



On the ferroelastic nature of the scheelite-to-fergusonite phase transition in orthotungstates and orthomolybdates

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ABSTRACT

New evidence supporting the ferroelastic nature of the pressure-induced scheelite-to-fergusonite phase transition in ABO_4 orthotungstates and orthomolybdates ($A = Ca, Sr, Ba, Pb, Eu$ and $B = W, Mo$) has been obtained from the analysis of Raman spectroscopy data. In the studied scheelite-type compounds, one external translational mode of B_g symmetry in the scheelite phase softens up to the transition pressure and then becomes a hard A_g mode in the fergusonite high-pressure phase. However, other scheelite-type compounds not undergoing the scheelite-to-fergusonite transition do not show softening of the B_g mode. The reported results have allowed us to establish a relationship between the square of the soft-mode frequency at ambient pressure and the transition pressure in the series $PbWO_4$, $BaWO_4$, $EuWO_4$, $SrWO_4$, and $CaWO_4$ and also in the series $PbMoO_4$, $BaMoO_4$, $SrMoO_4$, and $CaMoO_4$. This fact is in accordance with the soft-mode theory of second-order phase transitions. The conclusions drawn confirm a previous characterization of the phase transition obtained from the Landau theory.

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1. Introduction

There is a great deal of interest in the high-pressure (HP) transitions of zircon- and scheelite-structured oxides due to their possible geophysical implications. In particular, in the last years, several groups have investigated the effects of pressure on the properties of the scheelite-structured orthotungstates and orthomolybdates [1–19]. Nowadays it is well-known that these compounds undergo a reversible phase transition between the tetragonal scheelite structure ($I4_1/a$) and the monoclinic M-fergusonite structure ($I2/a$) in the range from 6 to 12 GPa [7–11]. It is also known that the scheelite-to-fergusonite transition competes with the scheelite-to- $P2_1/n$ transition in the compounds with the heaviest A cations [15,17,18,20]. The M-fergusonite structure, hereafter named fergusonite, is a distorted and compressed version of scheelite obtained by a small distortion of the cation matrix and significant displacements of the anions. Fig. 1 illustrates the changes that take place at the transition. Beyond this, it has been also recently established that in many compounds of the ABO_4 -type family

(silicates, germanates, molybdates, tungstates, niobates, vanadates, etc.) pressure induces structural transformations from tetragonal to monoclinic symmetry and to orthorhombic symmetry following the structural sequence: zircon → scheelite → fergusonite → $P2_1/n$ → $BaMnF_4$ → $Cmca$ [20].

It has been shown that the scheelite-to- $P2_1/n$ transition in orthotungstates is a first-order phase transition [11], but there is a debate regarding the first- or second-order character of the scheelite-to-fergusonite transition. In a previous paper, we showed that Landau theory predicts that the transition should be a second-order, proper ferroelastic transition [21]. In such a case, it should involve the softening of a Raman active B_g mode since the transition involves a strong coupling between a zone-centre optic mode and the ferroelastic strain of B_g symmetry (in the paraelastic scheelite phase) [22]. In this paper, we will analyze previous Raman experiments and show that indeed there is an external translational mode of B_g symmetry that softens upon compression in scheelite-structured orthotungstates and orthomolybdates. The analysis of Raman spectroscopy results supports the second-order character of the studied transition. The reported results permit to establish a systematic behaviour for the series $PbWO_4$, $BaWO_4$, $EuWO_4$, $SrWO_4$, and $CaWO_4$ as well as for homologous molybdates. In the following our arguments will be applied to scheelite-type

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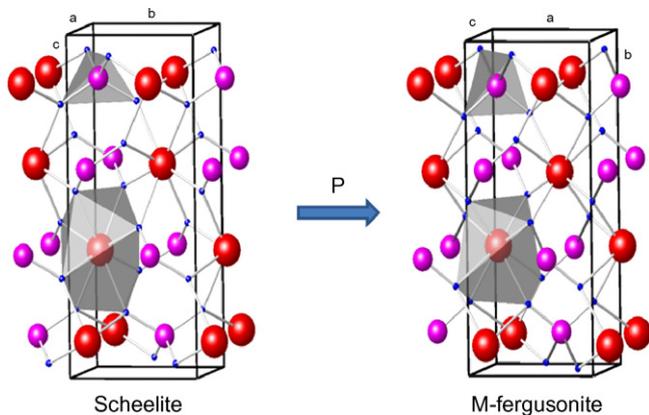


Fig. 1. The low-pressure scheelite and HP fergusonite structures of AWO_4 orthotungstates. Large red circles: A atoms, purple medium circles: W atoms, and small blue circles: O atoms. The A–O and W–O bonds are shown. The structures were drawn using the structural parameters of $CaWO_4$ at 1.4 GPa (scheelite) and 18.3 GPa (fergusonite).

orthotungstates but they can be similarly applied to scheelite-type orthomolybdates.

