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Abstract. In an earlier study, we showed that α-NaVO$_3$ undergoes a crystalline–amorphous phase transition at ~60 kbar. Below the amorphization pressure, some spectral changes were observed in the Raman spectra, but due to the polycrystalline nature of the samples used in these experiments, these changes were not clearly demonstrated. Here we report on high-pressure studies of α-NaVO$_3$ using single-crystal samples in the pressure range below 60 kbar. A first-order crystalline–crystalline phase transition occurred at 43 kbar. The transition was marked by the appearance of new Raman bands in both the internal and external vibrational regions, and the single-crystal sample shattered after the transition. Continuous spectral changes were observed for the Raman bands associated with the rocking, wagging and twisting motions preceding the transition.

1. Introduction

Sodium metavanadate (α) belongs to the pyroxene family, having infinite linear VO$_3^-$ chains formed by VO$_4$ tetrahedra sharing two corners with each other. It is ferroelectric under ambient conditions, and becomes paraelectric above 380 °C with a slight change in crystal structure. The crystal structures of α-NaVO$_3$ have been studied by x-ray diffraction techniques [3–7]. Marumo *et al* [3] studied the ambient condition phase, and they proposed a monoclinic structure of space group $C2/c$, with $Z = 4$. The samples they used were synthesized from a 1:1 mixture of Na$_2$CO$_3$ and V$_2$O$_5$ by the Bridgman method, and the crystals obtained were colourless and transparent. By slow cooling of the melt from 630 °C at the rate of 1 °C h^{-1} in a platinum crucible, Shaikh *et al* [4, 5] obtained plate like, yellowish brown α-NaVO$_3$ crystals. Their results showed that the ferroelectric low-temperature structure is monoclinic of space group C_c (C_s^4) with $a = 10.557$ Å, $b = 9.469$ Å, $c = 5.880$ Å, $\beta = 108.43°$ and $V = 557.653$ Å^3. There is no drastic structural change in the ferroelectric–paraelectric transition. The structure remains monoclinic but with space group $C2/c$ in the high-temperature paraelectric phase. The ambient condition structure may be described as being constructed from eight Na$^+$ ions and four different V$_2$O$_6$ chains (see figure 1). Both Na$^+$ and V$_2$O$_6$ chains occupy sites of C$_1$ symmetry. The V–O bond lengths along the chains involving the O atoms, O(3) and O(3^{iv}), which are shared by two neighbouring V atoms, are much longer than those involving the unshared O atoms, O(1) and O(2). The bond lengths of V–O(1) and V–O(2) are slightly different and can be attributed to the difference between the valency sums for O(1) and O(2) atoms. There are two types of Na atom in the unit cell, Na(1) and Na(2), each surrounded by six O atoms. The coordination around Na(2) is nearly octahedral, while the O atoms are arranged rather irregularly around Na(1). The mean Na(1)–O distance of 2.51 Å is somewhat longer than
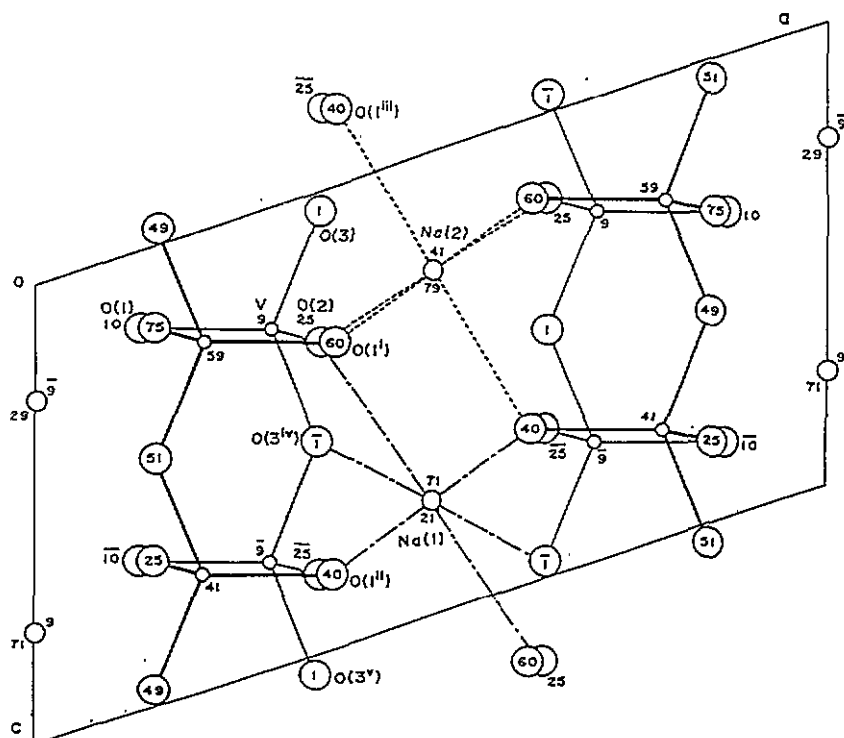
Figure 1. The crystal structure of α-NaVO$_3$, viewed along the b axis. The positions of atoms from the ac plane are indicated as percentages of the b length (after [3]).

