

High-pressure Raman study of alkaline-earth tungstates and a new pressure-induced phase transition in BaWO₄

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The pressure dependence of the Raman peaks of the scheelite-type alkaline-earth tungstates CaWO₄, SrWO₄, and BaWO₄ have been investigated to 90 kbar hydrostatic pressure, with the use of the diamond anvil cell. The (dv/dP) 's are all positive, except in the case of the lowest-frequency external mode. In BaWO₄, a new reversible first-order phase transition occurs near 65 kbar, where the Raman peaks shift abruptly to lower frequencies. From the observed decrease in the W—O bond-stretching mode frequencies and the increased number of W—O bond-bending modes it is concluded that the oxygen coordination for tungsten becomes octahedral, and the phase transition itself is postulated to be to the monoclinic HgWO₄ structure. The previously noted phase transitions in CaWO₄ and SrWO₄ are not confirmed in the present study.

INTRODUCTION

The alkaline-earth tungstates crystallize in the so-called scheelite structure, of which CaWO₄ is the archetype compound. The Raman and infrared spectra of scheelite-structure compounds have been investigated in a number of earlier studies¹⁻⁵ at ambient pressure. The observed phonon frequencies have been assigned in accordance with the phonon modes expected for the crystal symmetry and BO₄ tetrahedra, where *B* is Mo or W. In two pressure-Raman studies^{6,7} to 40 kbar, the effect of pressure on the scheelite-structure compounds CaMoO₄, CaWO₄, SrWO₄, and PbMoO₄ has been investigated. In the present study we have investigated BaWO₄ for the first time by high-pressure-Raman spectroscopy, and we present evidence for a new reversible first-order phase transition near 65 kbar at room temperature. This phase transition appears to be different from the phase transition reported in the high-pressure and high-temperature quenching studies of Fujita *et al.*⁸ and Kawada *et al.*⁹ Also, our results for CaWO₄ and SrWO₄ to 90 kbar hydrostatic pressure do not confirm the previously reported^{6,7} transitions in them. The results of these studies will be presented and discussed.

MATERIALS AND EXPERIMENTS

Because of their interest as laser hosts a large number of rare-earth-metal-doped tungstates and molybdates were grown in our laboratories. The tungstates CaWO₄, SrWO₄, and BaWO₄ were very lightly doped with rare earths. However, the percentage of doping was insignificantly small to affect the properties that we were interested in studying. The crystals were clear and were about a few millimeters in linear dimensions.

High pressure was generated in a gasketed diamond anvil cell¹⁰ with 4:1 methanol-ethanol mixture as the pressure-transmitting medium. Pressure was measured by the well-known ruby fluorescence technique.¹¹ For pressure-Raman studies a small crystal fragment of about 50–100 μm in linear dimensions and about 50 μm thickness was placed in the cell. No particular attention was paid to orient the crystal in the cell for polarized Raman

study.

Raman spectra with the pressure cell were recorded in the backscattering geometry using a Spex double monochromator and a conventional photon-counting system. For excitation, the 5145-Å radiation from an argon-ion laser was used at a power level of 30 mW. All measurements were carried out at room temperature, both on increasing and decreasing pressure.

The Raman spectra of BaWO₄ taken at four different pressures are presented in Fig. 1. In Fig. 2 the pressure dependence of the phonons are plotted. At a pressure near 65 ± 3 kbar, the crystal when viewed under a microscope turns abruptly to light brown in color and some texture is also evident. Remarkable changes are observed in the Raman spectrum. The high-frequency internal-mode region is strongly affected, involving the modes near 800, 840, and 920 cm⁻¹. Evaluated at 65 kbar, these mode frequencies abruptly jump from 815 to 794 cm⁻¹, 844 to 810 cm⁻¹, and 944 to 900 cm⁻¹ in the high-pressure phase. In the spectrum taken at 68 kbar, both sets are seen (see Fig. 1) and only at 85 kbar the peaks belonging to the low-pressure phase have almost vanished. This large abrupt change in the frequencies and the coexistence of two peaks over a range of pressure speak definitely for a first-order phase transition in BaWO₄ at about 65 ± 2 kbar. The phase transition is reversible but there is an ~20-kbar hysteresis. Another notable aspect is that the peaks at 810, 794, and 900 cm⁻¹ of the high-pressure phase are broader compared to the corresponding peaks of the low-pressure phase. The external as well as other internal modes are undoubtedly also affected in the phase transition, but it proved difficult to obtain all the peaks, because of the large background scattering (Rayleigh tail) caused by the coloration and texture of the sample. In Fig. 1 the peaks belonging to the high-pressure phase are marked by an arrow.

