



**Experiment title:**  
Tungstate scheelites at high pressures

**Experiment number:**  
HS2120

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## Report:

At ambient conditions,  $\text{MeWO}_4$  (Me: Ca, Sr, Ba, Pb) compounds, of which  $\text{CaWO}_4$  is the archetype, have a *scheelite* structure ( $I4_1/a$ ,  $Z = 4$ ), i.e., a superstructure of *fluorite*  $\text{CaF}_2$  ( $Fm\bar{3}m$ ,  $Z = 4$ ). The oxygen atoms are in a distorted simple cubic arrangement and the  $\text{Me}^{2+}$  and  $\text{W}^{6+}$  cations are eightfold and fourfold coordinated by oxygens, respectively.

The tungstate *scheelites* have been extensively studied at high pressures using Raman spectroscopy [1,2], energy-dispersive powder x-ray diffraction [3], and single-crystal x-ray diffraction [4]. Reversible phase transitions in  $\text{CaWO}_4$ ,  $\text{SrWO}_4$ ,  $\text{BaWO}_4$ , and  $\text{PbWO}_4$  occur near 12, 11.5, 6.5, and 4.5 GPa, respectively [1-3]. In the energy-dispersive study on  $\text{CaWO}_4$  [3], it was postulated that its high-pressure phase is of the *wolframite* type ( $P2/c$ ,  $Z = 2$ ), taken by  $\text{MgWO}_4$  at ambient conditions. In addition, a new crystalline modification of  $\text{CaWO}_4$  originating from the amorphous phase above 40 GPa and supposedly with the structure of  $\text{MnMoO}_4$  ( $C2/m$ ,  $Z = 4$ ) was suggested [5]. The high-pressure high-temperature forms of  $\text{BaWO}_4$  [6] and  $\text{PbWO}_4$  [7] are monoclinic ( $P2_1/n$ ,  $Z = 8$ ) with no resemblance to the *scheelite* or *wolframite* types.

Despite such a large number of experimental reports, the actual high-pressure behaviors of these compounds and their pressure-induced polymorphs are not known at all. The x-ray diffraction measurements on single crystals provided information on compressibilities of selected *scheelites* to about 6 GPa [4]. Results of the detailed Raman study on  $\text{CaWO}_4$  and  $\text{SrWO}_4$  [2], showing softening of several modes, cannot be reconciled with the first-order *scheelite*  $\rightarrow$  *wolframite* phase transition discussed in reference 3. In that study, four structural models were applied to index the powder pattern of the post-*scheelite* structure of  $\text{CaWO}_4$ :  $\text{MnMoO}_4$ -type ( $C2/m$ ,  $Z = 4$ ), *wolframite*-type ( $P2/c$ ,  $Z = 2$ ),  $\text{BaWO}_4$ -type ( $P2_1/n$ ,  $Z = 8$ ), and  $\text{HgWO}_4$ -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 the sample annealed at above 40 GPa, approximated with the  $MnMoO_4$  structure ( $C2/m$ ,  $Z = 4$ ) [5] reveals that several doublets were indexed as single peaks, e.g., the doublet near 22 keV.

In this study, we have re-examined details of the phase transitions in tungstate *scheelites* as observed with synchrotron angle-dispersive x-ray powder diffraction in diamond anvil cells loaded with different pressure media. Below we present our results on *scheelite*  $CaWO_4$ .

X-ray powder diffraction patterns of  $CaWO_4$  at selected pressures with helium as a pressure transmitting medium, are shown in Figure 1. 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, in particular the peak at about  $2\theta = 4.5^\circ$  (Figure 1 and 2), 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 [8]. Similar behavior of  $CaWO_4$  is observed upon compression at room temperature in the mixture of methanol and ethanol. In this case, however, the transformation occurs at slightly lower pressure of about 9 GPa.

