Raman spectroscopic studies on CeVO₄ at high pressures

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Abstract. Raman spectroscopic studies of zircon CeVO₄ is carried out at high pressures up to 13 GPa. Further pressurization leads to vanishing of Raman intensity. Changes in the Raman spectra across the zircon to monoclinic transition are reported. In addition, evolution of Raman spectra of the recovered monazite phase is reported.

1. Introduction

Rare-earth orthovanadates (ReVO₄) crystallize in zircon structure at ambient conditions [1] and follow a sequence of phase transitions from zircon → scheelite → fergusonite as a function of pressure in general [2,3]. Unlike the other members of this series, zircon CeVO₄ (which has a larger cationic radius) follows a different sequence of transitions from zircon → monazite → scheelite under pressure [4]. Apart from basic research interest in systematics of phase transitions, orthovanadates are technologically important as thermo-phosphors, scintillators, in photocatalysis and in lithium batteries. Though there are many structural and spectroscopic studies [2,3] on general high pressure behavior of orthovanadates, the trend in CeVO₄ is unusual. Recently XRD and Raman spectroscopic investigations have been reported in CeVO₄ at high pressure across the zircon to monazite transition [5,6]. Here we report Raman scattering investigations of zircon as well as recovered monazite phases CeVO₄ at high pressures. In addition, results of non-hydrostatic experiments which produced scheelite phase are also reported. Raman spectra of various phases of CeVO₄ are compared with that of other ReVO₄.

2. Experimental Details

Polycrystalline CeVO₄ was prepared by solid state reaction of CeO₂ and V₂O₅ and characterized by powder XRD [1]. High pressure Raman spectroscopic measurements were carried out as per experimental details given in reference [2].

3. Results and Discussion

3.1 High pressure behaviour of the zircon phase

In the ambient zircon phase, (space group I₄₁/amd, Z = 4), of the 33 expected modes, group theory predicts 12 distinct Raman active modes $2A_{1g}+4B_{1g}+B_{2g}+5E_g$. Raman spectra of CeVO₄ agrees with that reported [7]. Figure 1 shows Raman spectra of CeVO₄ compared with that of typical ReVO₄ like LuVO₄ in the zircon phase. In the spectra of CeVO₄, the strongest mode at 860 cm⁻¹ is the symmetric stretching mode ($v₁$) of $A_{1g}$ symmetry which is much lower than the symmetric stretching frequency (899 cm⁻¹) in LuVO₄ because of the larger ionic radius (114.3 pm) of Ce³⁺ as compared to that of Lu³⁺ (97.7 pm) resulting in reduced cation potential in the case of CeVO₄. The other two modes in CeVO₄ at 797 and 785 cm⁻¹ are the asymmetric stretching modes ($v₃$) of symmetry $E_g$ and $B_{1g}$ respectively. The V-O bending modes appear in the range 250-500 cm⁻¹. The mode at 376 cm⁻¹ is the symmetric bending ($v₂$) mode of $A_{1g}$ symmetry and that at 466 cm⁻¹ is the asymmetric bending mode.
(ν₄) of B₁₈ symmetry; the other asymmetric bending mode of E₈ symmetry could not be detected. The mode at 263 cm⁻¹ is the B₂g mode due to symmetric bending of the VO₄ tetrahedra. The external modes due to Ce-VO₄ vibrations appear at frequencies below 250 cm⁻¹.