the mean Na(2)–O distances of 2.36 Å. The interatomic distances and bond angles were reported by Marumo *et al* [3].

NaVO$_3$ has been also studied by other techniques [6–11], including Raman spectroscopic studies [9, 10]. We have studied α-NaVO$_3$ in powder form under pressure up to 168 kbar [1, 2]. A crystalline–amorphous phase transition was found at about 60 kbar, which is the lowest pressure for such transitions in ionic crystals. This phase transition was marked by a sudden appearance of very broad bands at the 800 cm^{-1} and 350 cm^{-1} regions, indicative of an amorphous phase. The amorphization involves the complete breaking up of the infinite chains of corner linked tetrahedral VO$_4$, most likely into VO$_3$. Below the crystalline–amorphous phase transition pressure, there are some subtle but definite spectral changes, but the powder samples used resulted in broader peaks with less well defined polarizations. A detailed study of these changes was not possible as a result. Thus, to investigate more closely the behaviour of α-NaVO$_3$ below the amorphization phase transition, we use single-crystal samples of α-NaVO$_3$ in this work.

2. Experimental details

The α-NaVO$_3$ single-crystal samples, yellowish brown in colour, were prepared from the powder form of the β-phase (Merck, 99%) by heating to 700 °C. The β-NaVO$_3$ transforms to α-NaVO$_3$ irreversibly at 405 °C, and the melt was allowed to crystallize by cooling at a rate of 3 °C h^{-1} to room temperature. The Raman spectra taken for the crystals obtained confirm
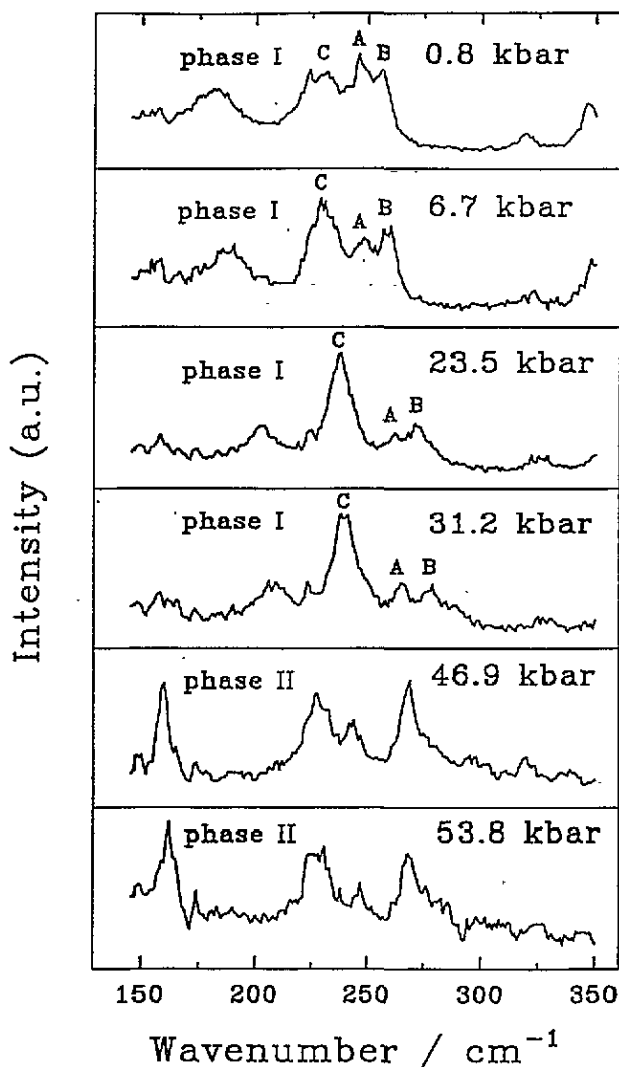
Figure 2. Raman spectra in the chain deformation region showing continuous changes preceding the I–II phase transition at 43 kbar.