2. Raman modes

The scheelite structure of AWO_4 compounds has four formula units per body centred unit cell of space group C_{4h}^{6} ($I4_1/a$). In this structure, the A and W atoms occupy S_4 sites and the oxygen atoms are on C_1 sites. Group theory predicts that scheelite-structured crystals will have thirteen Raman-active modes: $\Gamma = 3A_g + 5B_g + 5E_g$. These modes can be classified either as internal, if the WO_4 centre of mass does not move, or as external, if they imply movement of WO_4 tetrahedra as rigid units. In orthotungstates, there are six external modes that are located below 300 cm^{-1} at ambient pressure while the internal modes extend between 320 and 930 cm^{-1} . HP Raman spectroscopy measurements have been performed in $CaWO_4$, $SrWO_4$, $BaWO_4$, and $PbWO_4$ above the transition pressure (indicated by arrows) the new A_g mode shows no discontinuity in frequency with the $T(B_g)$ mode and begins to harden with increasing pressure. The soft-mode behaviour of the $T(B_g)$ mode in scheelite and the absence of discontinuities in the frequency of the parent A_g hard mode are consistent with a second-order phase transition. In addition, there is no hysteresis between the scheelite and the fergusonite phases when releasing compression from pressures close to the phase transition (before the precursor effects of a second pressure-induced transition appear; e.g. the scheelite-to- $P2_1/n$ transition in $PbWO_4$ and $BaWO_4$ [11,17,18]). This lack of hysteresis together

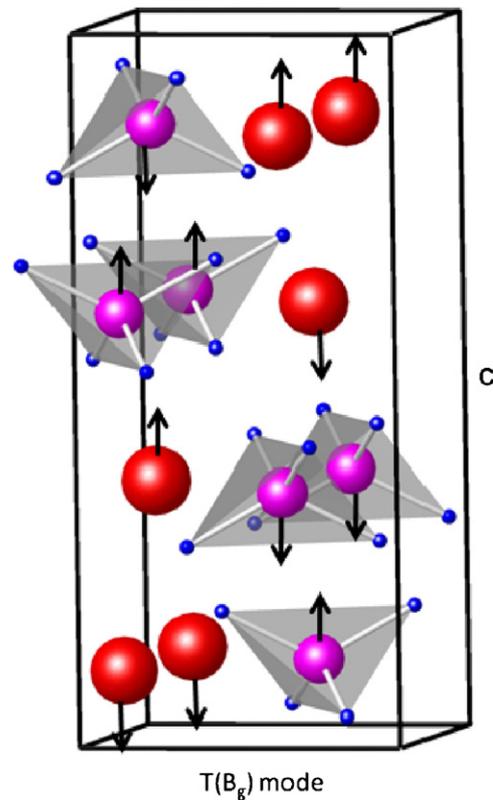


Fig. 2. Schematic representation of the $T(B_g)$ soft mode in scheelite. Atoms are represented following the same nomenclature used in Fig. 1.

After the tetragonal-to-monoclinic phase transition leading from the scheelite to fergusonite structure, there is an A_g mode in the HP phase arising from the $T(B_g)$ soft mode [17] according with the group relations between scheelite and fergusonite (see Table 1). In Fig. 3, it can be seen that in $CaWO_4$, $SrWO_4$, and $PbWO_4$ above the transition pressure (indicated by arrows) the new A_g mode shows no discontinuity in frequency with the $T(B_g)$ mode and begins to harden with increasing pressure. The soft-mode behaviour of the $T(B_g)$ mode in scheelite and the absence of discontinuities in the frequency of the parent A_g hard mode are consistent with a second-order phase transition. In addition, there is no hysteresis between the scheelite and the fergusonite phases when releasing compression from pressures close to the phase transition (before the precursor effects of a second pressure-induced transition appear; e.g. the scheelite-to- $P2_1/n$ transition in $PbWO_4$ and $BaWO_4$ [11,17,18]). This lack of hysteresis together

Table 1

Raman data for the soft mode of scheelite and the associated mode in the HP phase. P_T is also indicated, representing the average P_T of different experiments [1–19,25–28]. The scheelite (fergusonite) data correspond to ambient pressure (P_T).

