

# High pressure behavior of $\alpha$ - $\text{NaVO}_3$ : A Raman scattering study

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Received 23 March 2007; received in revised form 10 July 2007; accepted 23 July 2007

Available online 10 August 2007

## Abstract

The reported pressure-induced amorphization in  $\alpha$ - $\text{NaVO}_3$  has been re-investigated using Raman spectroscopy. Discontinuous changes are noted in the Raman spectrum above 5.6 GPa implying large structural changes across the transition. The decrease in frequency of the V–O stretching mode across the transition suggests that the vanadium atom may be in octahedral coordination in the high pressure phase. Excessive broadening of the internal modes is observed above 6 GPa. New peaks characteristic of a crystalline phase gain in intensity at higher pressures in the bending modes region; however, the transformation is not complete even at 13 GPa. Co-existence of phases is noted over a significant pressure range above the onset of transition. Pressure released spectrum is found to be a mixture of crystalline  $\alpha$ -phase, traces of crystalline  $\beta$ -phase and highly disordered phase consisting of V–O units in five- and six-fold coordination.

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**Keywords:** Raman spectroscopy; High pressure; Phase transition;  $\text{NaVO}_3$

## 1. Introduction

Vanadium exists in different oxidation states in different compounds. The interesting physical properties of the various vanadium oxides depend on the electronic structure, and in turn, on the valence state of the vanadium in the compound [1]. Consequently they find wide range of applications covering catalysis, gas sensors, phosphors, switching devices, [1,2] and also in rechargeable batteries [3]. Vanadium oxide-based compounds show rich variety of phenomena. Owing to the strong electron correlation, the  $\beta$ -vanadium bronzes have shown many interesting behavior such as charge ordering [4], pressure-induced superconductivity [5], etc. Orthovanadates of the type  $\text{M}_3(\text{VO}_4)_2$  (M: Ca, Sr, Ba) have excellent luminescence properties which are enhanced when doped with suitable rare-earth element, and find application as laser host materials [6]. Metavanadates of type  $\text{AVO}_3$  (A: Li, Na, K, Rb, Cs,  $\text{NH}_4$ ) have been reported to show ferroelectric and pyroelectric properties [7]. Basic research on the stability and phase

transition behavior of these compounds has led to high temperature–high pressure synthesis of novel phases [8,9]. Studies on the high pressure behavior of alkali metavanadates have shown that  $\text{KVO}_3$ ,  $\text{RbVO}_3$  [10] and  $\text{CsVO}_3$  [11] exhibit structural transitions at moderate pressure of 5–10 GPa. The observed trend in transition pressure was understood on the basis of cation sizes. All these compounds consist of corner-sharing  $\text{VO}_4$  tetrahedra forming infinite chains of  $(\text{VO}_4)^{3-}$ . Interestingly,  $\alpha$ - $\text{NaVO}_3$  was reported to exhibit pressure-induced amorphization (PIA) at around 6 GPa [12,13], while the structurally related compound  $\text{LiVO}_3$  showed a series of structural transitions, with no PIA during compression upto 20 GPa [14].

Compared to other metavanadates, high pressure behavior of  $\text{NaVO}_3$  appears to be complex. There exists another polymorph,  $\beta$ - $\text{NaVO}_3$ , which transforms irreversibly to the  $\alpha$ -form at temperature above 405 °C [15]. Structural similarities and differences of the two polymorphs may be briefly summarized as follows.  $\alpha$ - $\text{NaVO}_3$  crystallizes in a monoclinic structure (Cc) and is ferroelectric at ambient conditions [16,17].  $\beta$ - $\text{NaVO}_3$  is orthorhombic (Pnma) at ambient conditions and is made up of