that the β–α transformation was complete and only the α-form was present. High pressure was generated by a gasketed diamond anvil cell. The stainless steel gaskets used are 200 μm in thickness with a hole of 200 μm in diameter. The gaskets were predented before samples were loaded. A small sample and a ruby chip were loaded into the gasket hole together with a 4:1 mixture of methanol: ethanol, which acts as quasi-hydrostatic pressure transmitting medium. The pressure was calibrated by the ruby fluorescence technique [12]. Raman spectra were recorded in the backscattering geometry using a Spex double monochromator coupled to a conventional photon counting system. The 514.5 nm line of a Spectra-Physics Ar⁺ ion laser was used as the excitation source and the power at the sample was estimated to be below 250 mW. All high-pressure spectra were taken at room temperature.

The samples chosen were thin enough that they would not be crushed by the diamond

windows under high pressure. The use of a single crystal also allowed us to examine the sample optically using a polarizing microscope.

3. Results and discussion

The Raman bands observed at ambient pressure are listed in table 1, and the assignment of the peaks follows those of Seetharaman *et al* [10] and Adams and Fletcher [13]. The bands in the 200 cm^{-1} region (associated with chain deformation and the VO$_2$ rock, wag and twist motion) show the greatest changes below 40 kbar. This is indicated by the two bands initially at 246.6 cm^{-1} (band A) and 256 cm^{-1} (band B) shown in figure 2. As the pressure is increased, the intensities of these two bands show distinct changes. We started with the intensity of band A being higher than that of band B but very soon, at 6.7 kbar, there is an interchange and this change is maintained until 31.2 kbar. At this pressure, band A shows a comeback and is then of the same intensity as band B. It was also observed that band C at ~230 cm^{-1} has become much stronger as compared to the other bands in this region.

Table 1. The observed Raman bands and their assignments and pressure dependences in the α-phase.

Frequency (cm^{-1})	Assignment	$d\omega/dp$ (cm^{-1} kbar^{-1})	$[1/(d\omega/\omega)dp] \times 100$ (kbar^{-1})
61.5(m)			
69.9(w)			
88.1(m)	lattice		
92.3(m)	modes		
104.0(w)			
119.4(w)			
150.5(w)		0.17	0.11
179.4(m)	δVOV, ρ_r, ρ_t,	0.86	0.48
225.0(m)	ρ_w and chain	0.29	0.13
244.1(m)	deformations	0.59	0.24
253.1(sh)		0.79	0.31
316.6(w)		0.27	0.09
344.8(m)	δVO$_2$	0.38	0.11
358.5(w)		0.37	0.10
376.4(w)		0.47	0.12
507.9(s)	symmetric	0.66	0.13
547.2(w)	ν VOV	0.47	0.09
634.2(s)	antisymmetric ν VOV	0.53	0.08
905.6(w)	antisymmetric	0.45	0.05
917.8(s)	ν VOV	0.30	0.03
940.4(m)	symmetric	0.48	0.05
955.1(vs)	ν VO$_2$	0.51	0.05