Scheelite				Fergusonite			
Compound	Mode	ω (cm^{-1})	$d\omega/dP$ ($\text{cm}^{-1}/\text{GPa}$)	Mode	ω (cm^{-1})	$d\omega/dP$ ($\text{cm}^{-1}/\text{GPa}$)	P_T (GPa)
$CaWO_4$	B_g	84–86	–0.4	A_g	80		11 ± 1
$SrWO_4$	B_g	75	–0.4	A_g	70		10 ± 2
$EuWO_4$	B_g	69		A_g			8.5 ± 1
$BaWO_4$	B_g	62–63	–0.8	A_g	38	–0.6	7.5 ± 1.5
$PbWO_4$	B_g	56–58	–1.1	A_g	49	0.8	6.5 ± 2
$CaMoO_4$	B_g	112–113	–0.2	A_g	111	0.7	12 ± 4
$SrMoO_4$	B_g	98	–0.8	A_g	95	0.6	12.2 ± 1
$BaMoO_4$	B_g	79	–0.6				5.8 ± 1^a
$PbMoO_4$	B_g	72–75	–0.07	A_g	60	0.2	6.5 ± 3

^a The HP structure of $BaMoO_4$ has been not solved yet [28]. It likely undergoes a transition to a monoclinic phase previous to the scheelite-to-fergusonite transition, so this pressure is not exactly the value of the scheelite-to-fergusonite P_T .

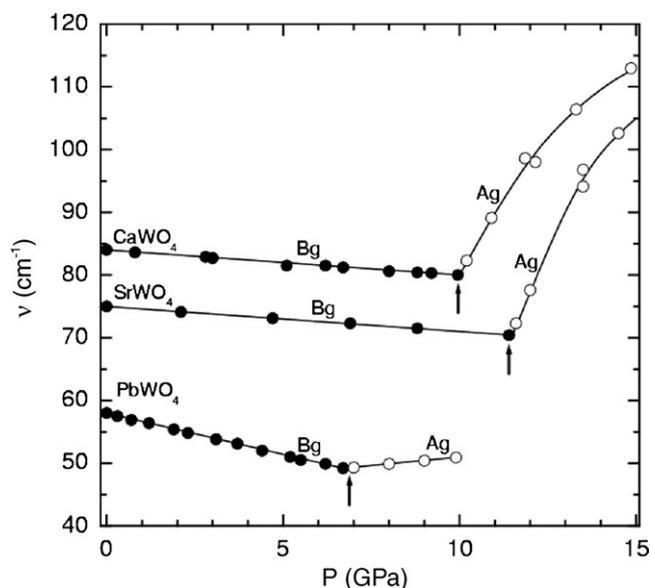


Fig. 3. Pressure evolution of the soft mode of scheelite CaWO_4 , SrWO_4 , and PbWO_4 and of the A_g mode of the HP phase arising from it. The data were taken from our experiments [18] and Refs. [3,4].

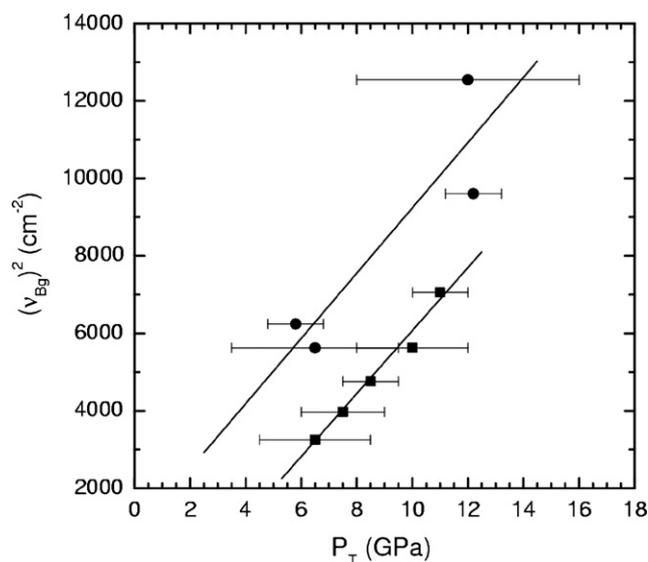


Fig. 4. Square of the $T(B_g)$ soft-mode frequency at ambient pressure as a function of P_T for tungstates (squares) and molybdates (circles). The error of the frequencies is smaller than the symbols size. The horizontal error bars illustrate the dispersion of transition pressures found in the literature. The lines illustrate the linear relation between $\nu_{B_g}^2$ and P_T . Data taken from Table 1.

