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Scheelite CaWO_4 at high pressures

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Abstract

The high-pressure room-temperature behaviour of scheelite CaWO_4 ($I4_1/a$, $Z = 4$) is studied using high-resolution synchrotron angle-dispersive x-ray powder diffraction in diamond anvil cells loaded with helium or a mixture of methanol and ethanol as the pressure-transmitting media. At about 10 GPa, there occurs a phase transition to the fergusonite type ($I2/a$, $Z = 4$) without any discontinuity in the pressure dependence of the unit cell volumes. These observations are discussed in relation to the high-pressure–high-temperature systematics of the AMX_4 and AX_2 type compounds.

1. Introduction

At ambient conditions MeWO_4 (Me: Ca, Sr, Ba, Pb) compounds, of which CaWO_4 is the archetype, have a scheelite structure ($I4_1/a$, $Z = 4$), i.e. a superstructure of fluorite CaF_2 ($Fm\bar{3}m$, $Z = 4$). The oxygen atoms are in a distorted simple cubic arrangement and the Me^{2+} and W^{6+} cations are respectively eightfold and fourfold coordinated by oxygens (figure 1). These tungstates are laser-host and luminescence materials, scintillators and oxide ion conductors [1].

The tungstate scheelites have been extensively studied at high pressures using Raman spectroscopy [2, 3], energy-dispersive powder x-ray diffraction [4], and single-crystal x-ray diffraction [5]. Reversible phase transitions in CaWO_4 , SrWO_4 , BaWO_4 and PbWO_4 occur near 12, 11.5, 6.5 and 4.5 GPa respectively [2–4]. In the energy-dispersive study on CaWO_4 [4], it was postulated that its high-pressure phase is of the wolframite type ($P2/c$, $Z = 2$), taken by MgWO_4 at ambient conditions. In addition, a new crystalline modification of CaWO_4 originating from the amorphous phase above 40 GPa and supposedly with the structure of MnMoO_4 ($C2/m$, $Z = 4$) was suggested [6]. The high-pressure–high-temperature forms of BaWO_4 [7] and PbWO_4 [8] are monoclinic ($P2_1/n$, $Z = 8$) with no resemblance to the scheelite or wolframite types.

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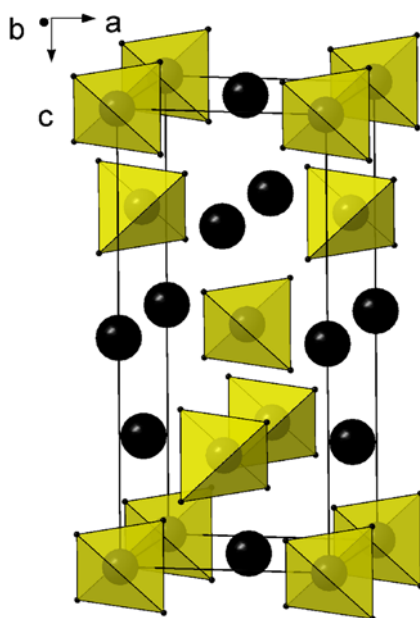


Figure 1. Crystal structure of scheelite CaWO_4 ($I4_1/a$, $Z = 4$) at ambient conditions. The tungstate atoms are tetrahedrally coordinated to the oxygen atoms.

(This figure is in colour only in the electronic version)

Despite such a large number of experimental reports, the actual high-pressure behaviours of these compounds and their pressure-induced polymorphs are not known at all. X-ray diffraction measurements on single crystals provided information on compressibilities of selected scheelites to about 6 GPa [5]. Results of a detailed Raman study on CaWO_4 and SrWO_4 [3], showing softening of several modes, cannot be reconciled with the first-order scheelite \rightarrow wolframite phase transition discussed in [4]. In that study, four structural models were applied to index the powder pattern of the post-scheelite structure of CaWO_4 : MnMoO_4 type ($C2/m$, $Z = 4$), wolframite type ($P2/c$, $Z = 2$), BaWO_4 type ($P2_1/n$, $Z = 8$), and HgWO_4 type ($C2/c$, $Z = 4$). On the basis of the quality of the unit cell fit, it was concluded that the high-pressure phase is of the wolframite type ($P2/c$, $Z = 2$). A close inspection of the energy-dispersive powder pattern, for a sample annealed at above 40 GPa approximated with the MnMoO_4 structure ($C2/m$, $Z = 4$) [6], reveals that several doublets were indexed as single peaks, e.g. the doublet near 22 keV.