The percentage frequency increments for these bands are larger than those for most of the other bands. Since the 200 cm^{-1} region is related to the chain deformation and VO$_2$ rocking motions, the drastic spectral changes in this region are an indication that the VO$_4$ chains are being severely distorted under pressure. Given the fact that the Raman
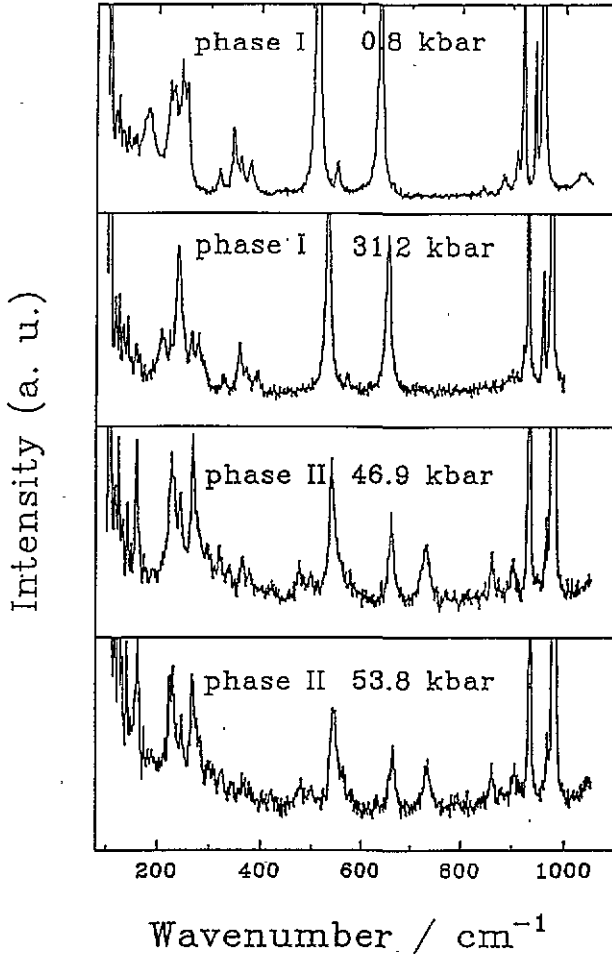
Figure 3. Representative high-pressure Raman spectra in different phases.

bands related to the bond vibrations at higher frequencies do not change much except that expected slight percentage frequency increase under compression, our result shows that the distortion of the chains should mainly involve bond angle changes and the relative motion of chains but no major changes in the bond lengths. This agrees well with the result on NH_4VO_3, which suggested that the initial increase in pressure has a direct effect on the O–V–O bonding angles in the chain [14].