The Raman spectrum of CaWO₄ and SrWO₄ taken at a pressure of about 42 kbar are shown in Fig. 3. Nicol and Durana⁶ and Ganguly and Nicol⁷ reported splitting of the *E_g* modes at 117 and 797 cm⁻¹ in the case of CaWO₄ above 15 kbar, and splitting of the corresponding modes in the case of SrWO₄ at 102 and 800 cm⁻¹ above 20 kbar.

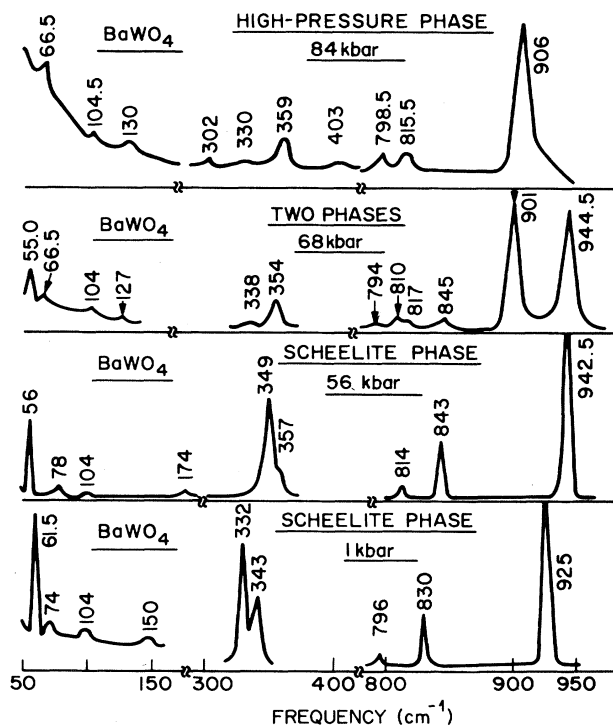


FIG. 1. Raman spectra of BaWO_4 at 1, 56, 68, and 84 kbar hydrostatic pressure. Spectrum at 68 kbar has Raman peaks from the high-pressure (marked by arrows) as well as the scheelite phase. Abrupt decrease in the internal-mode frequencies occurs in the high-pressure phase. Spectrum at 84 kbar is purely from the high-pressure phase. Frequency shifts are given in units of cm^{-1} .

In our spectra taken under hydrostatic pressure, there are no such splittings, and we believe that the use of a solid pressure-transmitting medium in the above two studies^{6,7} may have resulted in uniaxial stress and caused the splittings. The pressure dependence of the phonon frequencies in CaWO_4 and SrWO_4 are presented in Figs. 4 and 5. Table I presents the observed frequencies and their assignments from Ref. 5. The mode-Grüneisen parameters are also given.

DISCUSSION

For scheelite structure, group theory predicts 13 Raman-active phonons of the type $3A_g + 5B_g + 5E_g$. Of these, seven are internal modes of the WO_4 tetrahedra: stretching $\nu_1(A_g)$, $\nu_3(B_g)$, and $\nu_3(E_g)$; bending $\nu_2(A_g)$ and $\nu_2(B_g)$, and $\nu_4(B_g)$ and $\nu_4(E_g)$. The remaining six are external modes—two rotations A_g and E_g and four translations $2B_g$ and $2E_g$. The observed frequencies have been assigned by Liegeois-Duyckaerts and Tarte,⁵ from a detailed study of the infrared and polarized Raman spectra of pure compounds, their isotropic substitutions, and solid-solution systems. The Raman data obtained in the present study agree well with the previous work. Now the question is what is the nature of the high-pressure phase.

In high-pressure—high-temperature quenching experiments, Fujita *et al.*⁸ obtained a high-pressure form of

