

New pressure-induced phase changes in CdWO_4 from Raman spectroscopic and optical microscopic studies

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Pressure-induced phase transitions in ABO_4 tungstates and molybdates with scheelite and wolframite structure are of interest to materials science and mineral physics. High-pressure phases with interesting physical properties can be expected. Through a high-pressure Raman and optical microscopic study we have found two novel pressure-induced phase transitions in wolframite-type CdWO_4 . The first transition near 10 GPa is subtle, but easily observable under the polarizing microscope, as the crystal breaks into domains of colour, presumably due to a phase change accompanied by twinning, or ferroelasticity. At the second transition near 20 GPa, the Raman data clearly indicate a change in W–O coordination from basically tetrahedral to truly octahedral, a new finding of significance to high-pressure crystal chemistry.

PRESSURE-induced phase transformation in scheelite (tetragonal symmetry) ABO_4 compounds have been of current interest from the viewpoint of their high-pressure crystal chemistry¹. Recent high-pressure Raman spectroscopic studies^{2,3} have revealed that pressure-induced phase transformations are a rule in these systems. Another common structure adopted by ABO_4 tungstates at ambient pressure is the so-called wolframite type⁴ and to our knowledge these have not been studied under high pressure.

Two questions of great interest in the high-pressure behaviour of ABO_4 molybdates, tungstates and rehenates are (i) whether the scheelite-type compound would transform under pressure to the wolframite-type structure and (ii) how stable is the wolframite structure itself with respect to high pressure. The best candidates to study in this connection are CdMoO_4 and CdWO_4 , because the former crystallizes in the scheelite structure and sits on the border line between the scheelite–wolframite stability field⁴, and CdWO_4 has the wolframite structure and hence is a very good candidate for clarifying the second question. Therefore, we carried out high-pressure Raman spectroscopic studies on CdWO_4 and CdMoO_4 up to 40 GPa and optical microscopic studies on CdWO_4 up to 20 GPa. In this article we will discuss mainly our Raman results on CdWO_4 , and argue for a change in the coordination of tungsten to a truly octahedral

coordination with respect to oxygens at the pressure-induced phase transition observed near 20 GPa. We will briefly discuss our results on CdMoO_4 , which undergoes the anticipated scheelite to wolframite transformation as well as the phase transition involving the above-mentioned coordination change. Finally, we will present optical microscopic evidence for a subtle phase change near 10 GPa in CdWO_4 .

High-pressure Raman experiments on CdWO_4 were carried out in a gasketed Mao-Bell-type diamond cell, with 4:1 methanol–ethanol mixture as the pressure-transmitting medium. Pressure was calibrated by the well-known ruby fluorescence technique. Raman spectra were generally recorded using a Spex Raman instrument equipped with photomultiplier. In some experiments a Spex Triplemate instrument provided with a CCD diode array detector was used to record the spectra. Figure 1 shows the Raman spectra of CdWO_4 obtained at three different pressures. The bottom spectrum belongs to the wolframite phase, the middle one has Raman peaks belonging to a new high-pressure phase plus the wolframite phase, and the top spectrum represents purely the high-pressure phase. Figure 2a and b show a plot of the observed Raman peak positions as a function of pressure. Near 20 GPa the spectrum clearly changes due to a pressure-induced phase transition. Raman peaks of the wolframite phase extend beyond 20 GPa and disappear completely only above 30 GPa. Likewise, on release of pressure the high-pressure phase persists down to about 16 GPa. Below this pressure the sample is purely that of the wolframite phase. The appearance of the two-phase region shows very clearly that the transition is strongly first-order and that it is hysteretic. However, the transition is completely reversible at room temperature and the high-pressure phase is not quenchable. Now the question is what is the nature of the high-pressure phase? Only a high-pressure X-ray structure investigation can give a decisive answer, but the Raman results contain some important information regarding the structural building block, namely the coordination of the W–O polyhedra.