The full Rietveld refinement of the profile at 11.2 GPa with the *fergusonite* model is shown in Figure 2. The starting Ca, W, and O positions have been derived from the atomic coordinates in the *scheelite* type [4] using the  $I4_1/a \rightarrow I2/a$  subgroup relationship. The W-O bonds and next near-neighbor W-O distances are 1.66-1.82 Å and 2.7 Å. Therefore, the  $WO_4^{2-}$  tetrahedra are largely distorted but still isolated.

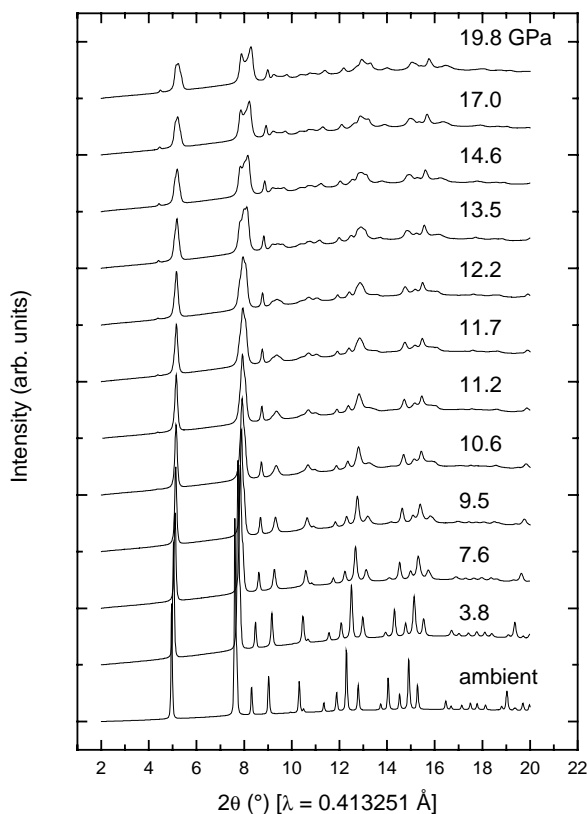
No discontinuities in the evolution of the unit cell volumes and the  $c$  tetragonal and  $b$  monoclinic axial parameters are observed during the phase transition (Figure 3). It indicates that unit cell volume changes between the two phases are negligible or not resolved in our x-ray powder diffraction experiments. The  $\beta$  angle and differences between the  $a$  and  $c$  lattice parameters (or  $b/a$  and  $b/c$  axial ratios) in the  $I2/a$  structure are the measure of the monoclinic distortion and increase with pressure. The evolution of all the parameters strongly depends on the pressure transmitting medium used for the experiments. Both *scheelite* and *fergusonite* polymorphs are less compressible when  $CaWO_4$  is loaded with the mixture of methanol and ethanol.

Our observation of the 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 [3]. Both *scheelite* and *fergusonite* structures are ordered superstructures of the *fluorite* type ( $Fm\bar{3}m$ ,  $Z = 4$ ). The oxygen atoms are in a distorted simple cubic arrangement and the  $Ca^{2+}$  and  $W^{6+}$  cations are eightfold and fourfold coordinated by oxygens, respectively. Our structure determination of the high-pressure polymorph of  $CaWO_4$  well explains the anomalous pressure dependence of Raman-active modes [2]. The temperature-induced ferroelastic  $I4_1/a \rightarrow I2/a$  transformation in rare earth niobates and

