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 gasketed 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 hysteretic.

Identifying the highest wave number peak with $v_1$ 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 $v_1$ mode of the octahedral WO$_6$ in Ba$_2$CaWO$_6$, 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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