Detailed structural investigations on the scheelite-type ABO_4 compounds have shown that the B cation is tetrahedrally coordinated to oxygens, while the A cations

are surrounded by eight oxygens^{4,5}. Raman and infrared spectra⁶⁻⁸ are consistent with the presence of isolated BO_4 tetrahedra in the structure⁷. In ABO_4 of the wolframite type, such as CdWO_4 , the B cation is regarded as sixfold-coordinated (approximately, octahedrally coordinated) with respect to oxygens, while the A cation is similarly situated with six oxygen neighbours⁴. The structure may be crudely described as hexagonally close-packed oxygens with certain octahedral sites filled with A and B cations in an ordered way⁴.

The wolframite-type CdWO_4 has monoclinic symmetry and belongs to the space group $\text{I}2/a$ (ref. 9). The usual view of the structural arrangement is that it consists of zigzag chains of edge-sharing WO_6 octahedra. But the description of the building blocks as octahedrally coordinated WO_6 is a highly distorted picture, for the two of the W-O distances are much larger than the four other distances to regard them as regular WO_6 units. For instance, in the isomorphous NiWO_4 these distances are found to be 1.79 Å for four W-O distances and 2.19 Å

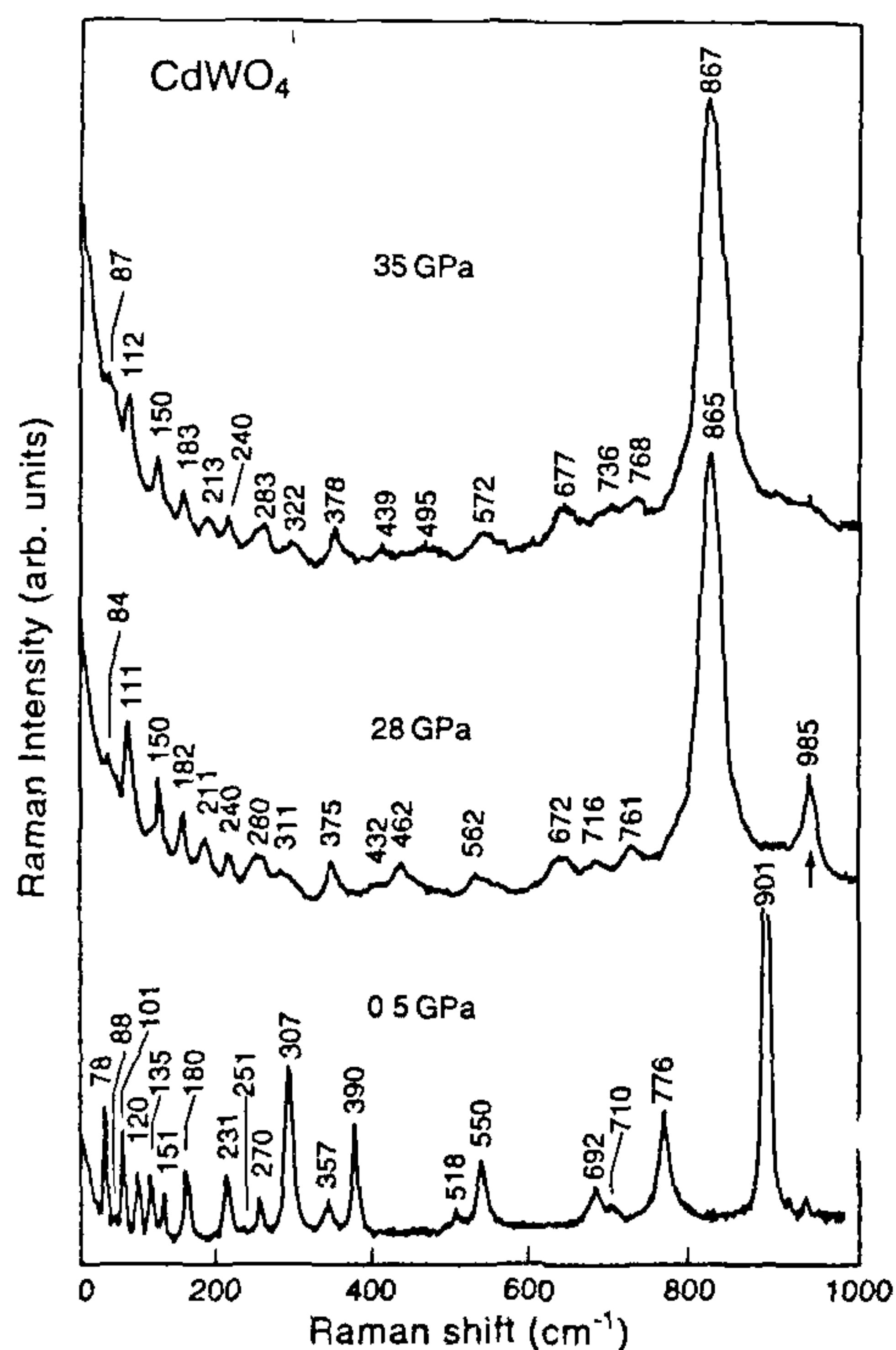


Figure 1. Raman spectra of CdWO_4 recorded at three different pressures with 514.5 nm line of the argon ion laser. The spectrum at 0.5 GPa is of the wolframite phase, which is the normal phase. The 28 GPa spectrum has changed and the strongest line representing the ν_1 mode frequency (865 cm^{-1}) has dropped by 120 cm^{-1} from that of the wolframite phase (985 cm^{-1}), seen to the right. The sample has not fully converted to the new phase. The wolframite peak is marked by an arrow. The spectrum at 35 GPa represents purely the new phase (see text for explanation)