A brief review of the literature on the high-pressure behaviours of scheelite-type compounds indicates that post-scheelite structures in oxides as well as in any other AMX_4 -type compound [2–10] are not fully known. In this study, we re-examine details of the phase transition in CaWO_4 at about 11 GPa at room temperature [3, 4] as observed with synchrotron angle-dispersive x-ray powder diffraction in diamond anvil cells. We then discuss our results in relation to the high-pressure–high-temperature systematics of the AMX_4 and AX_2 type compounds.

2. Experimental details

A sample of polycrystalline CaWO_4 scheelite (Chempur Feinchemikalien und Forschungsbedarf GmbH, Karlsruhe) was finely ground in ethanol and loaded into diamond anvil cells with

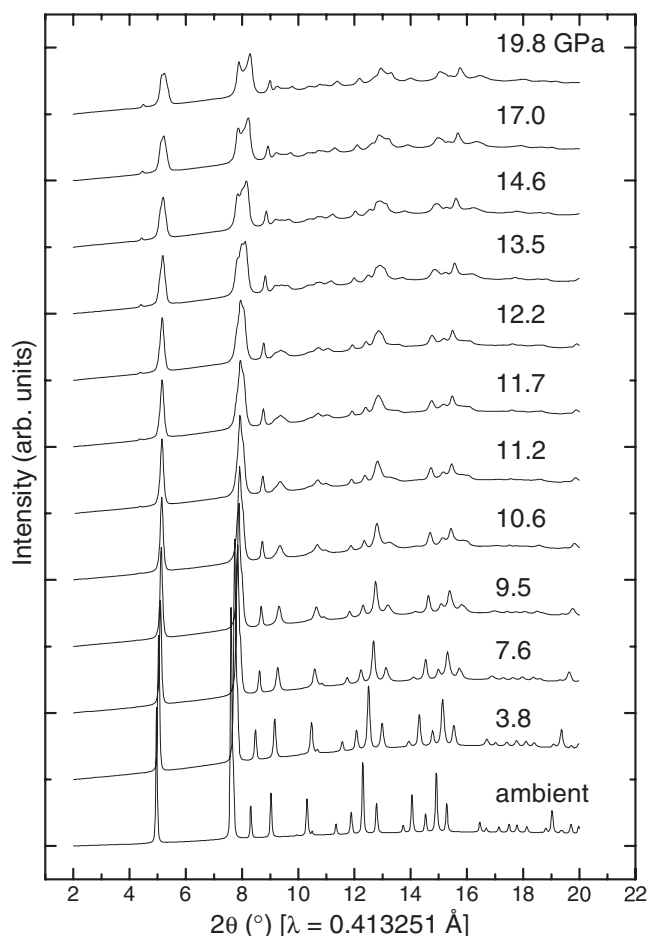


Figure 2. Selected x-ray powder patterns of CaWO_4 with helium as the pressure-transmitting medium.

helium or a mixture of methanol and ethanol as the pressure-transmitting media. The choice of these two media is based on the fact that helium ensures fully hydrostatic conditions, while the alcohol mixture has already been used for Raman scattering [2, 3] and single-crystal x-ray diffraction measurements of compressibilities [5] in tungstate scheelites. Angle-dispersive powder x-ray diffraction patterns were measured at room temperature on the ID09a beamline at the European Synchrotron Radiation Facility, Grenoble. Monochromatic radiation at $0.413\,251\text{ \AA}$ was used for pattern collection on image plates. The images were integrated using the FIT2D program [11] to yield intensity versus 2θ diagrams. The instrumental resolution, i.e. the minimum full width at half-maximum (FWHM) of diffraction peaks determined using a silicon standard, was 0.04° . The ruby luminescence method [12] was used for pressure measurements. At ambient conditions, the measured pattern matched perfectly the one calculated with the PowderCell program [13] using the structural data by Hazen *et al* [5].

A Rietveld refinement of the pattern collected at 11.2 GPa with helium as the pressure-transmitting medium was carried out using the GSAS program [14]. The refined parameters included the lattice parameters, fractional atomic coordinates, Chebyshev polynomial for the

Table 1. Structural parameters of fergusonite CaWO_4 at 11.2 GPa with helium as the pressure-transmitting medium: $I2/a$, $Z = 4$, $a = 5.0706(5)$ Å, $b = 10.8528(8)$ Å, $c = 5.0812(9)$ Å, $\beta = 90.082(13)^\circ$. Estimated standard deviations are given in brackets.

