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Quasi-hydrostatic X-ray powder diffraction study of the low- and high-pressure phases of $CaWO_4$ up to 28 GPa

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ABSTRACT

We have studied $CaWO_4$ under compression using Ne as pressure-transmitting medium at room temperature by means of synchrotron X-ray powder diffraction. We have found that $CaWO_4$ beyond 8.8 GPa transforms from its low-pressure tetragonal structure (scheelite) into a monoclinic structure (fergusonite). The high-pressure phase remains stable up to 28 GPa and the low-pressure phase is totally recovered after full decompression. The pressure dependence of the unit-cell parameters, as well as the pressure–volume equation of state, has been determined for both phases. Compared with previous studies, we found in our quasi-hydrostatic experiments a different behavior for the unit-cell parameters of the fergusonite phase and a different transition pressure. These facts suggest that deviatoric stresses influence on the high-pressure structural behavior of $CaWO_4$ as previously found in related compounds. The reported experiments also provide information on the pressure dependence of interatomic bond distances, shedding light on the transition mechanisms.

1. Introduction

Scheelite is a calcium tungstate mineral with chemical formula $CaWO_4$. At ambient pressure (10^{-4} GPa) and room temperature (RT), it crystallizes in a tetragonal structure with space group (SG) $I4_1/a$, $Z = 4$. Many orthotungstates, orthomolybdates [1], and other compounds are crystallographically isostructural to scheelite. They are technologically important materials and have a long history of practical application. Among various applications, orthotungstates are used as solid-state scintillators [2,3], laser-host materials [4], and in optoelectronic devices [5–7]. In particular, due to their large X-ray absorption coefficient and scintillation output, orthotungstates are very popular for detecting X-rays and γ-rays in medical applications.

The scheelite structure can be described as a highly ionic crystal with Ca^{+2} cations and tetrahedral WO_4^{-2} anions forming a cubic close-packed array [1]. It can be visualized as an assembly of isolated WO_4 tetrahedra that are corner connected by CaO_8 dodecahedra [8]. Fig. 1 illustrates the scheelite structure, which can be also seen as two intercalated diamond lattices, one for Ca atoms and other for W atoms. This results in a layered stacking in which the O atoms are connected with two Ca and one W.

After the pioneer work of Nicol and Durana [9], several high-pressure (HP) studies have been performed in scheelite-type tungstates [10–22]. They showed that compression is an efficient tool to improve the understanding of their physical properties [23]. Based upon Raman measurements, Nicol and Durana [9] discovered a pressure-induced transition at 1.5 GPa in $CaWO_4$. This study was carried out using NaCl as pressure-transmitting medium (PTM). The authors proposed a monoclinic wolframite structure (SG: $P2/c$, $Z = 2$) for the HP phase. Later Raman experiments, using a 4:1 methanol–ethanol mixture as PTM, located the transition at 10 GPa [10,11]. Energy-dispersive X-ray powder diffraction (EDXRD) experiments in $CaWO_4$ were performed at the beginning of the present century [12]. They were carried out without PTM and the wolframite structure was assigned as the HP phase of $CaWO_4$. However, posterior angle-dispersive X-ray powder diffraction (ADXRD) measurements found the HP structure of $CaWO_4$ to be fergusonite (SG: $I2/a$, $Z = 4$) [13]. Helium (He) or a 4:1 methanol–ethanol mixture was used as PTM in these experiments. This conclusion was confirmed by subsequent ADXRD experiments done using silicone oil as PTM [14]. It was also supported by *ab initio* total-energy calculations and X-ray

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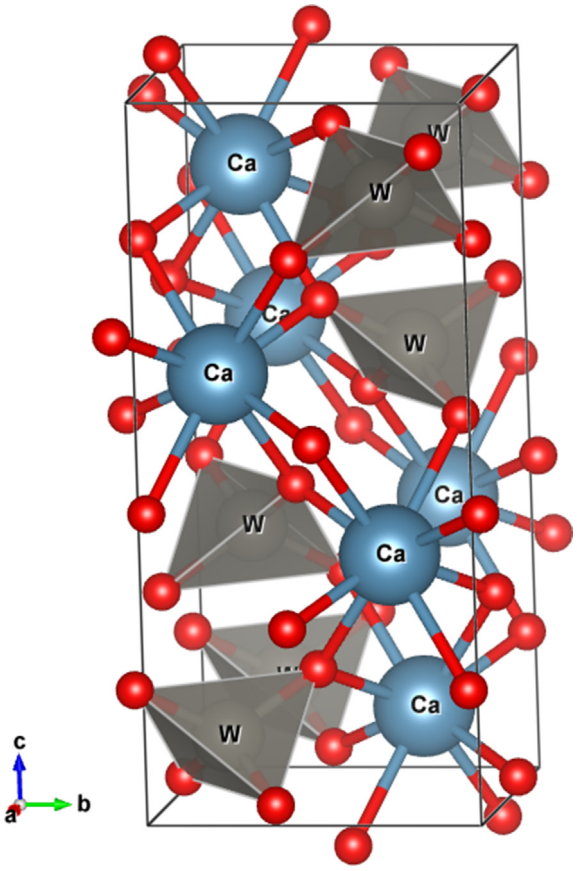

Fig. 1. Scheelite structure of $CaWO_4$. The bonds of the CaO_8 and WO_4 polyhedra are depicted.

absorption near-edge structure measurements [14,16]. However, a more recent EDXRD study, performed using 16:3:1 methanol–ethanol–water as PTM [19], concluded that scheelite $CaWO_4$ transforms to the wolframite structure. The above described results evidence that more efforts are needed to accurately determine the HP structural behavior of $CaWO_4$.