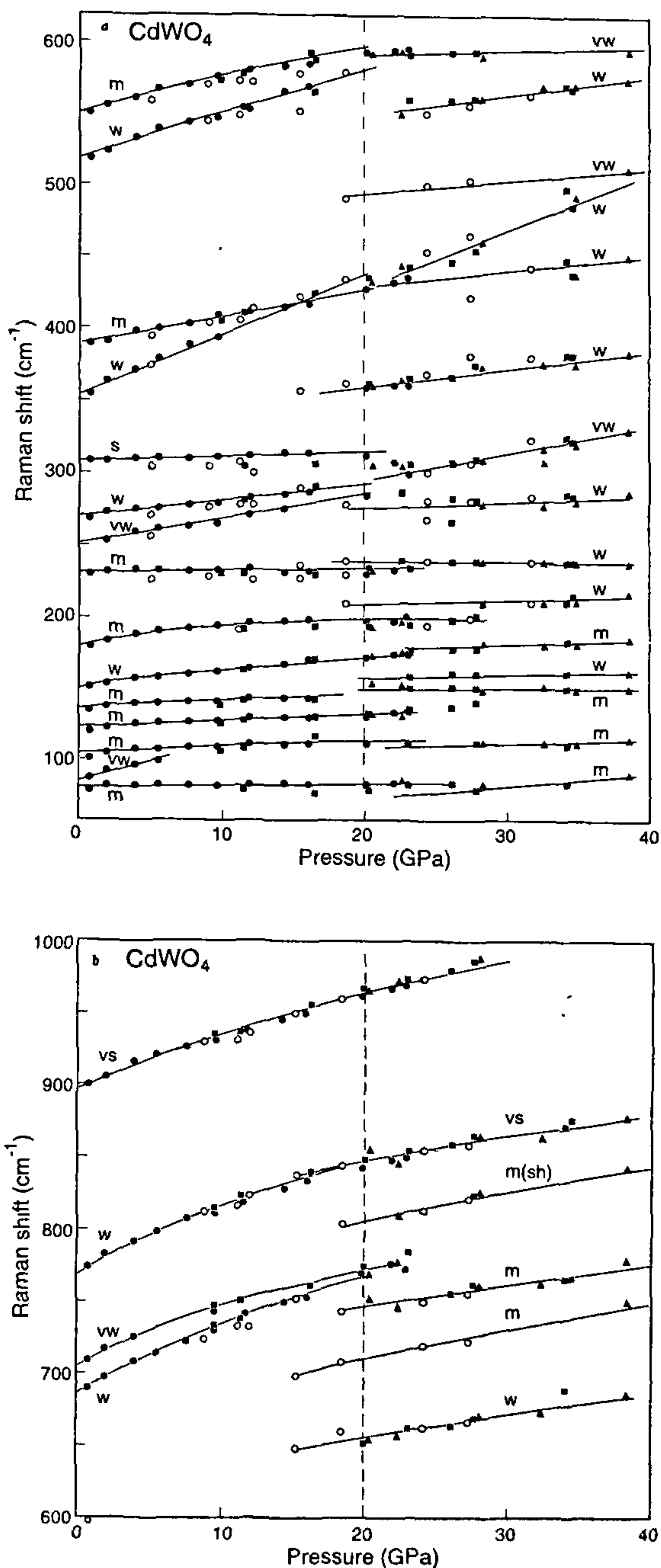


Figure 2a and b Pressure dependence of the observed Raman peaks in the wolframite phase as well as in the new high-pressure phase. A phase transition is marked by sudden shifts in the Raman peak frequency as well as appearance of new peaks and disappearance of old peaks. The dotted line marks the transformation pressure. The symbols s, m, w and vw appearing in the figure indicate the intensities of the Raman peaks, strong, medium, weak and very weak, respectively. Sh is shoulder. Solid lines have been drawn through the data points

for the other two¹⁰. Further, it has been pointed out⁷ that the Raman frequencies of WO_4 in wolframite-type CdWO_4 are consistent if the W–O coordination is regarded as tetrahedral rather than octahedral.

The remarkable feature in the Raman spectrum of the high-pressure phase is that the ν_1 mode frequency, which represents the totally symmetric W–O stretching vibration, drops by about 120 cm^{-1} from that of the wolframite phase at the corresponding pressure (see Figure 1) and dominates the spectrum. This is precisely what would be expected if the W–O coordination becomes truly octahedral. When the coordination increases, the bond lengths increase, and the result is a drop in mode frequency. For instance, the ν_1 mode frequency of the octahedral tungstate group (WO_6) in Ba_2CaWO_6 (refs 11, 12) crystallizing in the ordered perovskite structure is about 100 cm^{-1} lower compared to that of WO_4 in tetrahedral coordination⁷. Comparing our results with the above we conclude that in the high-pressure phase of CdWO_4 the coordination for W becomes truly octahedral. This would require that the WO_6 octahedrons form chains in the structure sharing four corners with neighbouring octahedra, or form zigzag chains sharing two edges, to preserve the W–O ratio. The Raman spectrum has other weak peaks in the high-frequency region which must be identified with the other internal modes appropriate for WO_6 as well as with the external modes. Obviously, the crystal symmetry will decide the splittings of both the internal and external modes. Input from a high-pressure X-ray diffraction study is needed to