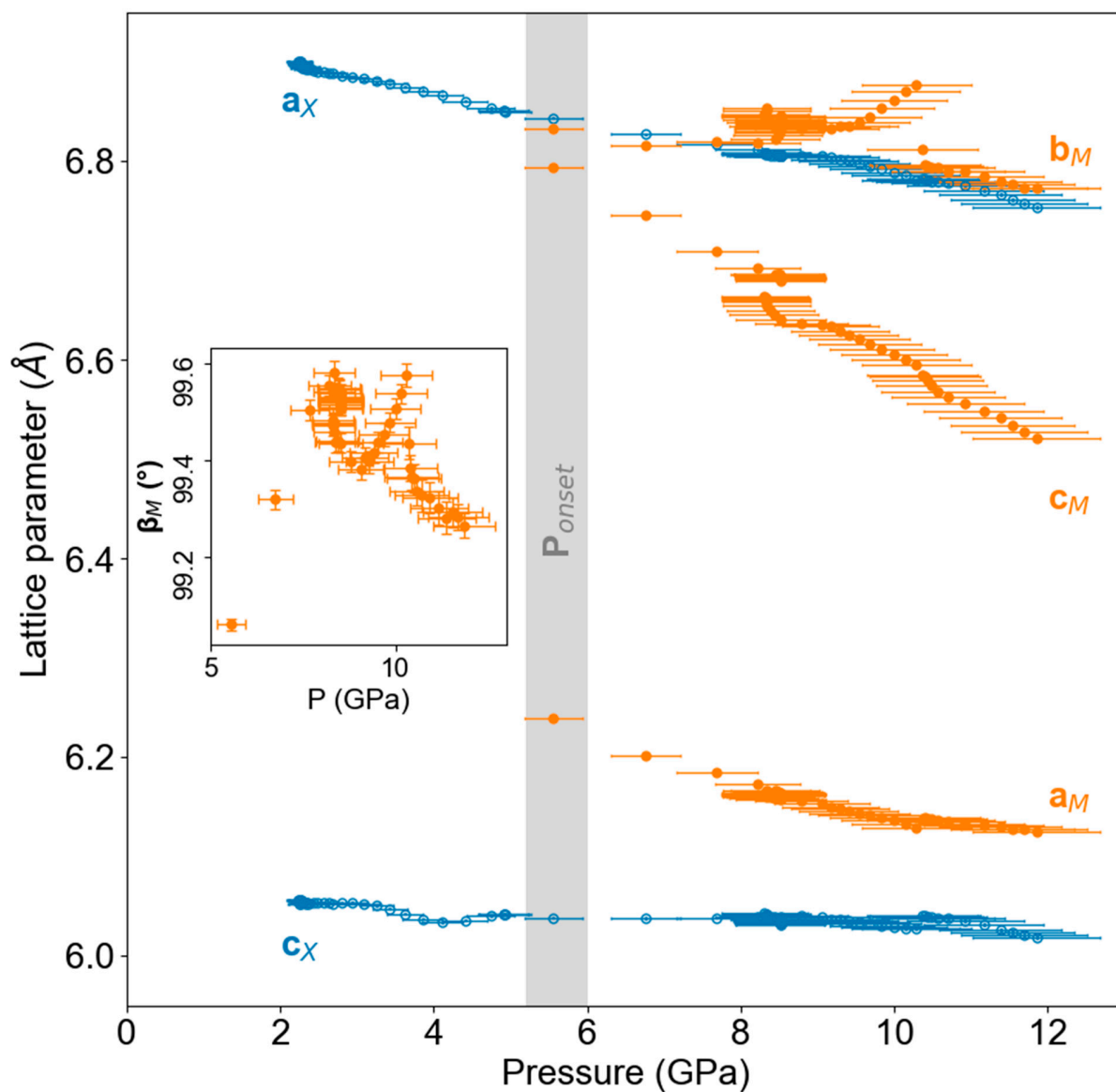
Figure S4. Pressure dependence of xenotime and monazite lattice parameters from the Tb-none experiment with standard deviation error bars. The grey rectangle indicates P_{onset}. The inset shows the monazite beta angle with standard deviation error bars. Lattice parameters shown in blue and orange/brown belong to the xenotime and monazite phases, respectively.