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infinite double chains parallel to the *b*-axis [18]. The two polymorphs have comparable volumes at ambient conditions; the volume per formula unit is  $69.7 \text{ \AA}^3$  for  $\alpha\text{-NaVO}_3$  [13], and  $69.18 \text{ \AA}^3$  for  $\beta\text{-NaVO}_3$  [19]. The main difference between the two is that in  $\alpha\text{-NaVO}_3$  the vanadium atom has four-fold coordination while in  $\beta\text{-NaVO}_3$ , it has five-fold oxygen coordination. High pressure behavior of both the polymorphs has been investigated using spectroscopic techniques [12,19].  $\alpha\text{-NaVO}_3$  has been reported to exhibit two transitions at pressures around 4.3 and 6 GPa. Based on the excessive broadening and weakening of the Raman bands, it was concluded that the new high pressure phase above 6 GPa is an amorphous phase [12]. Amorphization was found to be irreversible from pressures of about 17 GPa and recrystallization of  $\alpha$ -phase was reported upon heating the recovered amorphous sample [20]. Subsequent high pressure mid-infrared measurements suggested that the phase above 6 GPa could be a disordered phase where the vanadium atoms may have higher coordination [21]. On the other hand, spectroscopic studies on  $\beta\text{-NaVO}_3$  up to 16.6 GPa indicated three phase transitions at pressures 1.4, 4.4 and 8.0 GPa, with no signatures of any disorder in the high pressure phases [19]. Very different high pressure behavior of the two polymorphs leads to several questions such as what exactly is driving PIA in  $\alpha\text{-NaVO}_3$ . PIA is generally understood as arising due to kinetic hindrance of equilibrium transitions [22]. In this context, it would be of interest to know what is the stable high pressure crystalline form of  $\text{NaVO}_3$ . The present work is aimed at understanding the nature of high pressure phases in  $\alpha\text{-NaVO}_3$ , both the intermediate crystalline phase (4.3–6.0 GPa) and the subsequent amorphous phase, as reported in the earlier work [13], in relation to the behavior observed in other alkali meta vanadates.

## 2. Experimental details

Single crystals of  $\alpha\text{-NaVO}_3$  were grown by slow cooling the melt of  $\text{Na}_2\text{CO}_3$  and  $\text{V}_2\text{O}_5$  from  $630^\circ\text{C}$  at the rate of  $1^\circ\text{C/h}$  in a platinum crucible. Crystals were plate-like yellowish brown in color. Raman scattering measurements at high pressure were carried out using a diamond anvil cell (DAC), Diacell Products, UK, Model B-05 with octagonal diamonds  $400 \mu\text{m}$  diameter culet. A 4:1 methanol-ethanol mixture was used as pressure transmitting medium. Pressure inside the cell was measured using the standard ruby fluorescence technique. Raman spectrum of unoriented single crystal bits of  $\text{NaVO}_3$  from inside the DAC was excited using 532 nm line of power  $\sim 15 \text{ mW}$ . Scattered light was analyzed using a home built 0.9 m single monochromator, coupled with a super notch filter and detected by a cooled CCD (Andor Technology). Entrance slit was kept at  $50 \mu\text{m}$ , which gives a spectral band pass of  $3 \text{ cm}^{-1}$ .

## 3. Results

At ambient conditions,  $\alpha\text{-NaVO}_3$  exists in a non-centrosymmetric [15] structure with four formula units

per unit cell. Factor group analysis predicts 57 optic branches whereas only 22 distinct Raman modes have been experimentally observed [12]. The Raman spectrum of  $\alpha\text{-NaVO}_3$  at ambient conditions in the present studies agrees well with that reported [12,15]. Six lattice modes appear in the spectral range  $60\text{--}150 \text{ cm}^{-1}$ . Based on the comparison of the spectrum of crystalline compound and that of the aqueous solution, the Raman bands in the spectral range  $200\text{--}380 \text{ cm}^{-1}$  were identified to be due to  $\text{VO}_2$  rocking, twisting and chain deformation vibrations [15]. In the present studies, all the Raman modes appearing at frequencies above  $90 \text{ cm}^{-1}$  could be followed as a function of pressure. Fig. 1 shows the Raman spectra of  $\alpha\text{-NaVO}_3$  at various pressures. Frequencies of all the Raman modes increase monotonically with increasing pressure upto 5.6 GPa. Fig. 2 shows the pressure dependence of mode frequencies in  $\alpha\text{-NaVO}_3$ . The  $225 \text{ cm}^{-1}$  mode appears as a single broad band up to about 2.5 GPa, beyond which the second component at higher frequency separates out. Similar behavior is noted for the Raman band at  $256 \text{ cm}^{-1}$  above 3 GPa. It may be mentioned that in some of the crystal orientations, the broad band at  $225 \text{ cm}^{-1}$  (typical width of about  $20 \text{ cm}^{-1}$ ) appears clearly as two modes centered around  $222$  and  $231 \text{ cm}^{-1}$ , of width

