

Rapid Research Note

CaWO₄: A New High-Pressure and High-Temperature Phase

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Scheelite-type AWO₄ binary oxides are important materials due to their use as scintillator detectors, photoanodes, solid laser hosts, and in optical fiber applications. They crystallize in the scheelite structure (SG: I4₁/a, No. 88) [1], which may be regarded as a cubic close-packed array of A²⁺ and [WO₄]²⁻ units with the coordination number of 8 and 4 oxygen atoms for the A and W cations, respectively. CaWO₄ and other tungstates have been studied by high-pressure Raman spectroscopy [2], the occurrence of pressure-induced structural transitions being detected. In addition, the room temperature (RT) phase behaviour of CaWO₄ has been studied by X-ray diffraction up to 65 GPa [3]. These diffraction studies have determined that a pressure-induced transition to the wolframite-type structure (SG: P2/c, No. 13) takes place at 12 GPa [3] and have also established that CaWO₄ becomes amorphous at pressure exceeding 40 GPa [3]. At high pressure and high temperature a new phase has been found in BaWO₄ [4] and PbWO₄ [5], having a characteristic dense structure. In this note, we report the observation of a quenchable new high-pressure and high-temperature phase of CaWO₄ at 45 GPa after heating to 477 K.

The existence of this new phase was verified by energy dispersive X-ray powder diffraction (EDXD), using a focused beam of 10 μm by 10 μm , and its structure was tentatively determined using the XRDA [6] and GSAS [7] program packages. These studies were carried out at the X-17C beam line at the National Synchrotron Light Source (NSLS) using a white beam and a Ge detector. The powder X-ray patterns were all collected at a diffraction angle of $2\theta = 13^\circ$. CaWO₄ powder (99.78% purity) was compressed in a diamond anvil cell (DAC) to 45 GPa. No pressure medium was used in the experiments because it is known that alkaline earth tungstates are soft and can act as their own pressure medium [3, 8]. A gold standard (99% purity), which was used for pressure calibration, was loaded along with the sample. We compressed the crystalline CaWO₄ sample until reaching the amorphization of it [3]. At 45 GPa CaWO₄ was already amorphized, but after heating the DAC to 477 K during two hours in an off-line electrical furnace, and then quenching to RT, the crystalline structure was recovered, being the final new phase we obtained. This is illustrated in Fig. 1, where a sequence of the diffraction spectra obtained at 2 GPa and 45 GPa at RT as well as at 45 GPa after heating is shown. After releasing pressure, no other changes that shift the peaks to lower energies were observed in the X-ray diffraction pattern indicating that the new phase remains stable at ambient pressure.

A typical X-ray diffraction pattern for the new phase is given in Fig. 2. The general characteristics of the powder pattern are quite different from those of the scheelite and wolframite phase [3]. Decomposition of CaWO₄ can be ruled out since similar tungstates are thermodynamically stable with respect to their component oxides (CaO and WO₃ in the present case) up to about 1200 K [4, 5]. Then the X-ray pattern shown in Fig. 2 indicates the existence of a new CaWO₄ phase. The Bragg peaks of this new phase are broad. This is likely occurring because the sample is subject to significant non-hydrostatic stresses, due to the pressure medium used in the experiments, but may be also due to the presence of local disorders inherited from the amorphous phase. Under high pressure the AWO₄ compounds commonly assume monoclinic structures [2–5]. On the other hand, the only systematic absence among the reflections are in hkl for $h + k = 2n + 1$. The space group is hence C2 (No. 5), Cm (No. 8) or C2/m (No. 12). Evidence indicating that the space group is indeed C2/m is given by the refinement, in which a monoclinic phase (SG: C2/m, No. 12) with $a =$

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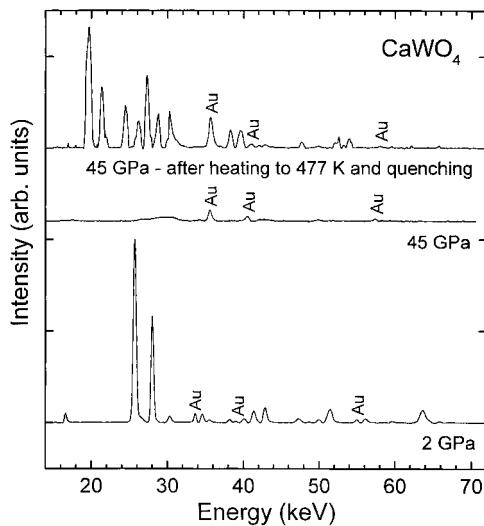


Fig. 1

Fig. 1. Diffraction patterns of CaWO_4 at 2 GPa (low-pressure scheelite phase), 45 GPa (amorphous) and after heating and quenching the amorphous CaWO_4 at 45 GPa. The background was subtracted and the Au peaks used to determine the pressure are marked

