Combined ADXRD, XANES, and *ab-initio* study of scintillating materials under high pressure

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Introduction

AWO_4 orthotungtates (A= Ca, Ba, Sr, and Pb) with scheelite structure ($I4_1/a$) are wide-gap semiconductors, which have attracted increasing interest due to their use as scintillators in high-energy physics. The study of the structural behavior of these materials is an important tool to improve the knowledge of their main physical properties. Thus, they have been extensively studied under pressure using Raman spectroscopy and x-ray diffraction [1]. However, a fully understanding of their structural behavior has not been achieved yet. Here, we present recent studies performed with the aim of exhaustively examinig the crystal stability of AWO_4 scintilatting orthotungstates.

Methods and Materials

$CaWO_4$, $SrWO_4$, $BaWO_4$, and $PbWO_4$ scintillating crystals were studied under pressure up to 25 GPa by angle-dispersive x-ray powder diffraction (ADXRD) and x-ray-absorption near-edge structure (XANES) using synchrotron radiation. ADXRD and XANES experiments were performed in a diamond-anvil cell at the APS (16-IDB) and the ESRF (ID24), respectively.

Results

The scheelite phase remains stable up to 10.5 GPa ($CaWO_4$), 9.9 GPa ($SrWO_4$), 9 GPa ($PbWO_4$), and 7.1 GPa ($BaWO_4$) where a reversible phase transition takes place [1,2]. A monoclinic unit cell is assigned to the high-pressure phase ($I2/a$, Z = 4). This phase remains stable up to 20 GPa for $CaWO_4$ and $SrWO_4$, but a second phase transition is observed in $BaWO_4$ and $PbWO_4$ near 10 GPa and 15 GPa, respectively. In order to illustrate the first phase-transition, Fig. 1 shows selected ADXRD data for $SrWO_4$. At the transition pressure some of the diffraction peaks split and additional diffraction peaks emerge. The appearance of a new peak at $2\theta \approx 4°$ is clearly distinguishable. A Rietveld analysis of the diffraction patterns of the high-pressure phase shows that they can be fitted with the fergusonite structure [1,2]. We also performed XANES experiments at the W L_3 edge (10.207 keV) in the four scintillating compounds [1,2]. Thus we investigated changes in W coordination induced by pressure. The obtained results also support the existence of a scheelite-to-fergusonite structural transition. We also observed that the monoclinic distortion triggered at the phase transition increases continuosly upon compression. The small changes of the local environment around the absorbing atom make XANES sensitive to the phase transition at slightly higher pressures than ADXRD; e.g. around 11.3 GPa in $CaWO_4$. According with our XANES and ADXRD measurements, upon further compression $BaWO_4$ and $PbWO_4$ transforms to a monoclinic structure with space group symmetry $P2_1/n$ near 10 and 15 GPa, respectively [2]. This transition occurs together with a large volume collapse, which reflects the fact that the $P2_1/n$ structure consists of densely packed networks of distorted WO_6 octahedra; i.e. the W-O coordination increase from 4 to 6 at the second transition. In addition, based on the observed data we obtained an equation of state (EOS) for the four AWO_4 compounds; see Table I.

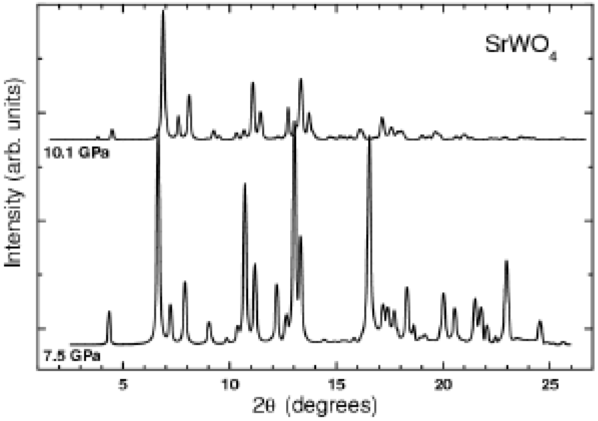

Fig.1:High-pressure ADXRD patterns of $SrWO_4$, λ=0.3679Å. Lower (upper) trace: scheelite (fergusonite) structure.

Further to experiments the structural stability of the AWO_4 orthotungstates was theoretically studied by means of total-energy calculations performed within the framework of the density functional theory with the Vienna *ab initio* simulation package [1,2]. The obtained results are in reasonable agreement with the experiments, but in $SrWO_4$, $BaWO_4$ and $PbWO_4$ we found small discrepancies. Our *ab initio* calculations indicate that the scheelite structure transforms upon compression directly to $P2_1/n$. We attribute the occurrence of the fergusonite phase in the sequence of structural transitions to the existence of a kinetic barrier that prevents the $I4_1/a$-to-$P2_1/n$ for taking place [2]. Beyond 25 GPa, our calculations predict the occurrence of additional phase transtions to denser structures like $Cmca$ [1,2].

Table I: EOS parameters for different AWO_4 compounds.

Compound	V_0 [Å^3]	B_0 [GPa]	B_0’
$CaWO_4$	312(1)	74(7)	5.6(9)
$SrWO_4$	347.4(9)	63(7)	5.2(9)
$BaWO_4$	402.8(9)	52(5)	5(1)
$PbWO_4$	357.8(6)	66(5)	5.6(9)

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[1] D. Errandonea, J. Pellicer-Porres, F. J. Manjón, *et al.*, Phys. Rev. B **72**, 174106 (2005); and references therein.
[2] D. Errandonea, *et al.*, Phys. Rev. B **73** (2006).