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ARTICLES

High-pressure Raman investigation on $CdMoO_4$ and pressure-induced phase transformations

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Cadmium molybdate ($CdMoO_4$) has been investigated by high-pressure Raman spectroscopy to 40 GPa in the diamond cell. Changes in the Raman spectral features reveal two pressure-induced phase transitions in the pressure range investigated. Detailed analysis of the Raman data and comparison with the spectra of $CdWO_4$ confirm that the first transition near 12 GPa is from the scheelite phase to the wolframite phase. The second phase change occurring near 25 GPa from the wolframite phase is marked by a large downward shift (120 cm^{-1}) of the v_1 mode frequency of Mo-O polyhedron. By comparison with the v_1 mode frequency of the WO_6, it is concluded that the Mo-O coordination becomes truly octahedral in the new high-pressure phase (phase III) of $CdMoO_4$. The behavior is compared with that of $CdWO_4$ which undergoes an analogous pressure-induced phase transition near 20 GPa. Our recent high-pressure x-ray diffraction study on $CdMoO_4$ fully supports the above conclusions.

INTRODUCTION

The pressure-induced phase transformation in ABO_4 compounds with scheelite structure has been of considerable interest lately.[1-3] In this connection Raman spectroscopic studies[1-3] have been quite informative in revealing phase transitions and in some cases identifying the nature of the high-pressure phases, although the determination of the symmetry and structure analysis require high-pressure x-ray-diffraction data. One of the interesting questions is whether the scheelite-type phase would transform to the wolframite type under pressure. To date such a transformation has not been reported.

Our motivation to study $CdMoO_4$ stems from the fact that this scheelite-structured compound sits very close to the scheelite-wolframite instability.[4] The corresponding tungstate $CdWO_4$ has the wolframite structure at ambient pressure. If the latter is denser than the scheelite, as is believed from their structural features, $CdMoO_4$ would be the most favorable case to observe a pressure-induced transition directly from scheelite to wolframite under pressure. The question of relative stability and metastability can also be studied conveniently with Raman spectroscopy. Further, any post wolframite structure, where the BO_4 ion becomes truly octahedrally coordinated (BO_6), would be of great interest, and this is a reasonable expectation since we have already found this pressure-induced transformation in $CdWO_4$.[5]

We have therefore investigated $CdMoO_4$ to pressures over 40 GPa by high-pressure Raman spectroscopy in the diamond anvil cell. We believe that we have strong Raman evidence for a pressure-induced scheelite to wolframite type structural transition near 12 GPa and another phase change near 25 GPa in which Mo becomes octahedrally coordinated to oxygens. The results will be presented and discussed in this paper.

EXPERIMENTS

Single-crystal samples of $CdMoO_4$ were made available to us from AT&T Bell Laboratories, where they had been grown a long time ago as laser hosts for rare-earth ions. The scheelite structure of $CdMoO_4$ was verified from its Raman and IR spectra by comparison with published IR data.[6] However, no published Raman data were available for $CdMoO_4$, but the nature of the Raman spectrum obtained and the Raman peaks of the internal modes of the MoO_4 group provided the basis for the identification of its structure as scheelite type.[7] The crystals were colorless and clear, and samples for high-presssure Raman studies were obtained by fracturing them. Hence no orientation or polarization studies were attempted.

For high-pressure generation a gasketed Mao-Bell-type diamond anvil cell was used, with 4:1 methanol-ethanol mixture as pressure medium. Pressure was calibrated by the well-known ruby fluorescence techique.[8] For recording the Raman spectra, a Spex Raman double monochromator provided with a photomultiplier tube for photon counting was used, in conjunction with the Ramalog data-acquistion system. A Spex Triplemate spectrometer equipped with a charge-coupled-diode (CCD) array detector was also employed for recording spectra especially at the high-pressure end, where the Raman intensity was drastically reduced by the change in the color of the sample to a dark brown color. This change also necessitated the use of 647.1-nm line of krypton laser for Raman excitation. In general, the 514.5-nm line of the argon laser proved to be ideal for excitation at power levels in the range of 30–60 mw.