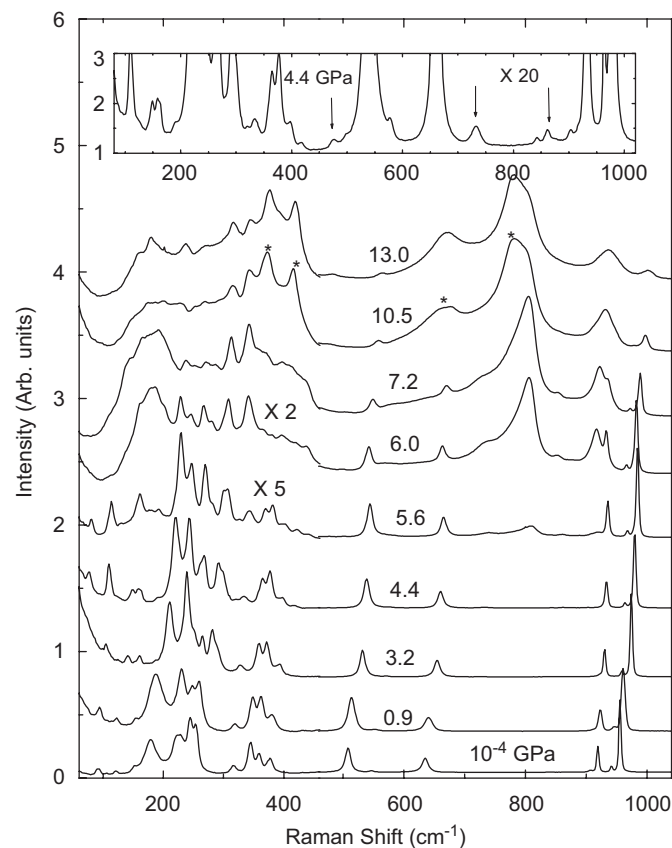


Fig. 1. Raman spectra of  $\alpha\text{-NaVO}_3$  at different pressures. Spectrum in the range  $60\text{--}460 \text{ cm}^{-1}$  have a scale factor of 5 up to 5.6 GPa, and a factor of 2 thereafter. Inset shows the appearance of weak peaks above 4.4 GPa indicated by arrows. \*Indicates the modes that increase in intensity above 9 GPa.

