High Pressure phase transitions in $NdVO_4$

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Abstract : Raman-scattering measurements on $NdVO_4$ suggest a pressure-induced zircon to monazite phase transition beyond 5.9 GPa. The monazite phase undergoes a second phase transition to a yet unknown phase at 18.1 GPa. Lattice-dynamics calculations well support the experimental findings and predict a possible orthorhombic structure for the post-monazite structure of $NdVO_4$.

Keywords : Phase transition, High pressure, Raman scattering
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INTRODUCTION

AVO_4 (with a trivalent cation) vanadates mostly crystallizes in a tetragonal zircon-type structure (space group: $I4_1/amd$, Z = 2)[1]. They are technologically important materials with applications as cathodoluminescent, scintillators, photocalysis, and thermophosphors materials as well as in lithium ion batteries[2,3].

$NdVO_4$ crystallizes in the zircon structure which can be view as alternating edge-sharing NdO_8 dodecahedra and VO_4 tetrahedra forming chains parallel to the *c*-axis. Among zircon structured orthovanadates, most of them undergo zircon to scheelite and then consequently to fergusonite phase transitions.[4] However, compounds like $CeVO_4$ undergo zircon to monazite phase transitions[5]. Similarly x-ray diffraction studies in phosphates, viz. YPO_4 and $ErPO_4$, report a zircon to monazite phase transition[6]. In the present investigation we present Raman scattering measurements and *ab initio* lattice-dynamics calculations in $NdVO_4$ up to 30.8 GPa.

EXPERIMENT

$NdVO_4$ was loaded in a pre-indented inconel gasket with a 150-μm diameter hole inside a diamond-anvil cell. A 16:3:1 methanol-ethanol-water mixture was used as pressure medium. Pressure was determined using ruby fluorescence.[7] HP Raman measurements were performed in the backscattering geometry using a 632.8 nm HeNe laser and a Horiba Jobin Yvon LabRAM HR UV microspectrometer in combination with a thermoelectric-cooled multichannel CCD detector with spectral resolution below 2 cm^{-1}.

RESULT & DISCUSSION

For the zircon structure group theory predicts 12 Raman-active modes at the center of the BZ with symmetries $\Gamma = 2A_{1g} + 4B_{1g} + B_{2g} + 5E_g$.[8]. Raman spectra of $NdVO_4$ in zircon phase at various pressures are shown in **Figure 1.** 11 Raman modes are clearly discernable at ambient conditions out of the 12 predicted Raman modes. The

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symmetry assignment for the Raman modes has been performed in accordance with our lattice dynamics calculations. The external $T(E_g)$ mode at 113 cm^{-1} shows a very small pressure coefficient and the internal $\nu_2(B_{2g})$ mode at 260 cm^{-1} has a negative pressure coefficient.

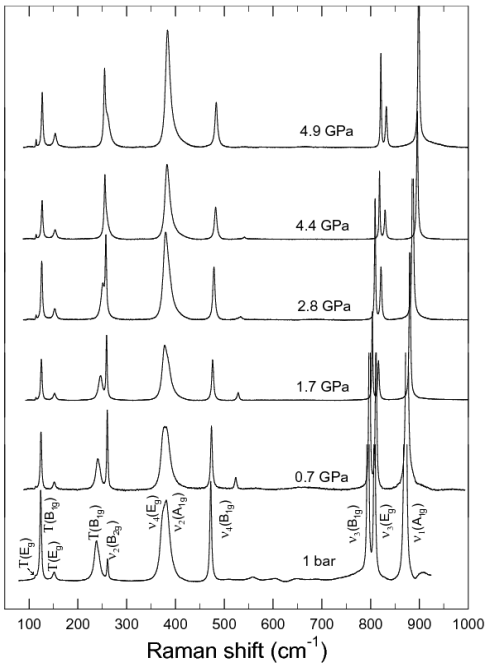

FIGURE 1. Raman spectra of $NdVO_4$ in the zircon phase till 4.9 GPa

Figure 2 shows the Raman spectra of $NdVO_4$ in the monazite phase at few representative pressures. It can be seen that at 5.9 GPa we have observed noticeable changes in the Raman spectrum with emergence of new Raman bands, accompanied by the broadening of many Raman modes. These changes in the Raman spectra are indicative of a structural phase transition towards the lower-symmetry monoclinic monazite phase. This is in quite agreement with our lattice dynamics calculations and recent x-ray diffraction studies.[9] Zircon to monazite phase transitions were also observed in $CeVO_4$[4], $PrVO_4$[10], and phosphates like YPO_4 and $ErPO_4$[5]. We have observed 21 Raman modes at 6.3 GPa out of 36 Raman modes predicted for the monazite phase of $NdVO_4$. Along with these first order Raman modes few second order Raman modes were also recorded. They are marked by asterisks in **Figure 2.** The mode assignment of the observed Raman modes of monazite $NdVO_4$ was done by comparing the experimental and calculated values of mode frequencies and pressure coefficients. As can be seen from **Figure 2**, the monazite phase happened to continue till 18.1 GPa.

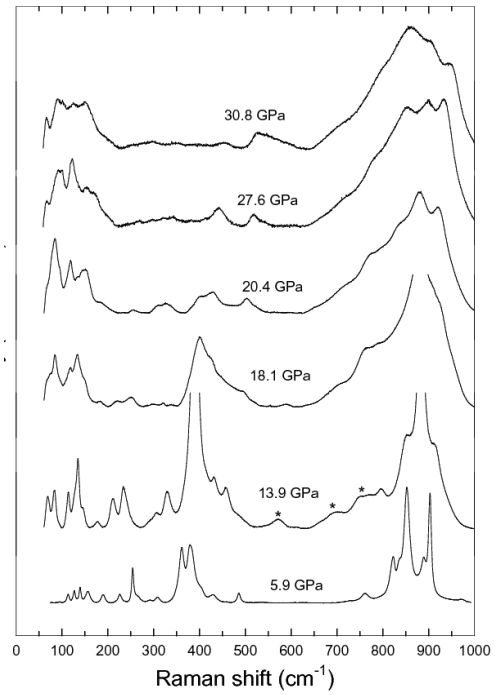

FIGURE 2. Raman spectra of $NdVO_4$ in monazite and new HP phase.

Beyond this pressure we have observed subtle changes in the Raman spectra of $NdVO_4$ with the appearance of new Raman bands in the 600-700 cm^{-1} frequency region along with the weakening of several Raman bands assigned to the monazite phase. Our lattice dynamics calculations suggest the possible occurrence of a new phase transition in $NdVO_4$ around this pressure. The post-monazite structure is proposed to have an orthorhombic structure as observed in related compounds[11,12]. However, the undoubtedly identification of the crystal structure of the new post-monazite phase is awaiting the confirmation of XRD experiments.

CONCLUSION

Our experimental Raman scattering, and theoretical lattice dynamics investigation of $NdVO_4$ up to 30.8 GPa respectively suggests that the low-pressure zircon phase undergo an irreversible zircon-to-monazite transition at 5.9 GPa. The symmetries of the Raman modes zircon

and monazite phases of $NdVO_4$ have been assigned in accordance with our lattice dynamics calculations. Beyond 18.1 GPa $NdVO_4$ is observed to undergo second phase transition. Our calculations predict the new phase of $NdVO_4$ to have an orthorhombic structure.

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