Figure 1 shows the Raman spectra of CeVO₄ in comparison with that of LuVO₄. With increase in pressure, all the modes except the B₂g mode at 263 cm⁻¹ increase in frequency. At around 4 GPa, abrupt changes in the Raman spectra are observed; around the same pressure as the observed zircon to monazite transition by XRD measurements [4]. Discontinuities in mode frequencies and appearance of new modes indicate first order nature of the transition. Softening of the B₂g mode in CeVO₄ is similar to that of B₁₈ mode seen in other vanadates also across the zircon to scheelite transition [2,3]. Co-existence of the two phases was found in a small pressure range 3.9 to 4.9 GPa. While the bending mode region shows a different set of modes, there is a small discontinuity in the stretching mode frequency. Overall there is a marked increase in the number of modes consistent with the transition to a low symmetry phase. Figure 2 shows the evolution of Raman spectra of CeVO₄ with pressure and the pressure dependence of mode frequencies. The Raman spectra were recorded up to 13 GPa beyond which all the peaks were very weak and only the symmetric stretching mode could be followed. The sample became dark and the signal became poor beyond 13 GPa probably due to transition involving reduction in bandgap. It may be noted that NdVO₄ which also follows the trend of CeVO₄; undergoes zircon to monazite transition [8] followed by transition to scheelite phase involving discontinuous decrease in bandgap across the transitions. A similar effect like band gap reduction is expected in CeVO₄ also which could be the reason for loss of intensity of the Raman modes.

When the pressure is released, CeVO₄ remains in the high pressure monazite phase. In vanadates like TbVO₄, DyVO₄ Elliott et al [9] have identified the softening of B₂g and B₁₈ modes to a distortion of the primitive cell along [110] or [100] directions, respectively. The softening of the B₂g mode could be indicative of similar structural distortion in the system leading to monazite phase.

3.2 High pressure behaviour of the monazite phase

Figure 3 shows the evolution of Raman spectra of the pressure quenched CeVO₄ which is in monazite phase at ambient conditions. It may be noted that one of the modes exhibits further softening with pressure. As in the previous case, complete loss of Raman intensity was observed above 13 GPa.
Figure 2(a) and (b)  Raman spectra of CeVO$_4$ at various pressures showing the changes across the zircon to monazite transition. (c) Pressure dependence of mode frequencies. Arrow indicates the zircon to monazite transition pressure. Solid lines denote the linear fit of the data within a phase. Only the prominent mode frequencies in the high pressure phase are plotted.

Figure 3. Pressure evolution of monazite phase of CeVO$_4$. Arrow mark indicates continuous softening of a mode in the monazite phase

3.3 Non-hydrostatic experiments

In order to recover other phases, non-hydrostatic pressure was generated in a diamond anvil cell without any pressure transmitting medium. Pressurising to 8 GPa without any pressure transmitting medium resulted in a mixture of zircon and scheelite phase as discussed in reference [5]. Figure 4 shows the Raman spectra of CeVO$_4$ in the three phases along with that of scheelite LuVO$_4$ for comparison. Though the zircon CeVO$_4$ stretching frequencies are very much different from that of LuVO$_4$, in the scheelite interestingly, the V-O stretching frequencies are nearly same. This indicates the interatomic bond strength is similar in spite of larger ionic radius of Ce$^{3+}$ which implies that the
scheelite phase of CeVO$_4$ has shorter V-O bonds compared to that of LuVO$_4$. While the V-O interaction strength in zircon phase in CeVO$_4$ is less than that of LuVO$_4$, it is same in the scheelite phase in CeVO$_4$ and LuVO$_4$. Panchal et al in their calculations of band structure have shown that bandgap depends on the V-O distances in this class of orthovanadates [8]. It would be possible to estimate the band gap using V-O stretching frequency. It appears that CeVO$_4$ which has the lowest bandgap in the zircon phase among the orthovanadates, undergoes transitions involving discontinuous decrease in bandgap similar to NdVO$_4$, resulting in loss of Raman intensity above 13 GPa. In analogy with NdVO$_4$, the loss intensity above 13 GPa could be due to a phase transition.

![Figure 4. Raman spectra of CeVO$_4$ in zircon, monazite and scheelite phases. Arrow mark indicates the symmetric stretching mode in scheelite CeVO$_4$.](image)

4. Conclusion

Raman spectroscopic studies have been carried out on zircon phase and monazite phases of CeVO$_4$ at high pressures up to 13 GPa beyond which there is a loss of Raman intensity. Raman spectra of CeVO$_4$ in various phases is compared with other ReVO$_4$.

5. References

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