It is well known that the use of different PTM generates, in a diamond-anvil cell (DAC) and other HP devices, not only hydrostatic pressure but also deviatoric stress components [24,25]. Deviatoric stresses usually influence the HP structural behavior of materials [26]. In the particular case of scheelite-type oxides, the different deviatoric stresses caused by the use of different PTM leaded to discrepancies in the determination of the crystal structure of the HP phases [22,27]. This could be probably the cause of the finding of either the fergusonite or wolframite structure in $CaWO_4$ in different HP experiments. To clarify this issue, we performed an ADXRD study on $CaWO_4$ up to 28 GPa under quasi-hydrostatic conditions using neon (Ne) as PTM. The reported results will be compared with previous measurements carried out under several pressure environments. In particular, we will provide convincing evidence that beyond 8.8 GPa the scheelite structure transforms to fergusonite. The axial and bond compressibilities and the pressure–volume (P–V) equation of state (EOS) of $CaWO_4$ will also be presented. Our results are relevant for the understanding of the HP behavior of materials isomorphic to scheelite.

2. Experimental details

Powder $CaWO_4$ samples used in the present experiments were obtained from a high-purity $CaWO_4$ single crystal, which was grown by Czochralski method [5]. The HP experiments were performed using a symmetric DAC. The culet size of diamond anvils was 400 μm and T301 stainless steel served as gasket material. The gasket was preindented to a thickness of 40 μm and a hole with a diameter of 100 μm was drilled in its center to act as pressure chamber. The sample together with a ruby ball was loaded into this chamber. Ne was used as PTM and pressure was determined from ruby fluorescence [28].

HP ADXRD measurements were carried out at the 16-IDB station of HPCAT at the Advanced Photon Source (APS). Monochromatic synchrotron radiation with a wavelength of 0.40695 Å was employed. X-ray powder diffraction (XRD) was collected using a MAR345 image-plate detector located at 349.9 mm from the sample. The X-ray beam was focused down to 5 × 5 μm^2 using Kirkpatrick–Baez mirrors. The acquisition time was 20 s for each pressure. FIT2D was used to convert the collected two-dimensional XRD images into one-dimensional intensity versus 2θ diffraction patterns [29]. Indexing, structure solution, and refinements were performed using UNITCELL [30], POWDERCELL [31], and GSAS [32].

3. Results and discussion

Fig. 2 shows a selection of diffraction patterns of $CaWO_4$. These patterns can be assigned to the scheelite structure up to 8.8 GPa

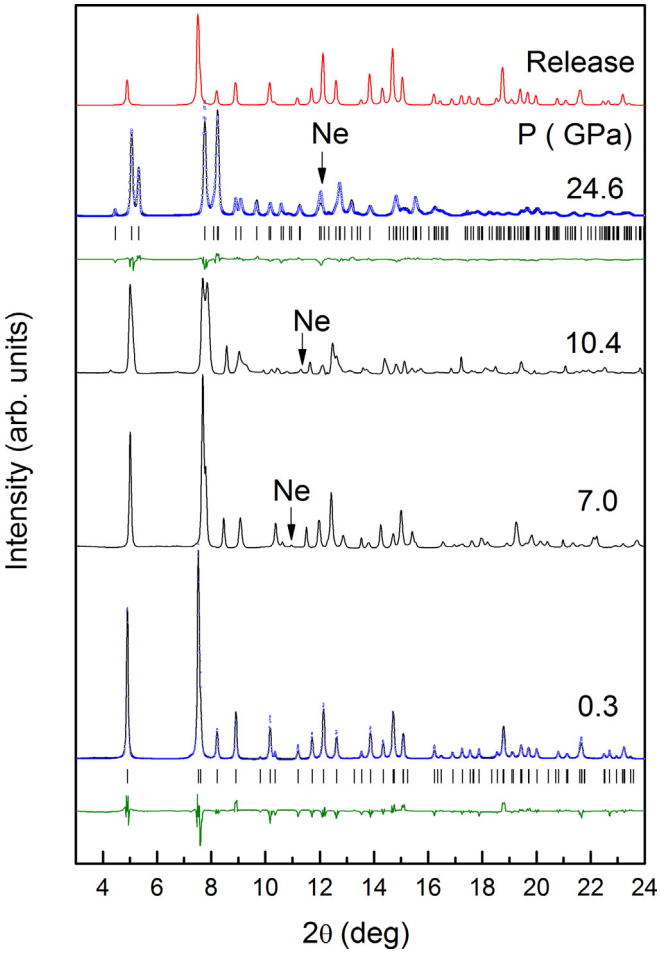

Fig. 2. Selected XRD patterns collected using Ne as pressure-transmitting medium. Rietveld refinements are shown for the scheelite structure at 0.3 GPa and for the HP fergusonite phase at 24.6 GPa with the experimental data plotted as solid lines and the calculated profiles as squares. In all of the cases the background has been subtracted. Residuals are also shown as solid lines. Vertical ticks indicate the position of Bragg reflections. Reflections of Ne are shown by arrows.