with the gradual increase of the intensity of the fergusonite A_g mode and the gradual decrease of the scheelite $T(B_g)$ mode (see Fig. 5 in Ref. [18]) also supports the displacive second-order character of the scheelite-to-fergusonite transition [17,18]. To close this section, we would like to comment on the apparent anomalous behaviour of the fergusonite BaWO_4 . In this compound, there is a jump between the frequencies of the B_g mode of scheelite and the A_g mode of fergusonite. In addition, the A_g mode has a negative pressure coefficient. We think, these phenomena are probably related to the fact that fergusonite is a thermodynamically unstable phase, which is only observed upon compression due to the presence of kinetic barriers that hinder the first-order scheelite-to- BaWO_4 -II ($P2_1/n$) transition [11].

3. Discussion

Based upon the analysis of the spontaneous strain induced in the monoclinic fergusonite structure and applying the Landau theory, we concluded in a previous work that the scheelite-to-fergusonite transition has a second-order character [21]. According with the soft-mode theory [23], in a second-order ferroelastic phase transition, the soft mode in the paraelastic and ferroelastic phases should have the following pressure dependence:

$$\nu_{p(f)}^2 = k_{p(f)} |P - P_{p(f)}| \quad (1)$$

where P_p and P_f are the pressures at which the modes of each phase become unstable and k_p and k_f are constants. The pressure at which the two lines intersect is the transition pressure (P_T). The relation given above has been proven to be valid in ferroelastic transitions in compounds related to scheelite, like rutile-structured oxides [24]. In Fig. 3, for CaWO_4 and SrWO_4 , it can be seen that the A_g modes in the fergusonite structure follows clearly a quadratic dependence as expected if a ferroelastic transformation would take place. Similarly, a quadratic dependence on pressure has been found for the lowest frequency mode in CaMoO_4 above 8.2 GPa [25] and a non-linear dependence is also observed for the lowest frequency mode in SrMoO_4 [26]. In fact, the scheelite-to-fergusonite transition in SrMoO_4 has been recently confirmed by X-ray diffraction [27]. However, in the other two orthotungstates, BaWO_4 and PbWO_4 , unfortunately a second transition occurs very close to the scheelite-to-fergusonite transition [9,11] and therefore it is difficult to distinguish whether the dependence of the A_g hard mode is quadratic or linear. As regards PbMoO_4 , only a few points of the HP phase have been measured [2] so the pressure dependence of the fergusonite A_g mode cannot be discussed here. Finally, in BaMoO_4 a phase transition to a monoclinic structure, previous to the scheelite-to-fergusonite transition, is likely to occur on the basis of the large number of modes observed above 6 GPa, avoiding the clear observation of the fergusonite-like modes [28]. We refer the readers to Refs. [17,18] for a detailed discussion of the phase transitions in Ba and Pb orthotungstates that are likely the same expected for orthomolybdates.

Assuming that Eq. (1) holds for the scheelite-structured orthotungstates and orthomolybdates and selecting the ambient pressure to compare different compounds, we expect that, in a ferroelastic transition, the square of the frequency of the $T(B_g)$ mode measured at ambient pressure is proportional to the phase transition pressure between the scheelite and fergusonite phases ($\nu_{B_g}^2 \propto P_T$). Fig. 4 shows the plot of $\nu_{B_g}^2$ versus P_T for the different scheelite-type tungstates and molybdates. It can be seen that for each family of compounds a linear relation can be established. This systematic behaviour observed in scheelite-type tungstates and molybdates supports the idea that they undergo a second-order phase transition driven by a $T(B_g)$ soft mode. It is important to note here that the softening observed in the $T(B_g)$ mode of scheelite implies a vanishing restoring force against the corresponding deformation. The scheelite-to-fergusonite transition in AWO_4 compounds is of martensitic nature [29], being the initial structure partially conserved while certain sheets of it are slightly shifted [12]. In particular, it involves a shift in the zigzag chains of W cations either along $[1\ 0\ 0]$ or $[0\ 1\ 0]$ directions. This shift is strongly favoured by the weakening of the restoring force of the B_g mode.