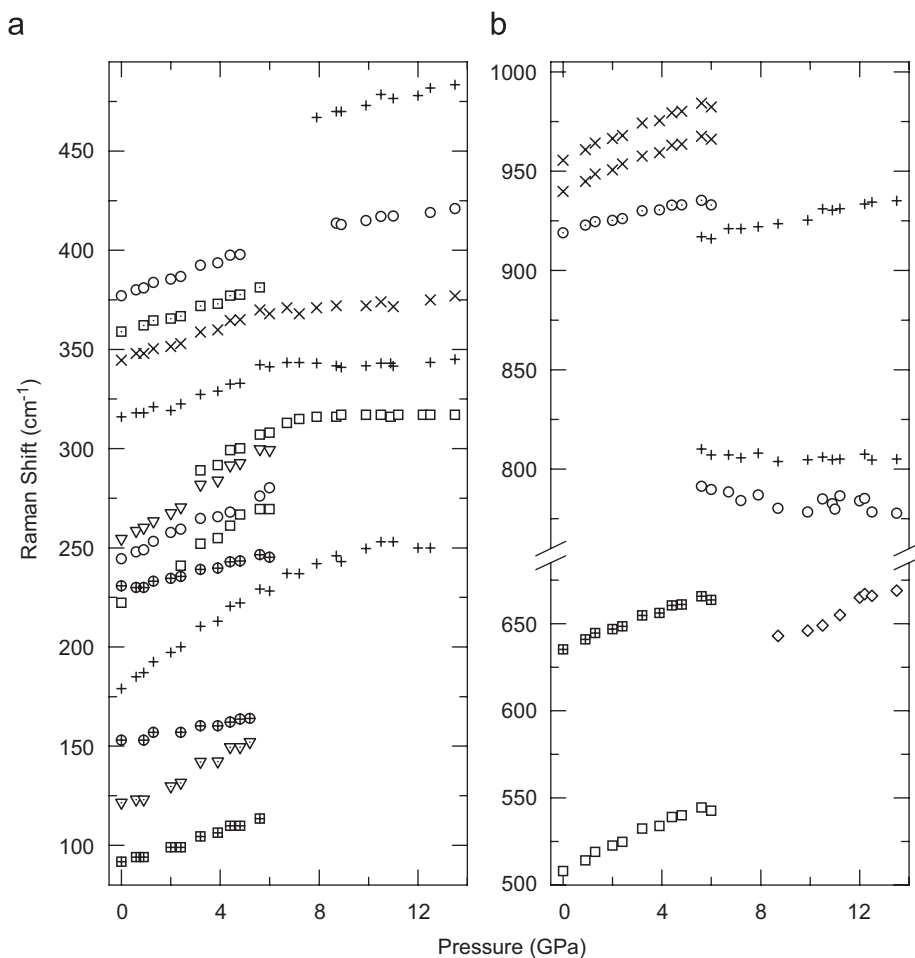


Fig. 2. (a, b) Pressure dependencies of mode frequencies in  $\alpha$ - $\text{NaVO}_3$ . Note that the two modes around  $800\text{ cm}^{-1}$  have a weak negative pressure dependency in the  $\gamma$ -phase.

$20$  and  $11\text{ cm}^{-1}$ , respectively, even at ambient conditions. Raman measurements in higher alkali vanadates by Adams and Fletcher [10] had shown more number of bands in this spectral range at low temperatures, partly due to line narrowing of the otherwise broad Raman bands. Appearance of new modes in the pressure range  $2.5$ – $3.5$  GPa (Fig. 2) is understood as due to gradual separation of the overlapping modes owing to different pressure dependencies. Line width of the  $179\text{ cm}^{-1}$  mode gradually decreases from  $\sim 22\text{ cm}^{-1}$  at ambient pressure to  $11\text{ cm}^{-1}$  at  $3.2$  GPa, accompanied by an increase in intensity.

Around  $4.0$  GPa, new peaks of rather weak intensity appear at frequencies around  $475$ ,  $497$ ,  $730$ , and  $862\text{ cm}^{-1}$ . Inset in Fig. 1 shows the new modes that appear around  $4$  GPa. Earlier high pressure Raman studies [13] had reported subtle spectroscopic changes around  $4$  GPa, relating to intensities and pressure dependence of mode frequencies, as well as appearance of new weak bands. This was attributed to a first order phase transition. However, mid-infrared studies at high pressure, did not find any noticeable spectral changes around this pressure [21]. In the present work also, no significant changes are noted in the pressure dependence of mode frequencies. Relative inten-

sities of the modes in chain deformation region ( $350$ – $420\text{ cm}^{-1}$ ) are noted to gradually change and above  $3.9$  GPa, the mode at  $377\text{ cm}^{-1}$  appears with strongest intensity among the set of four bands. It may be mentioned that in some of the high pressure runs, the band at  $345\text{ cm}^{-1}$  appears with a lesser intensity compared to that at  $360\text{ cm}^{-1}$  even at ambient conditions. Further decrease in intensity of the other three modes around  $3.9$  GPa results in only one of the mode in this region to be observed at higher pressures. It is difficult to comment whether these changes in relative intensities and increased separation of some of the overlapping modes are due to any phase transition, as these are rather gradual changes and appear over a range of pressure, from  $2.5$  to  $3.9$  GPa. Intensities of these new weak peaks (inset in Fig. 1) do not show increase upon further pressurization. Possible origin of these peaks will be discussed in the subsequent section.