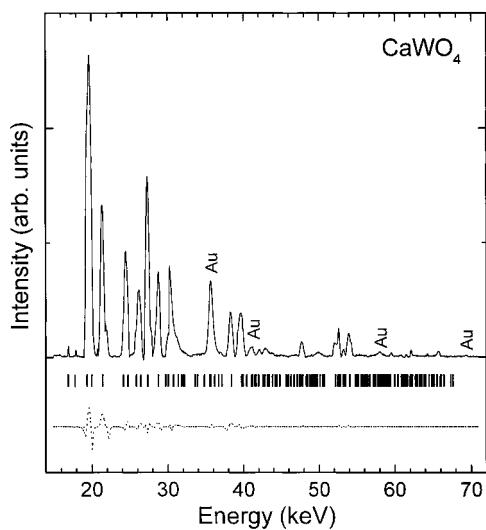


Fig. 2

Fig. 2. EDXD pattern of CaWO_4 at 45 GPa after heating to 477 K and quenching. The background was subtracted. Au marks the gold diffraction lines. The lowest curve represents the difference between the measured data and the refined profile. The bars indicate the calculated positions of the reflections

$(10.38 \pm 0.02) \text{ \AA}$, $b = (6.11 \pm 0.01) \text{ \AA}$, $c = (7.41 \pm 0.02) \text{ \AA}$, $\beta = (104.2 \pm 0.2)^\circ$, and with eight chemical units per unit cell, is the one which gives the best fit for the X-ray pattern presented in Fig. 2. These lattice parameters were obtained using the LeBail extraction technique [9] available in the GSAS program [7]. The $\text{C}2/\text{m}$ structure has been observed previously in other binary oxides related to CaWO_4 , being its prototype MnMoO_4 [10]. Therefore we have assumed the atomic position parameters of MnMoO_4 to perform the LeBail refinement. The result of the structure refinement (obtained by considering the displacement parameter $U = 0.05 \text{ \AA}^2$) is shown in Fig. 2 and the structure is illustrated in Fig. 3. We obtained qualitative good agreement with the experimental diffraction pattern and a low value of the residual for the intensities, $R(F^2) = 0.151$ (for 146 reflections).

The differences between the measured and simulated intensities observed in the lowest trace of Fig. 2 could be related to the induction of preferred orientations during the recrystallization process, which were not considered during the refinement.

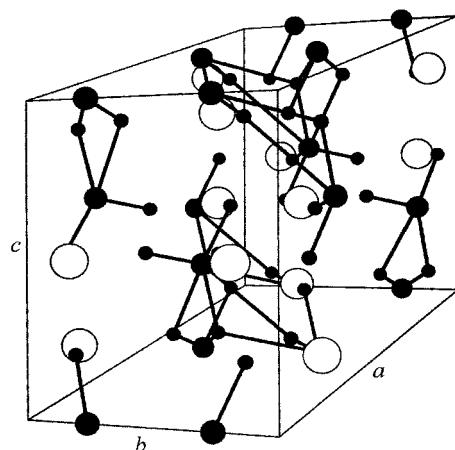


Fig. 3. Perspective drawing of the atomic arrangement for the new phase of CaWO_4 in the proposed $\text{C}2/\text{m}$ (SG: No. 12) structure. Spheres represent the atomic positions. The white spheres are the Ca sites, the large black spheres are the W sites, and the small black spheres the O sites. The bonds of the W-O polyhedra are indicated by solid thick lines

The proposed structure for the new phase of CaWO_4 gives a volume of $34.28 \text{ cm}^3 \text{ mol}^{-1}$, which represents a volume decrease of about 8% in going from the RT wolframite phase (the one observed before the amorphization at 40 GPa [3]) to the new observed phase. In this phase, the Ca atoms occupy the two crystallographically independent Wyckoff positions 4h (0, 0.183, 0.5) and 4i (0.8, 0, 0.142) and are surrounded by deformed oxygen octahedra, whereas the W atoms occupy the Wyckoff positions 4g (0, 0.25, 0) and 4i (0.267, 0, 0.4) at the centers of somewhat distorted octahedra with two short ($1.32 \pm 0.02 \text{ \AA}$) and four long ($1.82 \pm 0.02 \text{ \AA}$) W–O distances. An increase in the density was also observed in the high-pressure quenched phase of BaWO_4 [4], being related to an augment of the packing efficiency of the W–O polyhedra. In the present study, the observed new phase of CaWO_4 also provides a logical response to the demand of compression for more efficient packing by increasing the effective W–O coordination as compared with either the scheelite or the wolframite RT phases [1, 3]. In view of the evidence obtained from the structural refinement, the proposed $\text{C}2/\text{m}$ structure appears as the most probable for the new phase of CaWO_4 reported here.

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