The evidence obtained from the analysis of the Raman data supporting the second-order ferroelastic nature of the scheelite-to-fergusonite transition reinforces the conclusions drawn from the Landau theory [21]. An analogous ferroelastic phase transition was found at low temperature in scheelite-type CaMoO_4 [30] showing a softening of an acoustic mode observed in Brillouin experiments [31]

what gives additional support to our conclusion. Furthermore, the splitting of peaks in X-ray diffraction experiments at the scheelite-to-fergusonite transition observed in tungstates and the negligible volume discontinuity between both phases suggests also the occurrence of a second-order transformation [9,11]. We think that all these facts are enough evidence to conclude that in scheelite-structured orthotungstates and orthomolybdates a ferroelastic phase transition is induced upon compression despite the fergusonite nature of the HP phase in BaMoO₄ and PbMoO₄ still has not been experimentally checked. It is important to note here, that it could be argued against our conclusions that in BaWO₄ there is a hysteresis on release of pressure and that hysteresis is only observed in first-order phase transitions. However, the mentioned hysteresis is only observed when releasing pressure from the post-fergusonite BaWO₄-II phase, which has a structure different than fergusonite [11]. Indeed, the scheelite-to-BaWO₄-II transition is well-known to be a first-order phase transition [11], which takes place together with a large volume collapse.

The similarities in the structural and vibrational properties of scheelite orthotungstates and other scheelite-structured compounds, like orthomolybdates and orthovanadates, suggest that the soft-mode behaviour should be also found in these compounds. In the double-scheelite-structured compounds NaSm(WO₄)₂, NaTb(WO₄)₂, and NaHo(WO₄)₂ the lowest frequency T(B_g) mode is located close to 76 cm⁻¹. As reported by Jayaraman et al. [32], these modes clearly soften upon compression. In these compounds the scheelite structure becomes unstable around 10 GPa, which is reasonable since the soft-mode frequency is very close to that of SrWO₄. In the case of the vanadates, the scheelite-to-fergusonite transition has been recently detected as a second pressure-driven transition in LuVO₄ and YVO₄ [33,34]. In particular, Raman experiments in YVO₄ detected the softening of the scheelite-type T(B_g) mode with the lowest frequency and the hardening of the associated A_g mode after the scheelite-to-fergusonite phase transition [34]. In YVO₄, the frequency of the scheelite-type T(B_g) mode at ambient pressure (~166 cm⁻¹) is higher than in tungstates and molybdates, and therefore it is reasonable that the scheelite-to-fergusonite transition would be located at higher pressures (16–20 GPa) than in the other compounds in good agreement with experimental observations [33,34]. The fact that the same behaviour has been detected in many different scheelite-type oxide minerals suggest that the softening of the T(B_g) mode can be used to predict the occurrence of unknown phase transitions in other members of this family like CaCrO₄ and YCrO₄. In both of them a softening of the lowest frequency mode was detected in the scheelite-structured HP phase [35], but no phase transition was detected in the pressure range covered by the experiments. Therefore, the phase transition from scheelite to fergusonite would probably take place at higher pressures.

4. Concluding remarks

In conclusion, from the analysis of HP Raman spectroscopy measurements on scheelite-type ABO₄ compounds (A = Ca, Sr, Ba, Pb and B = Mo, W) we found evidence that a second-order, proper ferroelastic transition occurs in these compounds towards the M-fergusonite structure. A systematic relation between the square of the ambient pressure frequency of the T(B_g) soft mode in the scheelite phase and the transition pressure of the compounds is identified. The comparison of other scheelite-type oxides indicates that the HP behaviour of molybdates, vanadates, and chromates could closely mirror that of their homologous tungstates. Furthermore, the presence or absence of a soft T(B_g) mode in scheelites could help in discriminating phase transitions to fergusonite or to other structures. For instance, in scheelite-type YLiF₄ there is a soft mode

but of E_g symmetry [36]. This mode is consistent with the fact that this compound does not undergo a phase transition to the M-fergusonite phase but to the M'-fergusonite (P2₁/c) [37], a structure that cannot be obtained by a ferroelastic distortion of scheelite. The pressure softening of different Raman modes in scheelite-structured oxides (B_g) and fluorides (E_g) basically suggest that upon compression they share along different symmetry axes, leading thus to different HP structures. Finally, in AgReO₄ and KReO₄, it has been evidenced that the lowest modes do not have a negative pressure coefficient so a transition from scheelite to a structure different than fergusonite could be expected [38].

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