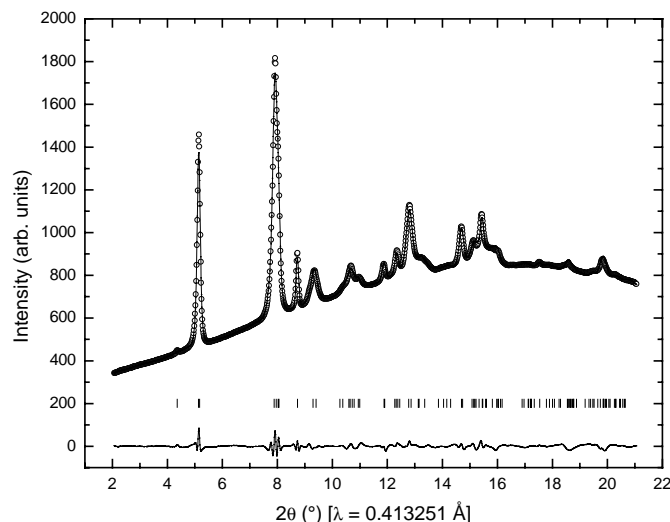
tantalates at atmospheric conditions is associated with the anisotropic phonon softening of a transverse acoustic mode at the Brillouin zone center [8]. Like in lanthanide niobates and tantalates [8], it remains to be seen whether this  $I4_1/a \rightarrow I2/a$  transition is of the first or second order.

## References

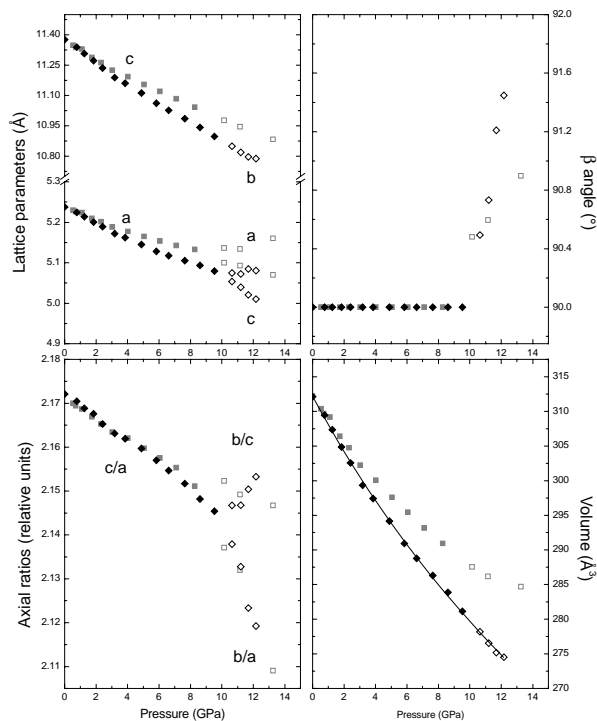
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**Figure 1** Selected x-ray powder patterns of  $\text{CaWO}_4$  with helium as a pressure transmitting medium.



**Figure 2** Observed, calculated, and difference x-ray powder patterns for *fergusonite*  $\text{CaWO}_4$  at 11.2 GPa with helium as a pressure medium -  $I2/a$ ,  $Z = 4$ ,  $a = 5.0706(5) \text{ \AA}$ ,  $b = 10.8528(8) \text{ \AA}$ ,  $c = 5.0812(9) \text{ \AA}$ ,  $\beta = 90.082(13)^\circ$ ,  $R_{\text{wp}} = 2.51\%$ ,  $R_p = 1.4\%$ ,  $R(F^2) = 3.82\%$ . Vertical markers indicate Bragg reflections. The residuals  $R_{\text{wp}}$  and  $R_p$  have been calculated with the background eliminated, see the GSAS manual for more details.



**Figure 3** Pressure dependence of lattice parameters of  $\text{CaWO}_4$ . Full and open symbols represent the parameters for the *scheelite* ( $I4_1/a$ ,  $Z = 4$ ) and *fergusonite* ( $I2/a$ ,  $Z = 4$ ) polymorphs, respectively. Black diamonds and gray squares are for the data collected with helium or a mixture of methanol and ethanol as pressure transmitting media, respectively. The line in the pressure dependence of the unit cell volumes for both the *scheelite* and *fergusonite* phases represents the Birch-equation-of-state fit with  $V_0 = 312.2(7) \text{ \AA}^3$ ,  $B_0 = 74(6) \text{ GPa}$ , and  $B' = 3.89(1.0)$ .