Figure S5. Pressure dependence of xenotime and monazite lattice parameters from the Dy-none experiment with standard deviation error bars. The grey rectangle indicates P_{onset}. The inset shows the monazite beta angle with standard deviation error bars. Lattice parameters shown in blue and orange belong to the xenotime and monazite phases, respectively.
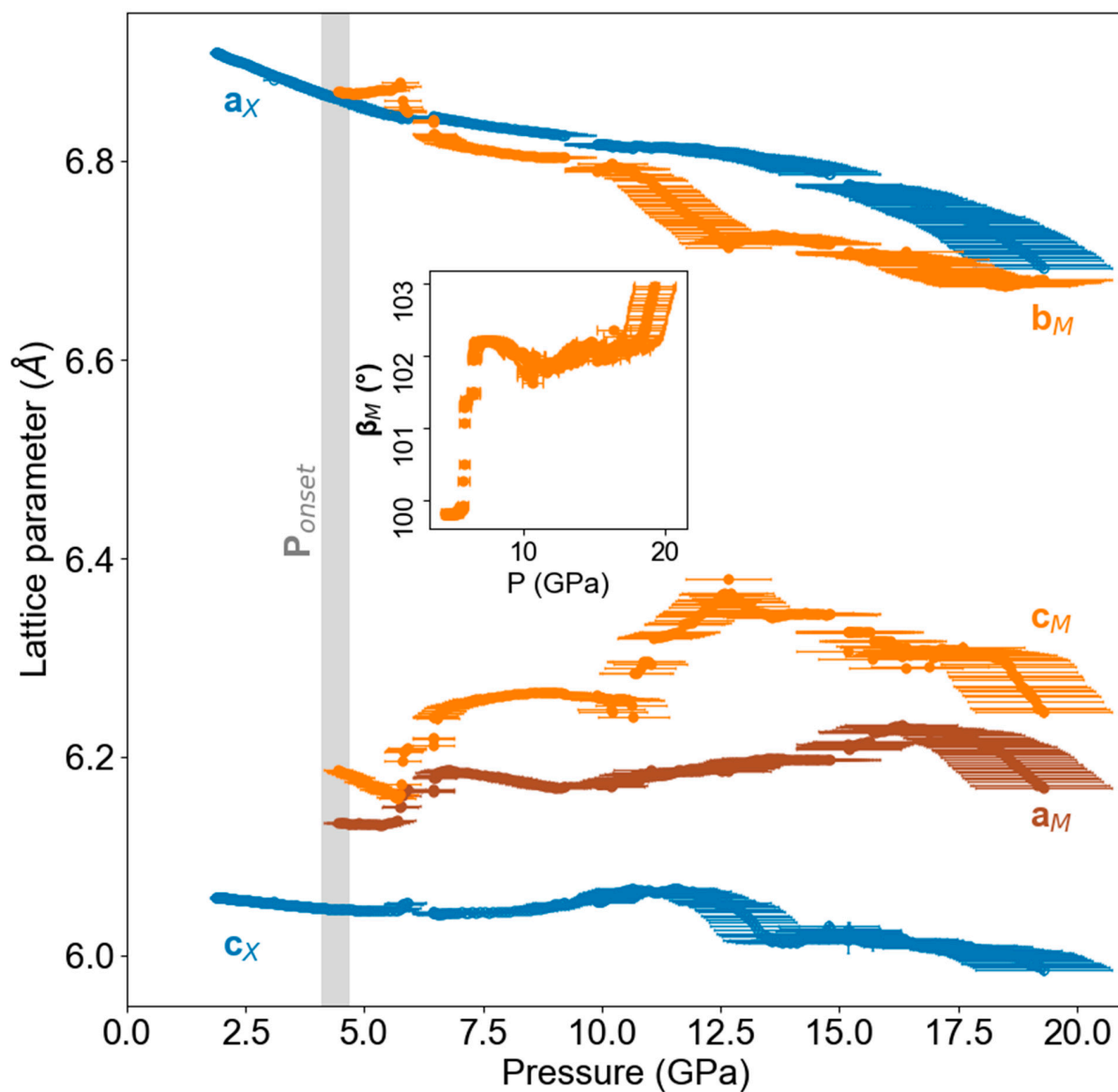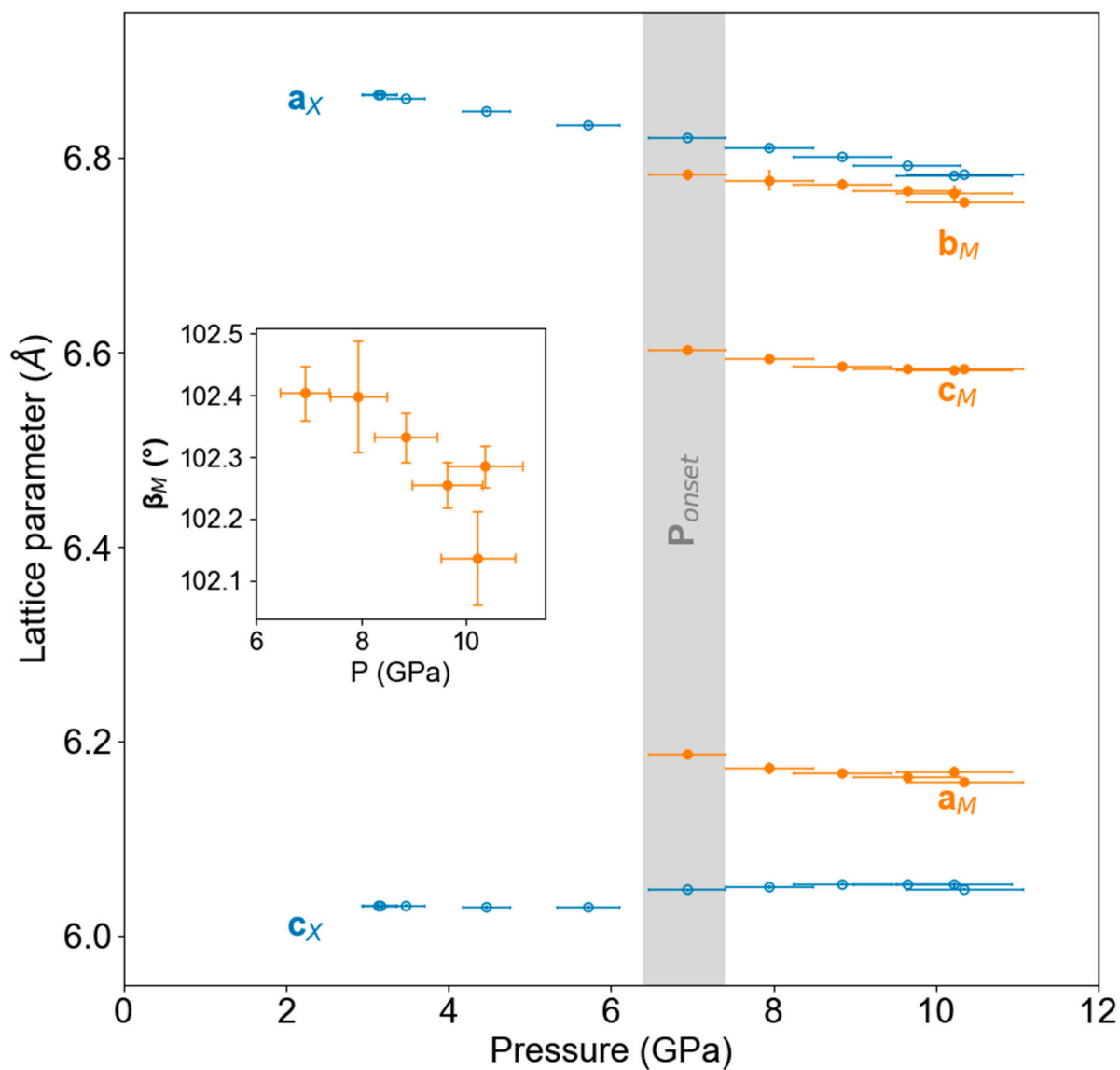
Table S1. Axial compressibility values (Å,° /GPa) x10^3 for each lattice parameter of each phase under each pressure-transmitting medium (PTM) for TbPO$_4$ and DyPO$_4$. Negative values indicate compression while positive values indicate expansion. Numbers in parentheses after a value represent the standard deviation of the last digit of the value. 'X' indicates xenotime, while 'M' indicates monazite. Compressibilities are determined using pressure ranges in which the data are monotonic, making a linear fit suitable. When a linear fit is not suitable or a phase does not have a certain lattice parameter, no compressibility is reported. *Data from Ref. [1].