identify the symmetry of the high-pressure phase, which will then enable one to assign the other observed peaks. But the identification of the highest wave number peak with the ν_1 mode of the WO_6 seems reasonable, and this is a valuable piece of information that we get from Raman spectroscopy, regarding the structure of the building block. Further, the change in colour of the sample after the 20 GPa transition would also be consistent with increase in coordination, for now the crystal field acting on the 5d states of W would be much larger, resulting in an enhanced 10DQ splitting. This would lower the conduction band and reduce the optical gap, causing the observed colour change.

Our high-pressure Raman studies on CdMoO_4 (ref. 13) show two pressure-induced phase transitions, one near 12 GPa and another near 25 GPa. From a detailed comparison of the Raman features of the first high-pressure phase with that of wolframite-type CdWO_4 it is clear that the first pressure-induced phase transition in CdMoO_4 is from scheelite to wolframite type. In the second transition near 25 GPa the behaviour is very similar to that observed in CdWO_4 . The ν_1 mode drops by about 120 cm^{-1} and the spectrum is similar to that of the high-pressure phase of CdWO_4 . This indicates that the wolframite phase transforms to a structure in which the

Mo–O coordination becomes octahedral. Thus, the results of CdMoO_4 and CdWO_4 are consistent.

We have made optical observations under a microscope on thick ($\sim 50\text{ }\mu\text{m}$) as well as thin ($\sim 20\text{ }\mu\text{m}$) samples of CdWO_4 in polarized and unpolarized white light. Remarkably, a pressure-induced phase transition that is not evident in the Raman results could easily be observed near 10 GPa. The sample is normally colourless in unpolarized white light and has a uniform colour in crossed polarization. The onset of the phase transition is marked by the sudden appearance of light grey bands inside the crystal when viewed in unpolarized light. In crossed polarization the effect is spectacular, for the sample transforms into parallel domains of different colours with sharp boundaries. These are illustrated in Figure 3 a–c.