Above  $5.6$  GPa, the Raman spectrum shows abrupt changes. The sharp intense bands around  $955$ ,  $920$ ,  $635$ , and  $508\text{ cm}^{-1}$  arising from the symmetric and antisymmetric stretching vibrations of V–O and V–O–V, respectively, show rapid decrease in intensity along with the appearance of new intense, broad bands around  $917$ ,  $810$

and  $791\text{ cm}^{-1}$ . The latter two are found to be broad, of width 20 and  $40\text{ cm}^{-1}$ , respectively, compared to those in  $\alpha$ -phase (typically  $\sim 5\text{ cm}^{-1}$ ) in this region. Intensity of these modes grows at the expense of those of the  $\alpha$ -phase bands suggesting nucleation and growth of a new phase, say  $\gamma$ , at this pressure. In the chain deformation mode region also, a new set of Raman modes appear (Fig. 1) riding over a broad background centered around  $300\text{ cm}^{-1}$ . At pressures typically about 7 GPa, the band at  $807\text{ cm}^{-1}$  appears as the strongest mode. Some of the strong Raman bands characteristic of the  $\alpha$ -phase could be detected with a weak intensity up to the highest pressure reached in the present investigations suggesting a rather sluggish nature of the transition. From the Raman spectra obtained from spatially different region of the sample, the set of bands corresponding to the  $\gamma$ -phase could be clearly differentiated from the bands of  $\alpha$ -phase. Pressure dependencies of only the  $\gamma$ -phase modes are shown beyond 5.6 GPa in Fig. 2. Besides the new set of modes, pressure dependencies of many bands show considerable decrease in the  $\gamma$ -phase. The excessive broadening of the stretching modes and increased background in the chain deformation mode region suggest that the new high pressure phase is disordered, which could be partly due to the sluggish nature of the  $\alpha$ - $\gamma$  transition. Well-defined lattice modes could not be observed beyond 6 GPa.

In the  $\gamma$ -phase, the mode at  $810\text{ cm}^{-1}$  has two components; both of them show weak decrease in frequency with further increase in pressure indicative of a gradual increase in V–O bond length evolving towards increasing V–O coordination. Above 9 GPa, a broad band centered around  $645\text{ cm}^{-1}$  and the shoulder at  $790\text{ cm}^{-1}$  gains in intensity. Raman bands in the chain deformation mode region ( $300$ – $450\text{ cm}^{-1}$ ) also appear with better intensity above this pressure. All these changes are found to be reversible with large hysteresis. Fig. 3 shows the Raman spectra of the compound in the pressure reducing cycle. The changes observed above 9 GPa, namely improved intensities of the V–O–V stretching and deformation modes, persist down to about 5.5 GPa, below which these bands reduce in intensity. Spectrum resembles that of the disordered  $\gamma$ -phase down to about 3.4 GPa. Below this pressure, a broad peak at around  $850\text{ cm}^{-1}$ , noted as a shoulder towards the higher frequency side of the V–O stretching band at  $820\text{ cm}^{-1}$ , gains in intensity. Around 2 GPa, the strongest Raman bands characteristic of the  $\alpha$ -phase start gaining in intensity, however, a few other bands such as the one around  $865$  and  $720\text{ cm}^{-1}$  (Fig. 3) also appear which neither belong to  $\alpha$ - $\text{NaVO}_3$  nor the high pressure  $\gamma$ -phase. Intensity of this broad feature is much reduced when the pressure is completely released. Raman spectrum of the pressure-released sample predominantly has the characteristic lines of  $\alpha$ -phase along with a few new modes, marked by arrows in Fig. 3. It is noted that the Raman intensities of the pressure-cycled sample are very much reduced when compared to that of the starting phase.