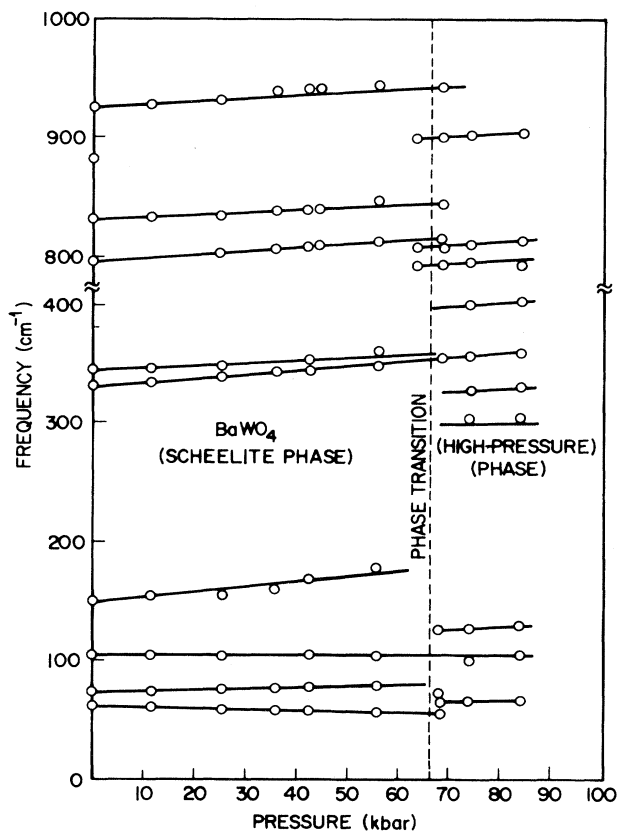


FIG. 2. Pressure dependence of phonon frequencies in BaWO_4 . Phase transition is indicated by the dotted line. Abrupt changes in the Raman frequencies at the transition is evident. Lowest-frequency external mode softens with pressure in the scheelite phase.

BaWO_4 which was retained at ambient pressure. From single-crystal x-ray-diffraction study of this quenched $\text{BaWO}_4(\text{II})$, Kawada *et al.*⁹ determined the structure as monoclinic with the space group $P2_1/m (C_{2h}^2)$; $a = 13.159 \text{ \AA}$, $b = 7.161 \text{ \AA}$, $c = 7.499 \text{ \AA}$, $\beta = 93^\circ 45'$, $z = 8$, and $D = 7.26 \text{ g/cm}^3$. The increase in density was found to

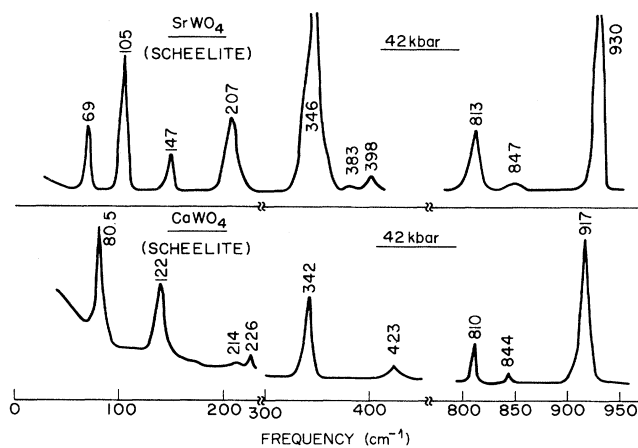


FIG. 3. Raman spectrum of CaWO_4 and SrWO_4 at 42 kbar are shown to indicate the absence of any splittings (see text).

TABLE I. Observed Raman frequencies and their mode-Grüneisen parameters. γ is the mode-Grüneisen parameter $d \ln \omega_i / d \ln v = (B_0 / \omega_i)(d \omega_i / dp)$, where B_0 is the bulk modulus, ω_i is the phonon frequency. For evaluating γ the following values for B_0 were used: $B_0 = 910$ kbar for CaWO_4 , $B_0 = 615$ kbar for SrWO_4 , and $B_0 = 400$ kbar for BaWO_4 ; the latter B_0 values were obtained from an Anderson-Nafe plot of the bulk-modulus data obtained by Hazen (private communication) for the scheelite-structure compounds CaWO_4 , CaMoO_4 , and CdMoO_4 from high-pressure x-ray data.

	CaWO_4	γ	SrWO_4	γ	BaWO_4	γ
Internal modes						
ν_1	912	0.14	921	0.16	925	0.12
$\nu_3(B_g)$	838	0.17	837	0.14	830	0.11
$\nu_3(E_g)$	797	0.34	800	0.25	796	0.16
$\nu_4(E_g)$			382	0.64	353 ^a	
$\nu_4(B_g)$	401	1.1	374	0.62	345	0.23
$\nu_2(A_g + B_g)$	334	0.65	336	0.58	332	0.38
Rotational modes						
E_g	273 ^a		238	1.7	191 ^a	
A_g	210	1.7	190	1.55	150	1.17
Translational modes						
X^2X^2	195	2.1	133	1.73	133 ^a	0
$\text{WO}_4(xy)\text{WO}_4(xy)$	117	1.1	102	1	74	0.43
$\text{WO}_4(z)\text{-WO}_4(z)$	86	-1.2	75	-0.32	62	-0.64

^aReported in Ref. 5.