Atom	Site	x	y	z
Ca	4e	1/4	0.6098(10)	0
W	4e	1/4	0.1320(5)	0
O1	8f	0.9214(44)	0.9661(17)	0.2337(29)
O2	8f	0.4807(23)	0.2164(16)	0.8529(51)
Selected bond distances (Å)				
Ca–O1	(2×)	2.24(2)		
Ca–O1	(2×)	2.30(2)		
Ca–O2	(2×)	2.44(2)		
Ca–O2	(2×)	2.54(2)		
W–O1	(2×)	1.82(2)		
W–O2	(2×)	1.66(2)		
W–O2		2.70(2)		

background, Stephens profile function parameters [15] and the overall intensity scaling factor. The isotropic thermal parameters U_i/U_e for Ca, W and O atoms were fixed at 0.01, 0.005 and 0.02 respectively, and not refined.

3. Results

X-ray powder diffraction patterns of CaWO_4 at selected pressures with helium as the pressure-transmitting medium are shown in figures 2 and 3. At pressures up to about 10 GPa, all reflections can be indexed with the scheelite polymorph ($I4_1/a$, $Z = 4$). At higher pressures, a peak splitting and the appearance of new weak reflections (figures 2–4), in particular the peak at about $2\theta = 4.5^\circ$, imply a continuous phase transformation to a low-symmetry fergusonite structure ($I2/a$, $Z = 4$) that is a distorted variant of the scheelite type, as previously observed for rare earth niobates and tantalates [16]. Similar behaviour of CaWO_4 is observed upon compression at room temperature in the mixture of methanol and ethanol (figures 5 and 6). In this case, however, the transformation occurs at a slightly lower pressure of about 9 GPa (figures 5–7).

The full Rietveld refinement of the profile at 11.2 GPa with the fergusonite model is shown in figure 4: $R_{\text{wp}} = 2.51\%$, $R_p = 1.4\%$, $R(F^2) = 3.82\%$ (the residuals R_{wp} and R_p have been calculated with the background eliminated, see the GSAS manual for more details [14]). The starting Ca, W and O positions have been derived from the atomic coordinates in the scheelite type [5] using the $I4_1/a \rightarrow I2/a$ subgroup relationship as implemented in the PowderCell program [13]. The corresponding structural parameters are given in table 1. The choice of origin for both figure 1 and the data in table 1 was made with PowderCell [13]. The W–O bonds and next nearest neighbour W–O distances are 1.66–1.82 and 2.7 Å. Therefore, the WO_4^{2-} tetrahedra are largely distorted but still isolated.

At ambient pressure, the lattice parameters for scheelite CaWO_4 studied here are $a = 5.2378(1)$ Å, $c = 11.3770(1)$ Å and $V = 312.12(3)$ Å³. The pressure dependence of the lattice parameters in the scheelite and fergusonite polymorphs is plotted up to about 13 GPa in figure 7. At higher pressures, regardless of the pressure-transmitting medium, the quality of the patterns has deteriorated significantly so that the extracted parameters are not reliable. No discontinuities in the evolution of the unit cell volumes and the c tetragonal and b monoclinic