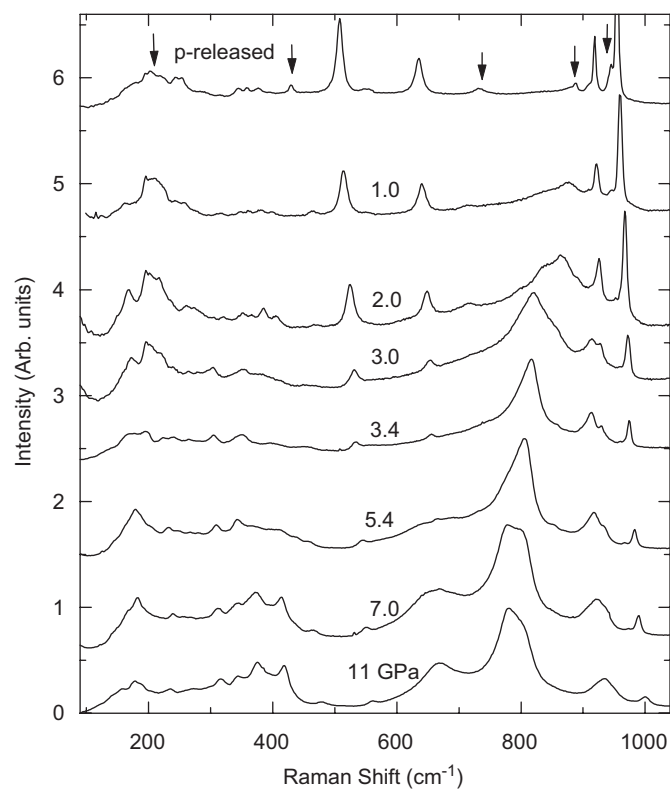


Fig. 3. Raman spectra of  $\text{NaVO}_3$  in the pressure reducing cycle. Arrows indicate the peaks identified to be due to  $\beta$ - $\text{NaVO}_3$ .

#### 4. Discussion

The spectral changes observed in  $\alpha$ - $\text{NaVO}_3$  around 6 GPa in the present work, by and large, agree well with that reported by Shen et al. [20]. It remains to be understood whether there is any intermediate structural transition around 4 GPa, as concluded by Shen et al. [13]. As mentioned earlier, appearance of weak peaks around  $475$ ,  $735$  and  $862\text{ cm}^{-1}$ , along with changes in intensities of some of the low frequency modes was taken as an indication for a phase transition. Appearance of new modes across a phase transition results either from correlation splitting or due to lowering of symmetry. In particular, loss of inversion symmetry leads to the infrared active modes becoming Raman active in the new phase, and such modes have poor Raman intensities. However,  $\alpha$ - $\text{NaVO}_3$  does not have inversion even at ambient conditions, hence such a possibility is ruled out. On close comparison of the frequencies of the new modes with those reported in  $\beta$ - $\text{NaVO}_3$ , these are identified as the strong Raman bands of  $\beta$ - $\text{NaVO}_3$  [19]. It is known that in  $\beta$ - $\text{NaVO}_3$ , vanadium atom has five-fold oxygen coordination forming a distorted trigonal bipyramid [18]; hence a  $\beta$ - $\text{NaVO}_3$  type of phase may be expected prior to transformation to a six-fold coordinated phase. However it is important to note that in the present studies, the intensities of these new modes do not grow upon further pressurization implying that it is not due to an equilibrium phase transition. Considering the fact that there is

nucleation and growth of  $\gamma$ -phase around 5.6 GPa, formation of traces of five-fold coordinated crystalline phase at a slightly lower pressure is not unexpected. There are a number of tetrahedrally coordinated framework structures such as  $\text{SiO}_2$  [23]; many of the tungstates and molybdates [24], which are reported to exhibit PIA due to highly, impeded transition to an octahedrally coordinated structure. Experimental studies of the evolution of local structure [25,26] as well as simulation studies [27,28] have shown that the intermediate disordered phase is often a mixture of four-fold (ambient), five-fold (intermediate) and six-fold (stable high pressure phase) coordinated. Hence, appearance of new modes of rather weak intensities around 4 GPa is quite possibly due to formation of a small fraction of  $\beta$ - $\text{NaVO}_3$  as an impurity phase prior to transformation to  $\gamma$ -phase. In the present studies, though the typical evolution of Raman spectrum was as described earlier, larger intensity of the  $\beta$ -phase was observed from some parts of the sample around 4 GPa in a few runs. Fig. 4 shows the typical (curve a) and  $\beta$ -rich spectrum (curve b) at 4.5 GPa. This  $\beta$ -rich region of the sample continued to show sharp crystalline lines, agreeing with the reported high pressure behavior of the  $\beta$ - $\text{NaVO}_3$  [19]. Pressure dependence of these ‘impurity’ phase modes are not shown in Fig. 2. These bands continue to be observed in the spectrum of the pressure-cycled sample also. It may be mentioned that Shen et al. [20] have also observed the spectral features of  $\beta$ - $\text{NaVO}_3$  along with those of the  $\alpha$ -phase upon heating the quenched high pressure phase.