Above 43 kbar, a set of new peaks appears, particularly at 474.4 cm^{-1}, 499.4 cm^{-1} and 730.3 cm^{-1} as shown in figure 3. Also, the peak at ∼980 cm^{-1} shows a splitting to give rise to two peaks, one at 974.3 cm^{-1} and the other at 980.7 cm^{-1}. At this pressure, the single crystal sample broke into a few pieces. All these observations indicate that there is a first-order phase transition and that the crystal has undergone a change in its crystal structure. The appearance of new peaks suggest that the high-pressure structure is of a lower symmetry. There is also a distinct change of the bands in the 200 cm^{-1} region (figure 2) and possibly a completely new set of bands exists after the phase transition as the intensities of these bands show vivid changes. In addition to this, a new band appears in the lattice
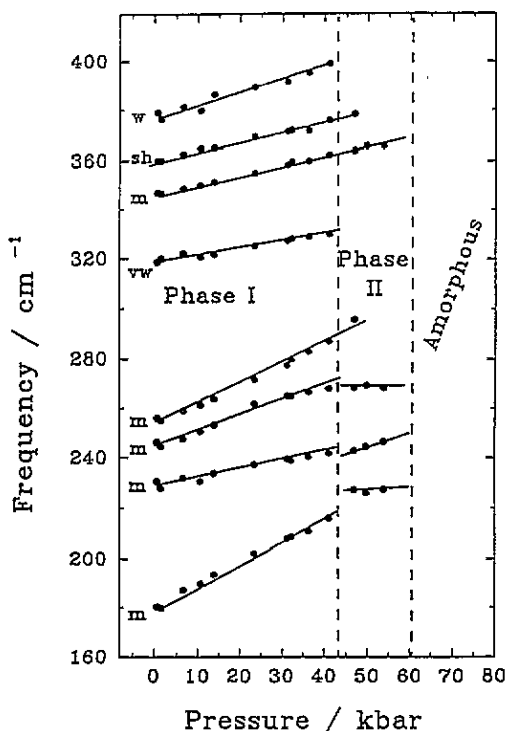
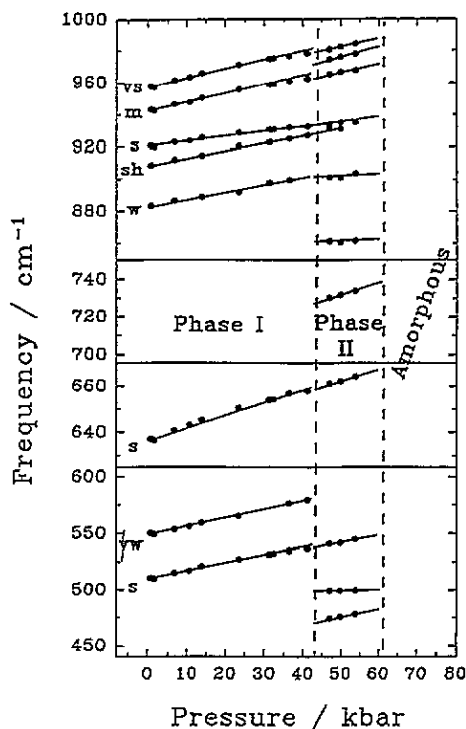Figure 4. The Raman frequency changes with pressure for this bands below 400 cm^{-1}.

Figure 5. The Raman frequency changes with pressure for the VOV and VO$_2$ stretch modes.

region at 159.5 cm^{-1}.

From the frequency against pressure graphs (figures 4 and 5), it is seen that there is a discontinuity in the frequency increase for most of the bands at 43 kbar, especially for the bands at lower frequencies. The slopes for the frequency increments for these bands are also observed to have changed after the phase transition.

In studying the thermal expansion behaviour of framework crystals, Megaw [15] and Taylor [16] have demonstrated that the relative tilting of the neighbouring tetrahedra or octahedra has a pronounced effect during temperature change, and can be the dominant contribution to the dimensional change. In our low-temperature studies of NaVO$_3$ and LiVO$_3$ [17], the main spectral changes also occur in the same spectral region, in agreement with Megaw and Taylor, and with the high-pressure result. The similar results for the high-pressure and low-temperature variations are not surprising since increasing pressure is generally analogous to decreasing temperature. Cartz and Jorgensen [18] have performed high-pressure time of flight neutron diffraction experiments on some network crystals. Their results show that the compressibility behaviour of such crystals depends markedly on their atomic structural arrangement. For flexible type framework structures, such as quartz, bond angle changes dominate the overall behaviour under moderate pressure. Incidentally, quartz also undergoes a pressure induced phase transition and has been studied intensively because of its physical and geophysical implications [19–21].

The experiment was terminated at 60 kbar just below the crystal–amorphous transition. This is because the sample became polycrystalline above 43 kbar and the results at higher pressure would repeat those of [1] and [2].

4. Conclusions

A first-order crystalline–crystalline phase transition was observed for α-NaVO$_3$ at 43 kbar. This phase transition was marked by the appearance of new peaks in the Raman spectra and the breaking up of the crystal into smaller pieces when observed under the microscope. There are also observed changes in the slopes of the frequency–pressure plots before and after the phase transition. The phase transition is preceded by gradual changes in the V–O–V bond angles as indicated by the spectral changes for the bands in the spectral region associated with the rocking, wagging and torsional vibrational modes. It has been proposed that pressure induced amorphization occurs in steps in quartz and it seems that the same mechanism is also true for α-NaVO$_3$. Thus this phase transition is the first step of change before the phase transition to an amorphous state at about 60 kbar.

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