RESULTS

Raman spectra of $CdMoO_4$ recorded at three different pressures are presented in Fig. 1. The low-pressure spec-

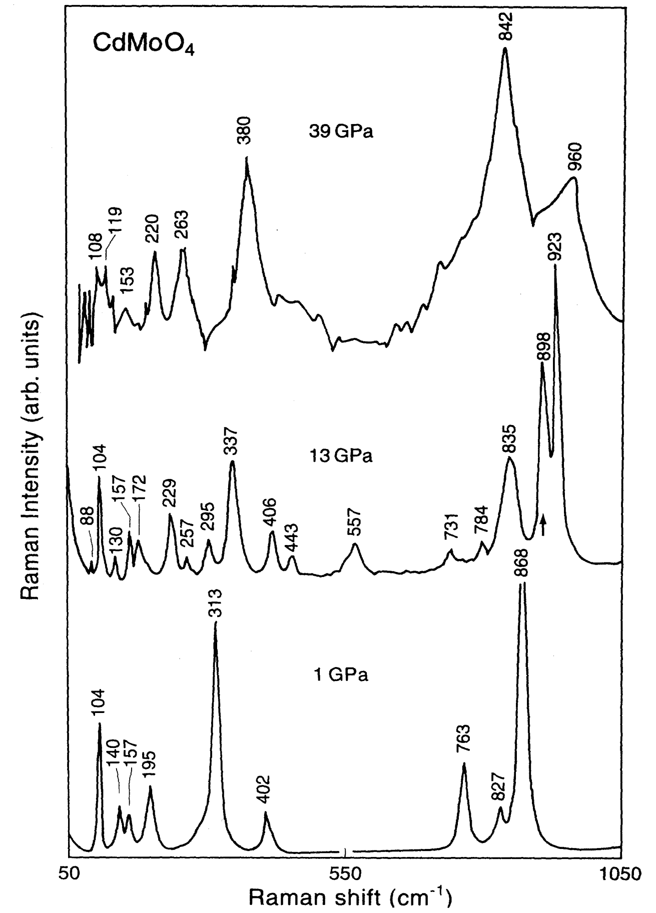

FIG. 1. Raman spectrum of CdMoO$_4$ recorded at three different pressures. The 1-GPa spectrum is scheelite phase and the 13-GPa spectrum is mixed phase, scheelite (marked by arrow) plus phase II (wolframite, see text). The 39-GPa spectrum is predominantly phase III with some untransformed phase II as shown by the 960-cm^{-1} peak on the right side of the 842 cm^{-1} peak. The latter is the strongest peak of phase III.