The other aspect to be understood is the nature of  $\gamma$ -phase. Rapid decrease in intensity of the  $984\text{ cm}^{-1}$  mode, that is typical of  $\text{V}=\text{O}$ , and appearance of the  $810\text{ cm}^{-1}$  characteristic of the  $\text{V}-\text{O}$  stretching vibration strongly suggest that the transition involves increase in vanadium coordination to six-fold across the transition. In many vanadium oxide-based compounds that are made up of tetrahedral  $\text{VO}_4$  units, transformation to an octahedrally

coordinated phase at high pressure is noted to be highly impeded often resulting in an amorphous phase [29]. Spectroscopic studies of  $\text{CsVO}_3$  at high pressure have shown evidence for partial disorder in the chain structure [11]. Disordered nature of  $\gamma$ -phase could be due to the sluggish nature of transition, and partly due to co-existence of different phases. In the present studies, it is noted that new Raman bands in the range  $350\text{--}450\text{ cm}^{-1}$  corresponding to chain deformation vibrations, gradually gain in intensity in the high pressure phase suggesting a tendency towards evolving into a more ordered structure. In the lattice modes region, the peak noted around  $180\text{ cm}^{-1}$  at 13 GPa (Fig. 1) is most likely from  $\beta$ -phase as discussed earlier. Another broad shoulder is noted at a lower frequency ( $160\text{ cm}^{-1}$  at 13 GPa) that is indeed a new feature; however, it is difficult to unambiguously assign it as the lattice mode of the new high pressure phase from the present results.

Further, increase in intensity of the  $\text{V}-\text{O}-\text{V}$  band (around  $645\text{ cm}^{-1}$ ) above 9.5 GPa indicate that the  $\text{V}-\text{O}-\text{V}$  linkages persist in the  $\gamma$ -phase. Shen et al. [20] have suggested that the chain structure could be broken in the high pressure phase. While the four-fold coordination of the vanadium atom in  $\alpha$ - $\text{NaVO}_3$  may be described as chains of the corner-shared  $\text{VO}_4$  tetrahedra, arrangements of structural units in five- and six-fold coordinated structures are different, often consisting of corner- as well as edge-shared polyhedral units. Such a transition may not necessarily involve breaking of chains. For example, heating the pressure amorphized  $\text{Ca}_3(\text{VO}_4)_2$  found to result in a crystalline monoclinic phase having three dimensional network structure unlike the parent phase [8]. Some other compounds such as  $\text{NaV}_2\text{O}_5$  [30],  $\text{CaV}_2\text{O}_5$  [31], etc., that has corner- and edge-sharing  $\text{VO}_5$  units at ambient conditions, also show a tendency for transformation to a structure of higher coordination at comparable pressures. In the case of  $\text{NaV}_2\text{O}_5$ , this transformation is understood