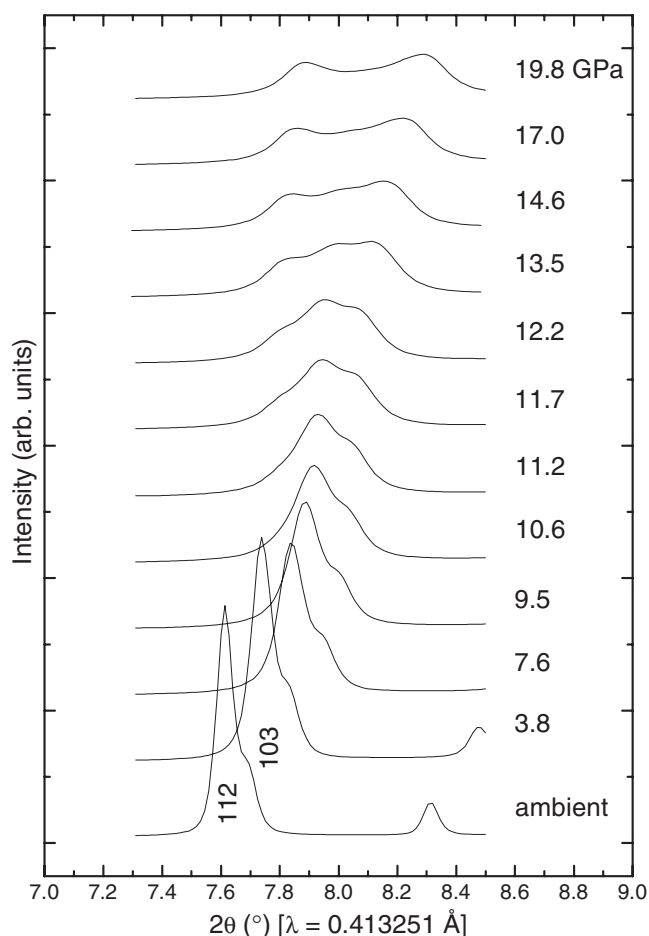


Figure 3. Selected x-ray powder diffraction patterns of CaWO₄ in the range $2\theta = 7.3^\circ$ – 8.5° with helium as the pressure-transmitting medium. The (112) and (103) reflections of the scheelite phase ($I4_1/a$, $Z = 4$) are marked.

axial parameters are observed during the phase transition. This indicates that changes in the unit cell volume between the two phases are negligible or not resolved in our x-ray powder diffraction experiments. The β angle and differences between the a and c lattice parameters (or b/a and b/c axial ratios) in the $I2/a$ structure are measures of the monoclinic distortion, and increase with pressure.

The compression data for both the scheelite and fergusonite polymorphs to 12.2 GPa in different pressure ranges with helium as the pressure-transmitting medium have been fitted by a Birch equation of state $P(V) = 1.5B_0(x^{-7} - x^{-5})(1 - y)$, where $x = (V/V_0)^{1/3}$ and $y = 0.75(4 - B')(x^{-2} - 1)$ [17], giving the zero-pressure bulk modulus B_0 , the first derivative of the bulk modulus B' , and the unit cell volume of scheelite at ambient pressure V_0 (table 2). The respective parameters for the scheelite phase only to 9.5 GPa are within the estimated errors. They represent the true compressibility of the scheelite polymorph up to the pressure-induced scheelite–fergusonite phase transition at 10 GPa with helium as the pressure-transmitting medium: $V_0 = 312.5(6) \text{ \AA}^3$, $B_0 = 68(6) \text{ GPa}$, $B' = 5.59(1.65)$.

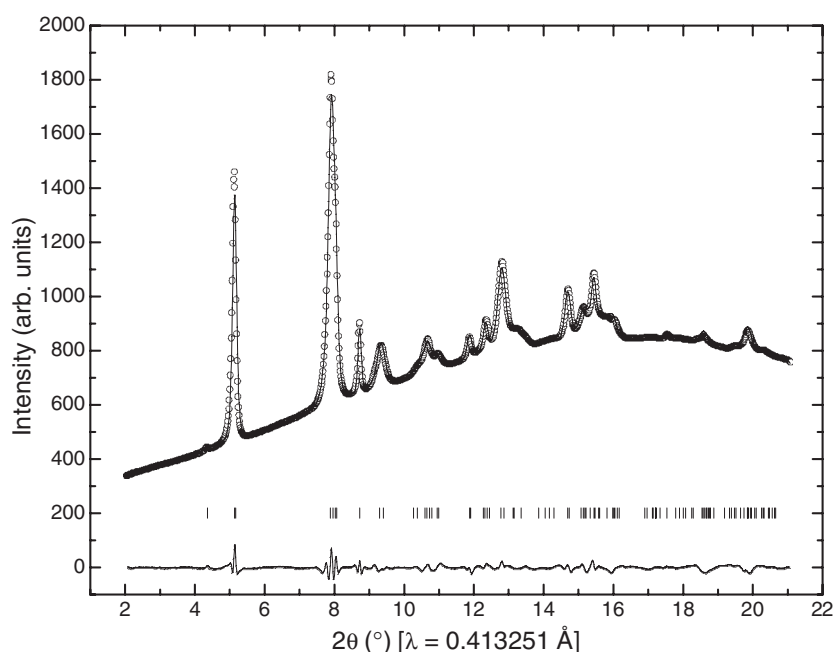


Figure 4. Observed, calculated, and difference x-ray powder patterns for fergusonite CaWO_4 at 11.2 GPa with helium as the pressure-transmitting medium: $I2/a$, $Z = 4$, $a = 5.0706(5)$ Å, $b = 10.8528(8)$ Å, $c = 5.0812(9)$ Å, $\beta = 90.082(13)^\circ$. Vertical markers indicate Bragg reflections.