In crossed polarization thin samples show the colour domain vividly. With increasing pressure numerous grey-coloured parallel bands develop in the sample when viewed in unpolarized light, which in crossed polarization has a colour pattern corresponding to the bands in Figure 3 c. At the 20 GPa transition the pattern breaks up and is replaced by dark spaghetti-like regions, the sample acquiring a yellow colour. The yellow progressively changes to a deep orange colour with increasing pressure. Figure 3 d illustrates the appearance of a thicker sample near 40 GPa as seen by transmission under white light illumination.

When pressure is released, the sample does not recover its original appearance, once it breaks up into domains. The grey bands are still seen and the originally observed uniform colour over the sample area in crossed polarization is not restored. After the 20 GPa transition a reversal to a single crystal is not expected and this is borne out from our observations.

The optical observations are strong evidence for a pressure-induced phase transition near 10 GPa. In fact, when the Raman data are examined critically, a few minor changes are seen, viz. small changes of slope in the pressure vs. Raman shift plot and a small (4 wave numbers) abrupt downward shift of the strong Raman peak near 304 cm^{-1} . Now the interesting question is: What is this subtle transition in the wolframite phase? A strong possibility is that the wolframite lattice $I2/a$ takes on the $C2/c$ symmetry of HgWO_4 . This would involve only a reorientation of the doubled unit cell of wolframite by a rotation around the b -axis, as shown by Jeitschko and Sleight⁵ for the reverse case, namely the relationship between wolframite structure and the structure of HgMoO_4 . In this transition the new unit cell volume would be the same, but the angle β is expected to be much larger than for wolframite CdWO_4 , $\sim 115^\circ$ vs. 91.5° . Jeitschko and Sleight⁵ describe the differences between the two structures as follows. In both the structures the oxygens form close-packed layers