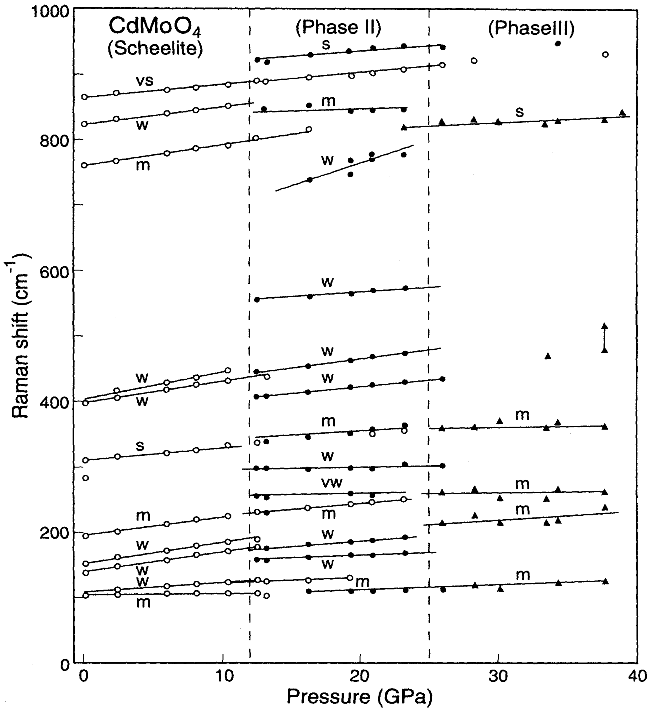

FIG. 2. Plot of the pressure dependences of the Raman peaks. Phase transitions near 12 and 25 GPa are indicated by the dashed line. Raman intensities: Vs, very strong; S, strong; M, medium; W, weak; and Vw, very weak.

trum (bottom) is typical of the scheelite phase. Near 12 GPa the spectrum started to change, with additional Raman peaks appearing. As pressure was increased, the scheelite Raman peaks decreased in intensity, while the Raman peaks of the new phase grew stronger. In Fig. 1 the spectrum recorded at 13 GPa is predominantly of the new phase. A small amount of the scheelite phase is still present as evidenced by the scheelite Raman peaks, which are marked by arrows in the spectrum. The top spectrum recorded at 39 GPa is quite different, signifying yet another phase change. In this spectrum a new peak near 842 cm^{-1} emerges as the strongest. The peak on the high-frequency side near 960 cm^{-1} is close to the position of the strongest peak of the wolframite phase expected at that pressure, indicating that there is still some untransformed wolframite phase. The detailed behavior of the Raman peaks indicates that the strong peak of phase III near 830 cm^{-1} starts to appear even while the phase I to II transition is not completed. We attribute this to pressure gradient over the sample area, for the pressure medium is no longer hydrostatic above 10 GPa. From measurements on ruby chips sitting in different areas around the hole, the gradient at pressures near 20 GPa could be as large as 15% depending on the geometry of the hole, the anvil alignment, and its position on the anvil flat.

TABLE I. Observed Raman peaks in CdMoO$_4$ under ambient pressure and temperature.

Vibration mode Type	Scheelite ν (cm^{-1})	Raman intensities[a]	$d\nu/dP$ (cm^{-1}/GPa)	Grüneisen[b] γ
ν_1 (A_g)	867	VS	1.8	0.2
ν_3 (B_g)	825	W	2.6	0.3
ν_3 (E_g)	761	W	3.1	0.4
ν_4 (E_g,B_g)	399	M	3.2	0.8
	401	M	4.6	1.2
ν_2 (A_g,B_g)	309	M	2.2	0.7
R	282	VW	3	1.1
R	193	M	3	1.6
R	154	VW	3	2.0
T	137	M	3.2	2.4
	107	M	1.3	1.2
T	103	S	0	

[a] VS, very strong; S, strong; M, medium; W, weak; VW, very weak.

[b] For calculating γ, the bulk modulus B_0 was taken as 104 GPa (Ref. 9), Raman intensities.

TABLE II. Observed Raman peaks in phase II (wolframite) and phase III of $CdMoO_4$.

	Phase II (20 GPa) ν(cm^{-1})	Phase II (1 bar)[a] ν (cm^{-1})	Phase III (28 GPa) ν (cm^{-1})
ν_1	941 VS	~900	834 VS
ν_3	849 M	~800	749 VW
ν_3	771–779 W	~650	
ν_4	569 M	~540	650 VW
ν_4	426 M	~386	491 W
ν_2	358 M	~320	370 M
ν_2	300 M	~292	332 VW
			294 W
R	248 M	~206	258 M
S	189 W	~160	215 M
	166 M	~146	114 M
T	142 VW		
	109 M	~94	78 W

[a] Extrapolated from the pressure dependence plot of Fig. 2.

[b] Notation as in Table I.