Table 2. Equation-of-state parameters for CaWO_4 determined in this study and compared with the parameters reported previously by Hazen *et al* [5] and Errandonea *et al* [6].

Pressure range (GPa)	Pressure medium	Polymorph	V_0 (Å ³)	B_0 (GPa)	B'
This work					
0–12.2	Helium	Scheelite + fergusonite	312.2(7)	74(6)	3.89(1.0)
			312.2(4)	73(1)	4.0 ^a
0–9.5		Scheelite	312.5(6)	68(6)	5.59(1.65)
			312.1(4)	74(2)	4.0 ^a
Hazen <i>et al</i> [5]					
0–4.1	Methanol:ethanol	Scheelite	312.6(4)	68(9)	4.0 ^a
Errandonea <i>et al</i> [6]					
0–12	None	Scheelite	47(0.26) ^b	77(8)	4.9(0.9)

^a B' fixed at 4.0 and not refined.

^b V_0 is in units of $\text{cm}^3 \text{mol}^{-1}$.

4. Discussion

Our observation of a continuous pressure-induced phase transition to the fergusonite structure ($I2/a$, $Z = 4$) in scheelite CaWO_4 ($I4_1/a$, $Z = 4$) at room temperature does not agree with the abrupt transition to the wolframite type ($P2/c$, $Z = 2$) suggested previously on the basis of low-resolution energy-dispersive x-ray powder diffraction measurements [4]. Both scheelite and fergusonite structures are ordered superstructures of the fluorite type ($Fm\bar{3}m$,

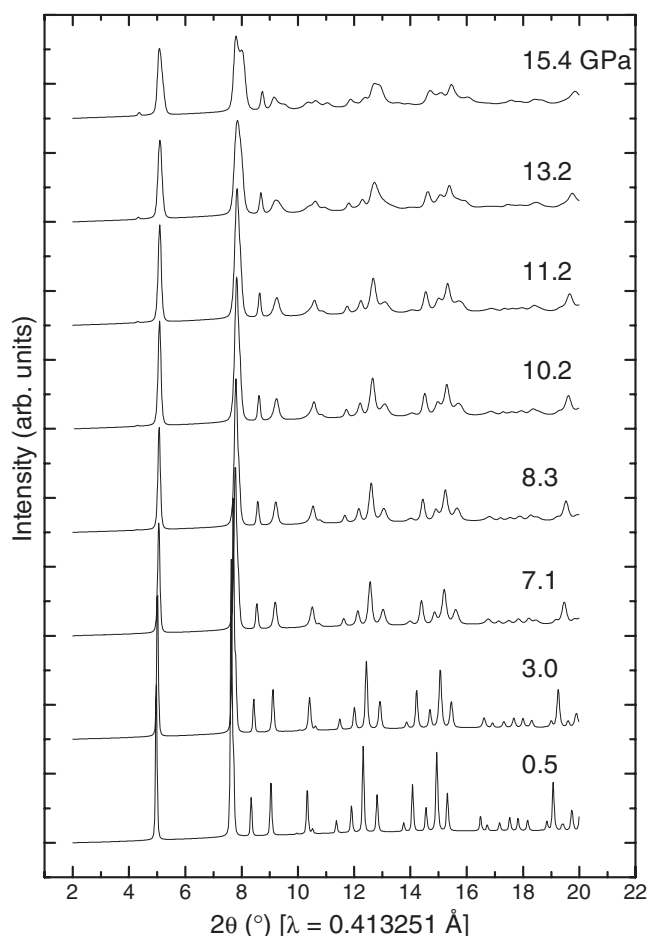


Figure 5. Selected x-ray powder diffraction patterns of CaWO₄ with a mixture of methanol and ethanol as the pressure-transmitting medium. The numbers stand for pressures in GPa.