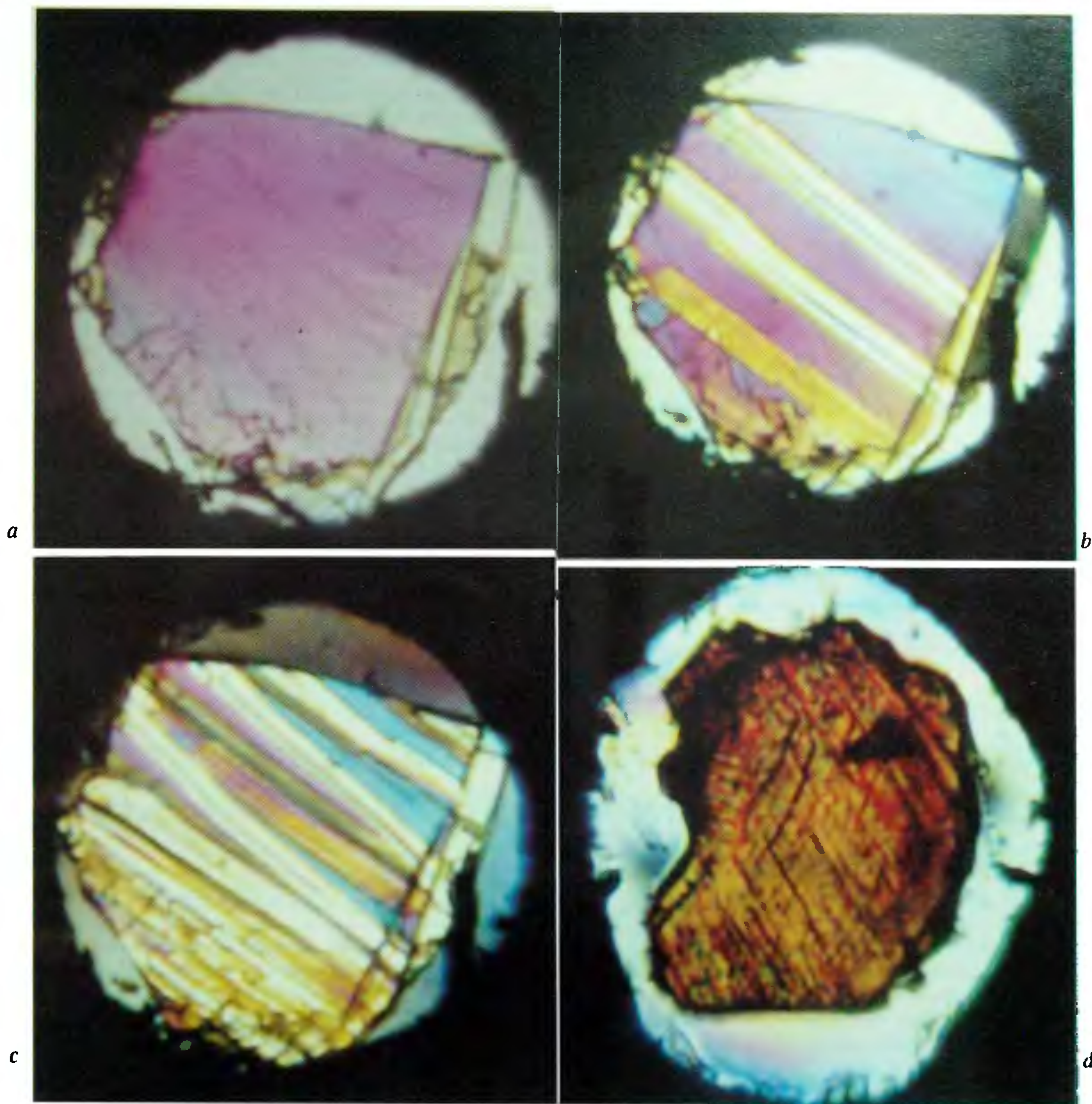


Figure 3. Photomicrographs (magnification $\times 400$) of two CdWO_4 samples in the form a thin plate *a*, *b*, *c*, taken with white light in crossed polarization at about 0.5 GPa, 9.7 GPa and 11 GPa, respectively. The uniform pink colour indicates that the sample is single crystal. In *b* the colour domains are due to a subtle phase transition (see text for explanation). In *c* the pressure has been increased and the result is that the domains multiply. The domains could be due to twinning or ferroelastic nature of the new phase. *d*, indicates the appearance of a thicker sample in transmission, with white light (unpolarized) as the source, at a pressure of about 38 GPa. The deep orange colour is believed to be connected with the second pressure-induced phase transition which involves a change in the W-O coordination, from basically tetrahedral to truly octahedral coordination. The latter transition occurs near 20 GPa and the colour of the sample progressively turns from yellow to deep orange. The sample is practically colourless and transparent before this phase transition.

parallel to the *b*-*c* plane. However, the stacking of these layers is almost perfectly hexagonal close-packed in the CdWO_4 wolframite structure, while it would be close to cubic close-packing in HgMoO_4 , and HgWO_4 . The wolframite-type CdWO_4 adopting the HgWO_4 structure would be consistent with the trends in high-pressure

crystal chemistry, namely that the structure of the compound down the column in the Periodic Table is a likely structure for the high-pressure phase of the analogous compound just above it in the same column. Single-crystal high-pressure X-ray diffraction on CdWO_4 would be very rewarding in this connection and it is quite

feasible in the present case, since the transition pressure is 10 GPa, within the reach of hydrostatic pressure.

The subtle nature of the transition as reflected in the Raman results and the observed optical property changes would fit in the above picture. It is very likely that multiple twinning occurs during the transition and the domains are a direct consequence of it. Twinning would also explain the fact that the sample does not regain its original single-crystal character on release of pressure after the 10 GPa transition. The other possibility is that they are ferroelastic domains. The optical observations under a polarizing microscope demonstrate the power of this technique in revealing subtle phase transitions.

Our picture then for the high-pressure transformation sequence in $A^{2+}B^{6+}O_4$ compounds is scheelite to wolframite, or wolframite-like phase and then to a phase with truly octahedrally coordinated BO_6 units. There are other monoclinic structures closely related to wolframite for ABO_4 compound⁵ and they are a possibility as intermediate high-pressure phases, before the transformation to the phase involving a change to octahedral coordination.