RE	Phase	PTM	a	b	c	β
Tb	X	Neon	-16.95(11)	-	-7.06(9)	-
		KCl	-14.30(9)	-	-	-
		None	-17.66(6)	-	-4.44(5)	-
	M	Neon	-13.7(7)	-7.1(12)	-11.6(11)	-
		KCl	-14.7(7)	-	-44.3(16)	-
		None	-	-15.9(2)	-	
Dy	X	Neon*	-14.12(18)	-	-5.26(7)	-
		KCl*	-16.16(26)	-	-8.35(29)	-
		None	-11.35(11)	-	-3.3(4)	-
	M	Neon*	-4.88(34)	-5.84(64)	-9.65(36)	-
		KCl*	-0.03(40)	0.06(7)	-0.09(8)	-
		None	-7.7(11)	-5.3(12)	-8.1(13)	-45.8(16)

Table S2. Whole pattern fit R-values (R_{wp}) for the selected patterns shown in Figs. 2b, 4b, 5b, and 6b in the main text. Numbers in parentheses after a pressure represent the standard deviation of the last digit of the pressure. The subscripts 'X,' 'M,' and 'S' indicate xenotime, monazite, and scheelite, respectively. We note that LeBail fits did not converge when incorporating all the phases potentially present in the XRD patterns (e.g., ruby, anhydrite, scheelite).

Experiment	Scan	P (GPa)	R_{wp} (%)
Tb-neon	Initial	1.6(1)	16.29
	$P_{onset, M}$	8.7(6)	14.62
	$P_{end, X}$	13.7(10	11.94
	Final	14.0(10	12.89
Tb-KCl	Initial	2.2(2)	19.56
	$P_{onset, M}$	5.6(4)	7.33
	Final	11.9(8)	8.50
Tb-none	Initial	1.9(1)	23.87
	$P_{onset, M}$	4.4(3)	7.83
	$P_{onset, S}$	10.2(7)	13.24
	Final	19.3(14	11.40
Dy-none	Initial	3.1(2)	29.10
	$P_{onset, M}$	6.9(5)	13.13
	Final	10.4(7)	7.83

Table S3. Xenotime zero-pressure bulk moduli (B_0) and zero-pressure derivatives (B_0') obtained by fitting volume vs pressure data to the 3rd order Birch–Murnaghan EoS using the EoSFit7-GUI program. The weighted chi square value (χ^2_w) is the measure of goodness of fit. Fits were performed by fixing B_0' to 4 or by letting it float between 2 and 7. Numbers in parentheses after a value represent the standard deviation of the last digit of the value. The xenotime volume at 0 GPa (V_0) is fixed to 292.25(3) Å^3. Data used for fitting were confined to pressures lower than the xenotime-monazite P_{onset}. *Data from Ref. [1].

Sample	PTM	$B_0' = 4$		$2 \le B_0' \le 7$		
		B_0 (GPa)	χ^2_w	B_0 (GPa)	B_0'	χ^2_w
TbPO$_4$	Neon	151(1)	0.55	155(1)	2.0(1)	0.40
	KCl	150(2)	0.51	153(2)	2.0(1)	0.50
	None	169(1)	0.22	172(1)	2.0(1)	0.16
DyPO$_4$	Neon*	144(1)	0.05	135(1)	7.0(1)	0.03
	KCl*	204(18)	154.86	209(17)	2.0(40)	152.90
	None	180(6)	0.88	174(5)	7.0(1)	0.72

References

1. Sharma, J.; Musselman, M.; Haberl, B.; Packard, C.E. In Situ Synchrotron Diffraction of Pressure-Induced Phase Transition in DyPO$_4$ under Variable Hydrostaticity. *Phys. Rev. B* **2021**, *103*, 184105, https://doi.org/10.1103/PhysRevB.103.184105.