$Z = 4$). The oxygen atoms are in a distorted simple cubic arrangement and the Ca²⁺ and W⁶⁺ cations are respectively eightfold and fourfold coordinated by oxygens. Our structure determination of the high-pressure polymorph of CaWO₄ well explains the anomalous pressure dependence of Raman-active modes [3]. The temperature-induced ferroelastic $I4_1/a \rightarrow I2/a$ transformation in rare earth niobates and tantalates at atmospheric conditions is associated with the anisotropic phonon softening of a transverse acoustic mode at the Brillouin zone centre [16]. As in lanthanide niobates and tantalates [16] and in the pressure-induced fergusonite phase in YLiF₄ [18], it remains to be seen whether this $I4_1/a \rightarrow I2/a$ transition is of the first or second order.

Understanding of the phase transitions in materials with a scheelite-type structure can be improved by a consideration of the crystal chemistry systematics in AMX₄ and AX₂ type compounds. The scheelite structure is the high-pressure form of the zircon ZrSiO₄ ($I4_1/amd$, $Z = 4$), monazite CePO₄ ($P2_1/n$, $Z = 4$) and CrVO₄ ($Cmcm$, $Z = 4$) types [9, 10]. The zircon structure is closely related to the rutile TiO₂ type ($P4_2/mnm$, $Z = 2$) [9]. Chains of edge-sharing TiO₆ octahedra in rutile become chains of alternating ZrO₈ bidisphenoids and SiO₄ tetrahedra in the zircon type. In the monazite structure, isolated PO₄ tetrahedra are linked

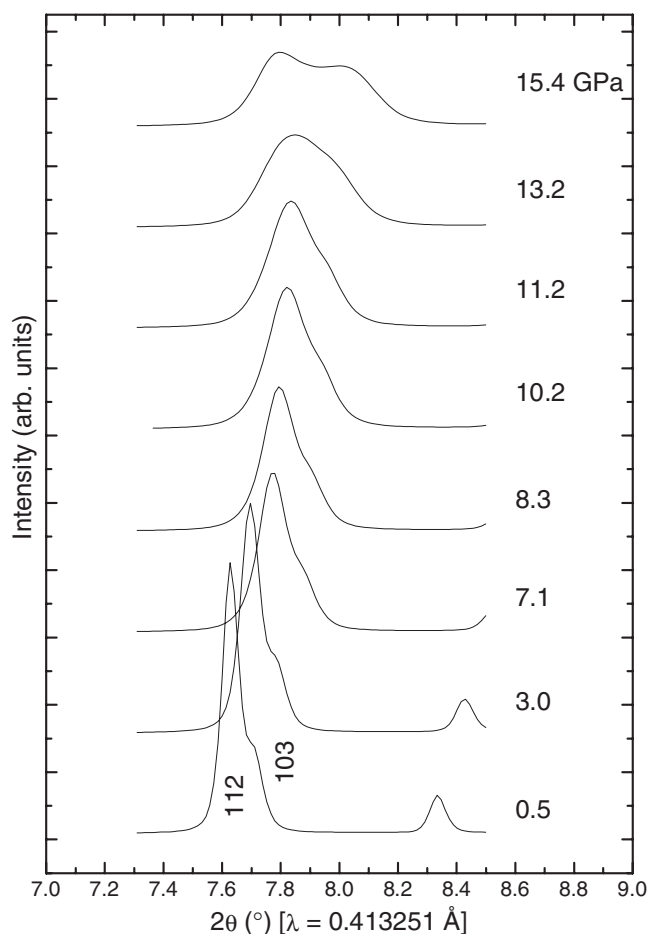


Figure 6. Selected x-ray powder patterns of CaWO_4 in the range $2\theta = 7.3^\circ$ – 8.5° with a mixture of methanol and ethanol as the pressure-transmitting medium. The numbers stand for pressures in GPa. The (112) and (103) reflections of the scheelite phase ($I4_1/a$, $Z = 4$) are marked.

together by CeO_8 polyhedra. Monazite is the high-temperature form of ThSiO_4 zircon [10]. Oxygen atoms in CrVO_4 form a distorted cubic close-packed array [10, 19]. Each CrO_6 octahedron shares two opposite edges with two neighbouring octahedra, forming octahedral chains parallel to the c axis linked together by VO_4 tetrahedra. Wolframite ($P2/c$, $Z = 2$) is an ordered superstructure of $\alpha\text{-PbO}_2$ ($Pbcn$, $Z = 4$), in which octahedra share edges to form zigzag strings along the c axis [9, 19].

