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Pressure-induced phase changes in $CdWO_4$

Studies in pressure-induced phase transformation in sheelite type ABO_4 compounds by Raman spectroscopy have demonstrated that such transformations are a rule in these systems. Do Wolframite type ABO_4 compounds exhibit pressure-induced transformation (PIT) is a logical question. A. Jayaraman *et al.* answer this question in their article 'New pressure-induced phase changes in $CdWO_4$ from Raman spectroscopic and optical microscopic studies' on **page 44**.

Employing a gasketted Mao–Bell type diamond cell, the behaviour of $CdWO_4$ (Wolframite structure) at high pressures have been studied up to 40 GPa with the help of high pressure Raman spectra. The results show that wolframite phase disappears above 30 GPa and reappears at 16 GPa on release of pressure. This transition is completely reversible at room temperature and the high pressure phase is not quenchable. It is a first order transition and is hysteritic.

Identifying the highest wave number peak with ν_1 mode of WO_6, the authors argue that the decrease of the frequency of this peak by about 120 cm^{-1} in the high pressure phase (as compared to the wolframite phase) is indicative of a truly octahedral W–O coordination in the high pressure phase. They point out that the description of octahedrally coordinated WO_6 as building blocks in wolframite $CdWO_4$ is a highly distorted picture. It should really be regarded as tetrahedral and that is also consistent with the Raman frequency of WO_4 in wolframite $CdWO_4$.

Comparing their results with the ν_1 mode of the octahedral WO_6 in Ba_2CaWO_6, they conclude that in the high pressure phase of $CdWO_4$, the coordination of W becomes truly octahedral. They suggest that the WO_6 octahedrons may form chains in the structure sharing four corners with the neighbouring octahedra or from zig-zag chains sharing the edges to preserve the W–O ratio. They point out the need for additional input from high pressure X-ray study to identify the other weak peaks of Raman spectrum.

Optical observations under microscopic (in unpolarized and crossed polarized light) with thick (~ 50 μm) as well as thin (~ 20 μm) samples of $CdWO_4$ revealed a remarkable PIT near 10 GPa. This is also shown in Raman spectra, in a less pronounced way, as small changes of slope in pressure vs Raman shift plot. This subtle transition in the wolframite phase is interpreted as the wolframite lattice 12/a taking on the C2/c symmetry of $HgWO_4$.

The authors show in the case of sheelite $CdMoO_4$, the sheelite to wolframite transition near 12 GPa. Near 25 GPa, $CdMoO_4$ exhibits another transition similar to that observed in $CdWO_4$.

Based on the above results, the authors suggest that the picture for the high pressure transition sequence in $A^{2+}B^{2+}O_4$ compounds is sheelite to wolframite or wolframite-like phase and then to a phase with truly octahedrally coordinated BO_6 units.

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