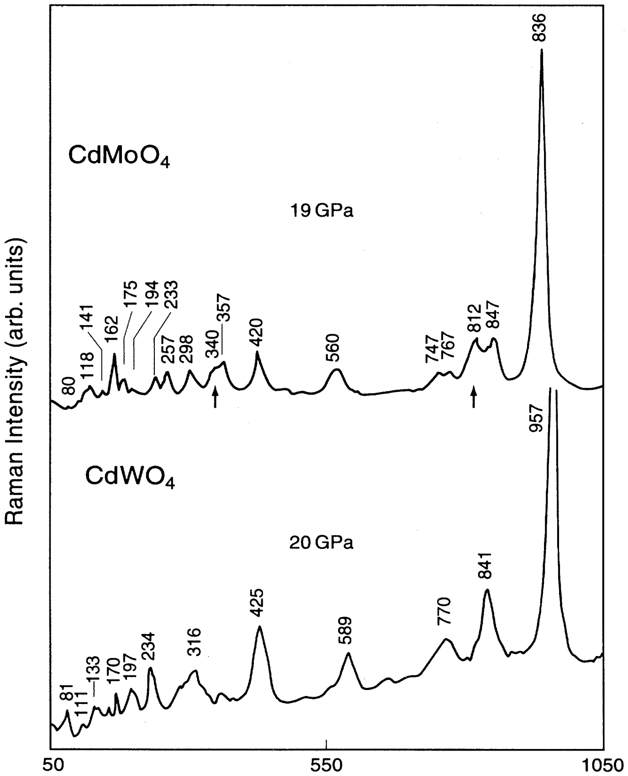

FIG. 3. Raman spectrum of nearly pure phase II at 19 GPa (wolframite phase) of $CdMoO_4$ is compared with the wolframite phase spectrum of $CdWO_4$ at 20 GPa. The close correspondence is clearly seen. The arrows in the top spectrum indicate that the peaks belonging to phases I and III, untransformed scheelite, and just the beginning of phase III, respectively.

On releasing the pressure the phase transitions are found to be reversible, but there is considerable hysteresis, in particular with phase II. The latter phase is present even down to 2–3 GPa. On releasing pressure to the ambient, the original scheelite phase spectrum is obtained. In Fig. 2 the pressure dependence of the observed Raman peaks is plotted against pressure to show the pressure-induced phase transitions near 12 and 25 GPa. In Table I, we present the Raman data for the scheelite phase and in Table II for the pressure-induced phases II and III, $CdMoO_4$. In Table I the measured $d\omega/dP$ and the mode Grüeisen parameters γ_i are presented for the scheelite phase. The interpretation of the scheelite phase spectrum of $CdMoO_4$ is straightforward, for the vibrational modes of scheelite structured ABO_4 oxides are well identified.[7] Following this, we indicate the assignments on the extreme left in Table I.

DISCUSSION

In Fig. 3 the Raman spectrum of phase II (top spectrum) of $CdMoO_4$ recorded at 19 GPa is presented, along with the Raman spectrum of the wolframite type $CdWO_4$ at 20 GPa. The Raman peak in the 500–600 cm^{-1} region is characteristic of the wolframite type. From the similiarity between the two spectra, we conclude that phase II of $CdMoO_4$ is of wolframite type. The Raman