The zircon \rightarrow scheelite and monazite \rightarrow scheelite transformations for the AMX_4 compounds [9, 10] are analogous to those for the AX_2 compounds as the rutile-type phases transform towards the fluorite type at high pressures [9, 20]. One of the possible intermediates in this process is the $\alpha\text{-PbO}_2$ -type structure. Hence, contrary to a recent report [4] and in accordance with the results of this study, the scheelite \rightarrow wolframite transformation in the AMX_4 compounds is not to be expected on the basis of the high-pressure–high-temperature systematics in the AX_2 group of materials. The analogies in the crystal chemistry of the AX_2 compounds and their AMX_4 superstructures [9, 10, 19] under pressure warrant further investigations to elucidate pressure-induced post-scheelite(–fergusonite) structures.

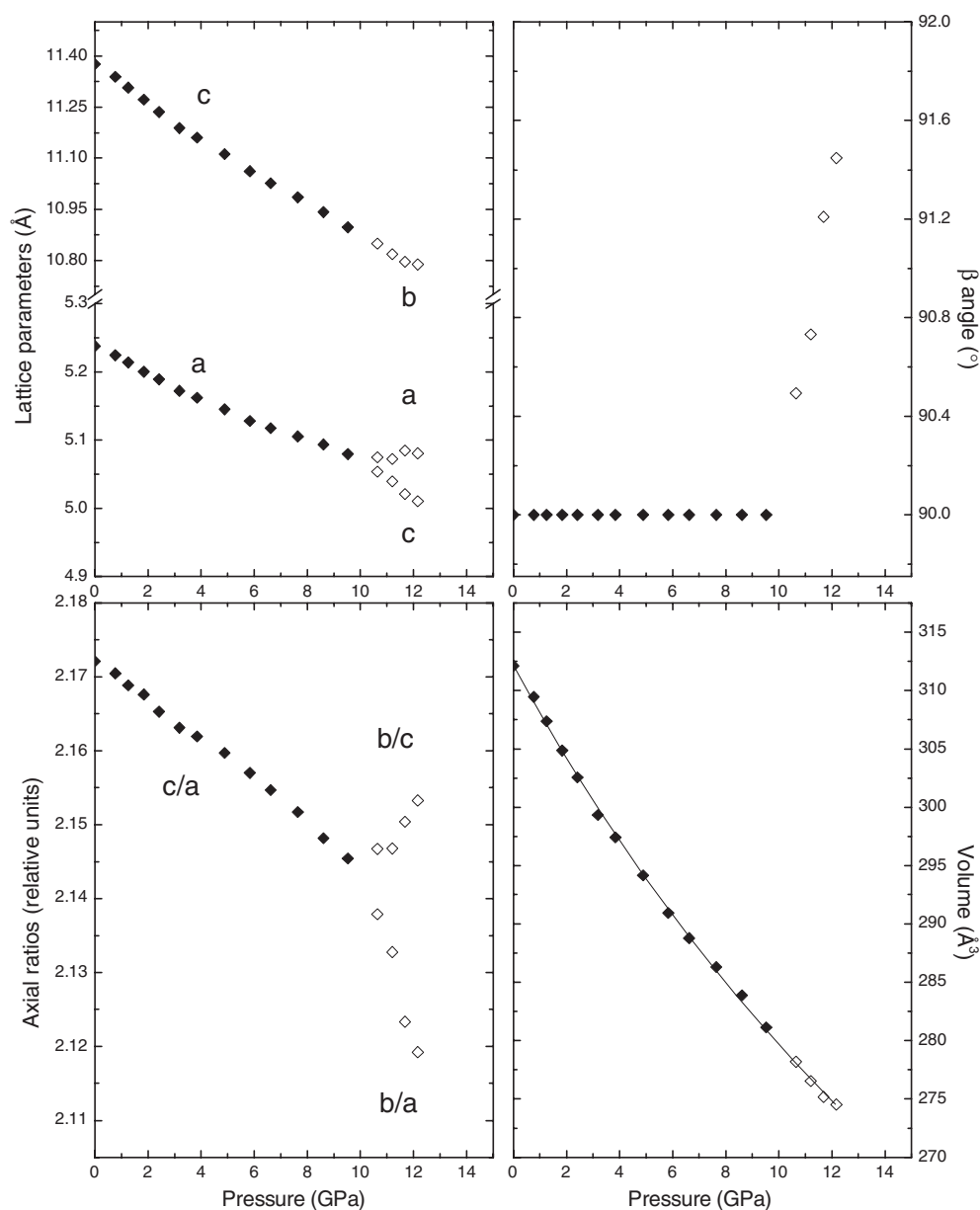


Figure 7. Pressure dependence of lattice parameters of CaWO_4 with helium as the pressure-transmitting medium. Full and open symbols represent the parameters for the scheelite ($I4_1/a$, $Z = 4$) and fergusonite ($I2/a$, $Z = 4$) polymorphs respectively. The curve in the pressure dependence of the unit cell volumes for both the scheelite and fergusonite phases represents the equation-of-state fit [17] with $V_0 = 312.2(7) \text{ \AA}^3$, $B_0 = 74(6) \text{ GPa}$ and $B' = 3.89(1.0)$.

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References

- [1] Lou Z and Cocivera M 2002 *MRS Bull.* **37** 1573
Liu B et al 2002 *J. Phys.: Condens. Matter* **14** 7065
Fujita M et al 2002 *Phys. Rev. B* **65** 195105
- [2] Jayaraman A, Batlogg B and VanUitert L G 1983 *Phys. Rev. B* **28** 4774
Jayaraman A, Batlogg B and VanUitert L G 1985 *Phys. Rev. B* **31** 5423
Jayaraman A, Sharma S K and Wang S Y 1998 *J. Raman Spectrosc.* **29** 305
- [3] Christofilos D, Ves S and Kourouklis G A 1996 *Phys. Status Solidi b* **198** 539