and $D = 7.26 \text{ g/cm}^3$. The increase in density was found to be 12.7%. According to Kawada *et al.*⁹ the W atom is surrounded by six oxygens and the WO_6 octahedra are slightly distorted, while the W atoms are slightly shifted from their centers, in the quenched phase [$\text{BaWO}_4(\text{II})$]. The Ba atoms apparently have also a higher coordination compared to the scheelite phase. Our attempts to synthesize $\text{BaWO}_4(\text{II})$ at 40 kbar and 600°C in a piston-cylinder device resulted in a quenched product which turned out to be a mixture of the scheelite phase and $\text{BaWO}_4(\text{II})$, and the Raman spectrum of this powder yielded the identifiable scheelite peaks as well as 23 peaks from the quenched high-pressure phase. However, the latter spectrum bears no resemblance to the presently obtained high-pressure phase. This and the fact that our phase transition is perfectly reversible at room temperature rules out the $\text{BaWO}_4(\text{II})$ structure. A high-pressure form of PbWO_4 has been reported,¹² again in quenching studies, but this is possibly also to a monoclinic phase akin to $\text{BaWO}_4(\text{II})$.

The other possibilities for ABO_4 structure compounds at high pressure are the wolframite and the HgMoO_4 structure, both of which are monoclinic, belonging to the space group $P2/c (C_{2h}^4)$ and $C2/c (C_{2h}^6)$ respectively.^{13,14} From packing-efficiency considerations Sleight¹⁵ has indicated that a pressure-induced scheelite-to-wolframite transition may be expected in ABO_4 compounds. This would result in an increase in coordination from tetrahedral to octahedral for W or Mo with respect to O.¹⁵ An increase in coordination is usually followed by an increase in the bond distance, a well-known effect, and this in turn should

abruptly decrease the W—O stretching vibration frequency. This is precisely what is observed; an abrupt decrease in frequency of ν_1 and ν_3 at the phase transition. In addition the number of phonons involving bond bending ($300\text{--}400 \text{ cm}^{-1}$) increases in the high-pressure phase, providing further evidence of a change in the W—O coordination. Hence our results would be consistent with a scheelite-to-wolframite transition. However, the difficulty is that the latter transition may be expected at even lower pressures for SrWO_4 and CaWO_4 and this does not seem to be the case. There is no pressure-induced phase transitions in SrWO_4 and CaWO_4 up to 90 kbar hydrostatic pressure.

The other alternative is that the transition in BaWO_4 is to the monoclinic HgMoO_4 -type structure [$C2/c (C_{2h}^6)$]. The latter structure is closely related to the wolframite structure and the B-cation—oxygen coordination is also octahedral.¹⁴ The observed frequency decrease would be consistent with this transition. Hence it may be that for heavy cation tungstates and molybdates, the HgMoO_4 structure is favored at high pressure, and the compression produced can never reach the radius-ratio—range favorable for the wolframite structure. That the high-pressure BaWO_4 can assume the HgWO_4 structure is in line with the general trends of the effect of pressure on elements and compounds, namely, that the lower-atomic-number species elements and compounds assume the ambient-pressure structure of the higher-atomic-number analogs at high pressure.¹⁶

Further pressure-Raman studies and *in situ* high-pressure x-ray-diffraction studies on scheelite-type

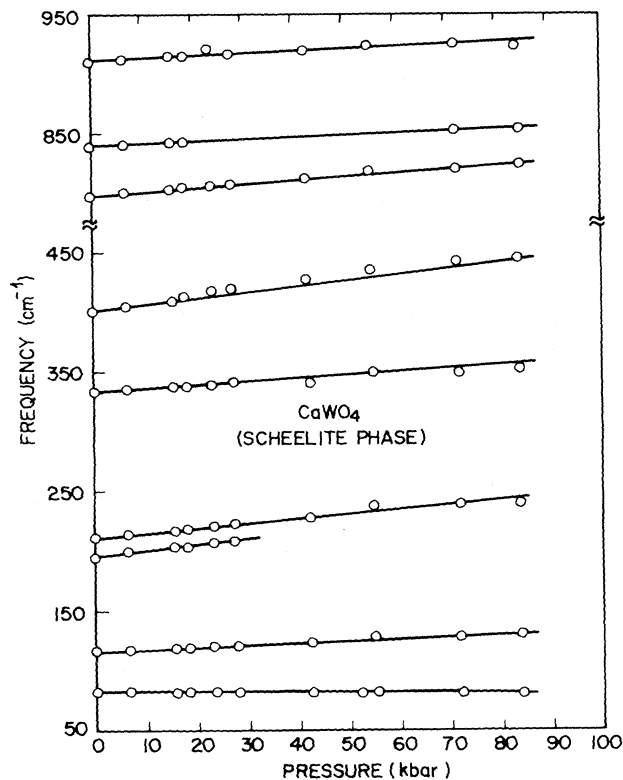


FIG. 4. Pressure dependence of the Raman peaks in CaWO_4 . Lowest-frequency external mode softens with pressure.