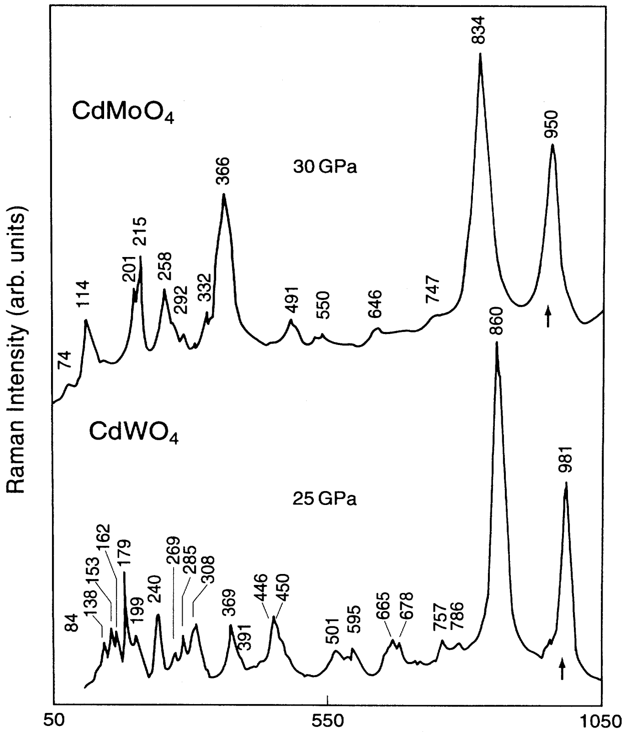

FIG. 4. Comparison of phase III of $CdMoO_4$ with phase II of $CdWO_4$. In both, a strong Raman peak downshifted by about 120 cm^{-1} emerges when the wolframite phase transforms to phase III. The untransformed wolframite peak (the strongest of this phase) is marked by an arrow, on the right side.

spectrum of the wolframite phase is more complex because of its lower symmetry. In Table II the Raman peaks observed in phase II at 20 GPa are listed. Also, the Raman peak positions of phase II at zero pressure obtained by extrapolation from the pressure dependence plot are given, for the ambient pressure values of the mode frequencies are of interest.

Detailed mode assignments for the ABO_4 wolframite compounds do not exist, but it has been suggested[10] from Raman and IR data, in the wolframite tungstates the internal mode frequencies are consistent when the anion is regarded as tetrahedrally coordinated, although from the structural point of view highly distorted edge-shared BO_6 units are believed to be present in wolframite compounds.[11] Following the former view that the tetrahedral coordination prevails, we assign the strongest peak in the spectrum of phase II of $CdMoO_4$ to the ν_1 mode of the MoO_4 ion. In fact, this frequency is slightly higher than in the scheelite phase (see Fig. 2), whereas it should have been lower if the Mo-O coordination had really increased. The rest of the internal mode ν_3, ν_2, and ν_4 peaks in the phase II spectrum lie at lower frequencies as for the scheelite phase, except that the symmetry of the crystal has now changed from $I4_1/a$ to $I2/a$. Our recent high-pressure x-ray-diffraction study has confirmed the wolframite-type structure for phase II and fully supports the above conclusion. The results of this study will be published elsewhere.

In Fig. 4 the spectrum of phase III of $CdMoO_4$ recorded at 30 GPa is compared with the Raman spectrum of the high-pressure phase of $CdWO_4$ at 25 GPa. The remarkable feature in both the above high-pressure phases is that the strong ν_1 peak is downshifted by about 120 cm^{-1} from the preceding wolframite-type phase. In the case of $CdWO_4$, the downshifting of the ν_1 peak has been attributed[5] to a change in W-O coordination from tetrahedral to octahedral (WO_4 to WO_6). This conclusion is based on a comparison of the ν_1 mode frequency of WO_6 taken from Ba_2CaWO_6 crystallizing in the ordered perovskite structure[12] with that of WO_4 in several ABO_4 tungstates at ambient pressure.[10] Therefore, we attribute the $\sim$120-cm^{-1} drop in the ν_1 mode frequency in phase III of $CdMoO_4$ to a pressure-induced Mo-O coordination change from tetrahedral to octahedral coordination. Further, crystal chemical considerations would require that the octahedral group (MoO_6) must share two edges or two corners in the arrangement to preserve the Mo-O ratio of 1:4. Thus Raman spectroscopy provides an important piece of information regarding the structural building block. However, from Raman data alone it is not possible to determine the crystal structure and symmetry of the phase in question. The results of our recent high-pressure x-ray-diffraction study on phase III are consistent with the $BaWO_4$ II-type[13] structure. In this structure Mo would be truly octahedrally coordinated to oxygens as is indicated by the Raman results.

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