- [4] Errandonea D, Somayazulu M and Häusermann D 2002 *Phys. Status Solidi b* **231** R1
- [5] Hazen R M, Finger L W and Mariathasan J W E 1985 *J. Phys. Chem. Solids* **46** 253
- [6] Errandonea D, Somayazulu M and Häusermann D 2003 *Phys. Status Solidi b* **235** 162
- [7] Kawada I, Kato K and Fujita T 1974 *Acta Crystallogr. B* **30** 2069
- [8] Richter P W, Kruger G J and Pistorius C W F T 1976 *Acta Crystallogr. B* **32** 928
- [9] Hyde B G and Andersson S 1989 *Inorganic Crystal Structures* (New York: Wiley)
- [10] Muller O and Roy R 1974 *The Major Ternary Structural Families* (Berlin: Springer)
- [11] Hammersley A P, Svensson S O, Hanfland M, Fitch A N and Häusermann D 1996 *High Pressure Res.* **14** 235
- [12] Piermarini G J, Block S, Barnett J D and Forman R A 1975 *J. Appl. Phys.* **46** 2774
Mao H K, Xu J and Bell P M 1986 *J. Geophys. Res.* **91** 4673
- [13] Kraus W and Nolze G 1998 *CPD Newsletter no. 20* International Union of Crystallography
- [14] Larson A C and von Dreele R B 2000 *GSAS: General Structure Analysis System* Los Alamos National Laboratory
- [15] Stephens P W 1999 *J. Appl. Crystallogr.* **32** 281
- [16] Tsunekawa S, Kamiyama T, Sasaki K, Asano H and Fukuda F 1993 *Acta Crystallogr. A* **49** 595
Tsunekawa S, Kamiyama T, Asano H and Fukuda T 1995 *J. Solid State Chem.* **116** 28
Borisov S V and Ipatova E N 1994 *J. Struct. Chem.* **35** 865
Kondrateva I A, Filatov S K, Andrianova L V and Korovkin A M 1989 *Inorg. Mater.* **25** 1446
Parlinski K, Hashi Y, Tsunekawa S and Kawazoe Y 1997 *J. Mater. Res.* **12** 2428
Kuroiwa Y, Aoyagi S, Shobu T, Nozawa K, Tsunekawa S and Noda Y 1999 *Japan. J. Appl. Phys.* **38** 600
- [17] Birch F 1978 *J. Geophys. Res.* **83** 1257
- [18] Grzechnik A, Syassen K, Loa I, Hanfland M and Gesland J Y 2002 *Phys. Rev. B* **65** 104102
- [19] Wells A F 1984 *Structural Inorganic Chemistry* 5th edn (Oxford: Oxford University Press)
- [20] Leger J M and Haines J 1997 *Eur. J. Solid State Inorg. Chem.* **34** 785