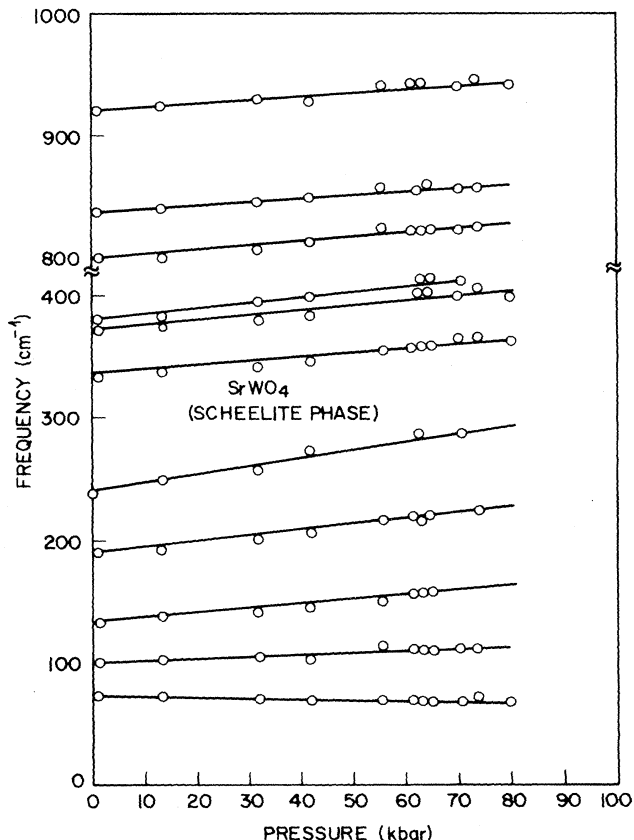


FIG. 5. Pressure dependence of the Raman peaks in SrWO_4 ; note softening of the lowest-frequency external mode.

BaMoO_4 , PbMoO_4 , and PbWO_4 , and possibly also HgMoO_4 and HgWO_4 may be expected to throw much light on this whole question of the nature of the pressure-induced transitions in $A(\text{Mo,W})\text{O}_4$ compounds. Since Raman studies alone cannot give a definite answer, *in situ* high-pressure x-ray-diffraction studies are especially needed.

ACKNOWLEDGMENTS

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- ¹J. P. Russel and R. Loudon, Proc. Phys. Soc. London **85**, 1029 (1965).
- ²S. P. S. Porto and J. F. Scott, Phys. Rev. **157**, 716 (1967).
- ³R. K. Khanna, W. S. Brower, B. R. Buscott, and E. R. Lippin Cott, J. Res. Natl. Bur. Stand. Sect. A **72**, 81 (1968).
- ⁴G. Blasse, J. Inorg. Nucl. Chem. A **37**, 97 (1975).
- ⁵M. Liegeois-Duyckaerts and P. Tarte, Spectrochim. Acta Part A **28**, 2037 (1972).
- ⁶M. Nicol and J. F. Durana, J. Chem. Phys. **54**, 1436 (1971).
- ⁷N. Ganguly and M. Nicol, Phys. Status Solidi B **72**, 617 (1977).
- ⁸T. Fujita, S. Yamaoka, and O. Fukunaga, Mater. Res. Bull. **9**, 141 (1974).
- ⁹I. Kawada, K. Kato, and T. Fujita, Acta Crystallogr. Sect. B

- 30**, 2069 (1974).
- ¹⁰G. J. Piermarini and S. Block, Rev. Sci. Instrum. **46**, 973 (1975).
- ¹¹J. D. Barnett, S. Block, and G. J. Piermarini, Rev. Sci. Instrum. **44**, 1 (1973).
- ¹²L. L. Y. Chang, J. Am. Ceram. Soc. **54**, 357 (1971).
- ¹³R. O. Keeling, Acta Crystallogr. **10**, 209 (1957).
- ¹⁴W. Jeitschko and A. W. Sleight, Acta Crystallogr. Sect. B **29**, 869 (1973).
- ¹⁵A. W. Sleight, Acta Crystallogr. Sect. B **28**, 2899 (1972).
- ¹⁶W. Klement and A. Jayaraman, in *Progress in Solid State Chemistry*, edited by H. Reiss (Pergamon, Oxford, 1967), Vol. 3, pp. 289–376.