- I. Nicol, M. and Durana, J. F., *J. Chem. Phys.*, 1971, 54, 1436–1440;
Ganguly, N. and Nicol, M., *Phys. Status Solidi B*, 1977, 79,

617–622.

2. Jayaraman, A., Batlogg, B. and van Uitert, L. G., *Phys. Rev.*, 1983, B28, 4774–4777, *ibid.*, 1983, B31, 5423–5427; Jayaraman, A., Kourouklis, G. A., van Uitert, L. G., Grodkiewicz, W. H. and Maines, R. G., *Sr. Physica*, 1988, A156, 325–340; Jayaraman, A., Wang, S. Y., Shieh, S. R., Sharma, S. K. and Ming, L. C., *J. Raman Spectrosc.*, June 1995.
3. Christofilos, D., Kourouklis, G. A. and Ves, S. (to be published).
4. Sleight, A. W., *Acta Crystallogr.*, 1972, B28, 2899–2902.
5. Jeitschko, W. and Sleight, A. W., *Acta Crystallogr.*, 1973, B29, 869–875.
6. Tarte, P. and Liegeois Duychaerts, M., *Spectrochim. Acta*, 1972, A28, 2029–2036, Liegeois-Duykaerts, M. and Tarte, P., *ibid.*, 1972, A28, 2037–2051.
7. Blasse, G., *J. Inorg. Nucl. Chem.*, 1975, 37, 97–99.
8. Clark, G. M. and Doyle, W. P., *Spectrochim. Acta*, 1966, 22, 1441–1446.
9. Chichagov, A. P., Ilyukhin, V. V. and Belov, N. V., *Dokl. Akad. Nauk SSSR*, 1966, 166, 87–89.
10. Keeling, R. O., *Acta Crystallogr.*, 1957, 10, 209–213.
11. Corsmit, A. F., Hoefdraad, H. E. and Blasse, G., *J. Inorg. Nucl. Chem.*, 1972, 34, 3401–3407.
12. Blasse, G. and Corsmit, A. F., *J. Solid State Chem.*, 1973, 6, 513–518.
13. Jayaraman, A., Wang, S. Y. and Sharma, S. K. (to be published).

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Analysis of a conformation-specific epitope of the alpha subunit of human chorionic gonadotropin: Study using monoclonal antibody probes

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Monoclonal antibodies (MAbs) have been used extensively for identification of sequence-specific epitopes using either the ELISA or/and IRMA methods. However, attempts to use MAbs for identification of conformation-specific epitopes have been very few as they are considered very labile. We have investigated the stability of conformation-specific epitopes of human chorionic gonadotropin (hCG) using a quantitative solid-phase radioimmunoassay (SPRIA) technique. Several epitopes are stable to mild modification (chemical and proteolytic) conditions, and epitopes show differential stability for these modifications. Based on these observations, a monoclonal antibody (MAb 16) for an α -subunit-specific epitope of hCG has been used to monitor changes at the epitopic site (identified as epitope 16) on modification of hCG, using SPRIA with

immobilized MAb 16. Modifications of amino groups, hydroxyl group of tyrosine as well as carboxyl group of Asp/Glu all bring about sufficient changes in the epitope integrity. Peptide bond hydrolysis at lysine residues damages the epitope, but not at arginine residues. Hydrolysis at tyrosine does not affect the epitope, though modification of the side-chain of tyrosine inactivates the epitope. Destruction of the epitope occurs on reduction of the disulphide bonds. Partial retention of the epitope activity is seen on modification of carboxyl or the ϵ -amino groups of lysine. Based on these results four to six amino acids have been identified to be at the epitopic site, and the data suggest that two peptide segments are brought together by the disulphide bond Cys10–Cys60 to form the epitope.

EPITOPES form a very important and specific immunochemical feature of a protein or a macromolecular

antigen, and this feature of the antigen is used extensively in the development of specific radioimmunoassays, immunodiagnoses, vaccines etc.^{1–4}. Epitopes are classified into sequence-specific (contiguous) and conformation-

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