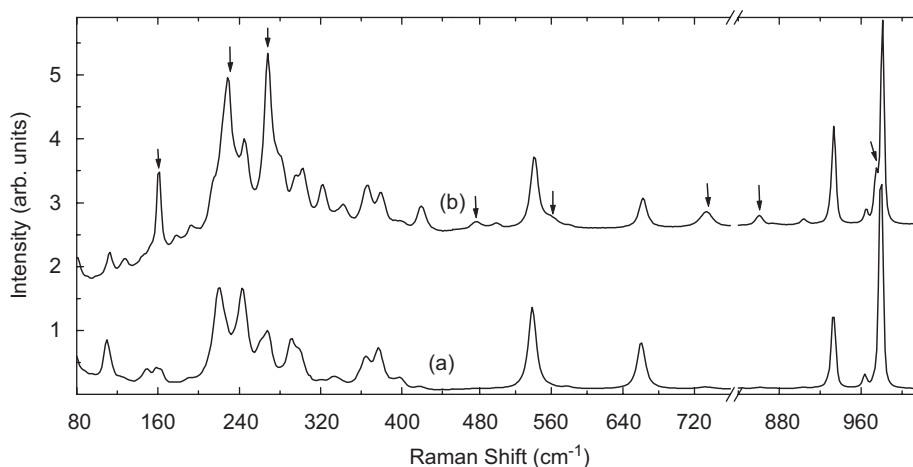


Fig. 4. Raman spectra of  $\text{NaVO}_3$  at 4.5 GPa in different regions of the sample. The peaks marked by arrows in (b) are the intense lines (phase III) of  $\beta$ - $\text{NaVO}_3$  (see Fig. 1 in Ref. [18]). Such a spatial inhomogeneity is noted only at high pressures, above 3.5 GPa. A larger fraction of  $\beta$ - $\text{NaVO}_3$  is recognized by the doublet structure of the  $981\text{ cm}^{-1}$  mode and a strong lattice mode at around  $160\text{ cm}^{-1}$ . These  $\beta$ - $\text{NaVO}_3$  modes continue to be present in the disordered  $\gamma$ -phase.

to be associated with the two dimensional chain structures becoming a three dimensional network structure [30]. Considering the trend in the high pressure behavior of other vanadates along with the present results which show evidence for the presence of V–O–V linkages, the  $\gamma$ -phase appears to have corner-linked structure in such a way as to achieve six-fold vanadium coordination, rather than breaking of the chain structure.

The high pressure behavior of  $\alpha$ - $\text{NaVO}_3$  may be compared with that of the other alkali metavanadates. In the case of  $\text{LiVO}_3$ , the first transition is reported to be around 3.5 GPa, across which the intensity of the  $980\text{ cm}^{-1}$  mode, characteristic of the  $\text{V}=\text{O}$  stretching decreases substantially in intensity and a new mode at around  $750\text{ cm}^{-1}$  appears as the strongest band [14] in the subsequent high pressure phases. Qualitative changes across this transition are very similar to those noted in the  $\alpha$ - $\text{NaVO}_3$  around 5.6 GPa in the present studies. The main difference is that while the  $\gamma$ -phase of  $\text{NaVO}_3$  is disordered,  $\text{LiVO}_3$  has sharp crystalline peaks in the high pressure phases suggesting the structural transition is far less hindered in the latter. Shen et al. [14] have attributed this difference to the smaller size of the alkali metal atom. Similarity of the behavior in the pressure reducing cycle is also striking, with the high pressure phase in  $\text{LiVO}_3$  persisting down to about 3 GPa and absence of any detectable Raman intensity upon pressure releasing [14]. Amorphization up on pressure releasing is known in some silicate perovskites [32] and is understood as the instability of the high pressure crystalline structure at ambient conditions combined with a large barrier for the reverse transformation.  $\text{KVO}_3$  and  $\text{RbVO}_3$  [10] are also reported to show only one transition at 5.6 and 5.3 GPa, respectively, not much of details are known about the spectral changes across these transitions.  $\text{CsVO}_3$  shows a different trend in the high pressure behavior, namely the Raman band characteristic of the  $\text{V}=\text{O}$  persists in all the high pressure phases [11] implying that in this compound, it is possible to transform in to more compact high pressure phases by suitable reorientation and repacking of the chain structure. Interestingly, high pressure behavior of  $\beta$ - $\text{NaVO}_3$  bears similarities with that of  $\text{CsVO}_3$  with the  $\text{V}=\text{O}$  band persisting in the high pressure phases [18] implying the basic chain structure is retained across the phase transitions. It may be noted that the compounds  $\text{KVO}_3$ ,  $\text{RbVO}_3$ ,  $\text{CsVO}_3$  and  $\beta$ - $\text{NaVO}_3$  crystallize in an orthorhombic structure while  $\text{LiVO}_3$  and  $\alpha$ - $\text{NaVO}_3$  crystallize in a monoclinic phase, and it would be interesting to study if there is a definite correlation between the high pressure behavior and the structure at ambient conditions.

## 5. Conclusion

High pressure Raman spectroscopic studies on  $\alpha$ - $\text{NaVO}_3$  have been carried out upto 13 GPa. Spectral changes at pressures around 4 GPa appear to be due to formation of

traces of  $\beta$ - $\text{NaVO}_3$ . Above 5.6 GPa, it transforms to a new phase  $\gamma$  and the spectral changes across the transition suggest that vanadium is in octahedral coordination in the  $\gamma$ -phase. The transition is noted to be sluggish with co-existence of phases observed over a large pressure range. Excessive broadening of the internal modes and absence of sharp lattice modes indicate that the  $\gamma$ -phase is highly disordered.

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