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Brief Reports

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Spectroscopic evidence of pressure-induced amorphization in α-NaVO$_3$

Z. X. Shen, C. W. Ong, S. H. Tang, and M. H. Kuok
Department of Physics, National University of Singapore, Lower Kent Ridge Road, Republic of Singapore 0511

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Raman spectra of α-NaVO$_3$ were recorded under pressures up to 170 kbar at room temperature. A crystalline-amorphous phase transition was found at ~61 kbar, much lower than the pressures of other ionic materials. This transition is marked by the sudden appearance of very broad bands at the 800- and 350-cm^{-1} regions. The amorphization involves the complete breaking up of the infinite chains of corner-linked tetrahedral VO$_4$, most likely into VO$_3^-$. On decompression, the amorphous phase transforms to another phase, probably also amorphous at ~40 kbar. It reverts to the stable ambient-condition α phase upon heating.

Pressure-induced amorphization has been the subject of intense study for the past few years because of its importance in materials science and solid state physics. A number of ionic crystals, including SiO$_2$,[1-4] CaAl$_2$Si$_2$O$_8$,[5] AlPO$_4$,[6] Ca(OH)$_2$,[7] and LiKSO$_4$,[8] have been found to undergo crystalline-amorphous transitions.

The structures of alkali metavanadates are unusual in that they have infinite VO$_3^-$ chains formed by VO$_4$ tetrahedra sharing corners. In this respect, they are similar to the better known and well studied materials, the silicates, which also have chain structures and are the best examples of amorphous materials. It is therefore interesting to see if the metavanadates become amorphous under pressure. High-pressure studies of many of these samples have been performed and they all undergo phase transitions up to about 100 kbar.[9-11] Disordered or partially disordered high-pressure phases have also been reported for NH$_4$VO$_3$ (Ref. 9) and CsVO$_3$.[10] Adams, Haines, and Leonard[9] have studied NH$_4$VO$_3$ to 106 kbar using Fourier transform infrared (FTIR) techniques and to 65 kbar by synchrotron x-ray powder diffraction. They suggest that the disordered phase above 49 kbar may be an amorphous phase, mainly based on the broadening of some of the IR bands. But their IR bands at low pressure are also quite broad. Kourouklis *et al.*[10] recorded Raman spectra up to 150 kbar and found phase transitions at 100, 115, and 130 kbar. They have concluded that the chain structure above 130 kbar is partially disordered. No high-pressure work appears to have been reported for NaVO$_3$.

NaVO$_3$ (α form) is ferroelectric below 380 °C and has the monoclinic space group C_c with the VO$_3^-$ chains parallel to the c axis. It is isostructural with the diopsides, CaMg(SiO$_3$)$_2$. NaVO$_3$ exists in another polymorphic form (β phase, $Pnma$, $Z=4$) which transforms irreversibly to the α phase at 405 °C.

α-NaVO$_3$ were prepared from the powder form of β phase (Merck, 99%) by heating to 450 °C. The Raman spectrum taken after heating confirms that the β to α transformation is complete. High pressure was generated by a gasketed diamond anvil cell, with 4:1 mixture of methanol-ethanol as pressure transmitting medium. 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 an Ar$^+$ laser was used as the excitation source and the power at sample was estimated to be below 250 mW. All spectra were taken at room temperature.

The ambient pressure Raman bands are listed in Table I. The grouping of these bands is from the work of Refs. 13 and 14. Our data agree well with the single-crystal work by Seetharaman, Bhat, and Narayanan.[13] The Raman spectra at different pressures are shown in Fig. 1. The spectra at 0 and 55 kbar are similar, apart from the gradual spectral change in the region around 200 cm^{-1} (Fig. 2) and the additional weak peak at 735 cm^{-1} above 35 kbar. Dramatic spectral changes occur at 61 kbar. A very strong and broad peak appears at 807 cm^{-1}, together with a weak shoulder at 779 cm^{-1}. There is also a new peak at 917.7 cm^{-1} and it is broader than the other peaks in this region. There are two new very broad peaks in the low-frequency region underneath the sharp bands, one extending from 430 to 200 cm^{-1} and the other below 200 cm^{-1}.

We interpret the results as follows: The 200-cm^{-1} region is associated with the chain deformation and the VO$_2$ rock, wag, and twist motions, which shows the greatest change below 60 kbar. The bands in other re-

TABLE I. Observed Raman frequencies, their assignments, and pressure dependencies in α phase.

Frequency (cm^{-1})	Assignment (Refs. 13 and 14)	$d\omega/dp$ (cm^{-1}/kbar)	$d\omega/dp\omega$ (10^{-2} kbar^{-1})
61.5(*m*)	Lattice modes		
69.9(*w*)			
88.1(*m*)			
92.3(*m*)			
104.0(*w*)			
119.4(*w*)			
150.5(*w*)	VO$_2$,ρ_r,ρ_t,ρ_w and chain deformations	0.17	0.11
179.4(*m*)		0.84	0.47
225.0(*m*)		0.33	0.15
244.1(*m*)		0.43	0.17
253.1(*sh*)		0.88	0.35
316.6(*w*)		0.37	0.12
344.8(*m*)		0.43	0.12
358.5(*w*)		0.37	0.10
376.4(*w*)		0.54	0.14
507.9(*s*)	δVO$_2$	0.59	0.12
547.2(*w*)	νV-O-V		
634.2(*s*)		0.50	0.08
905.6(*w*)	νVO$_2$ antisymmetric		
917.8(*s*)		0.28	0.03
940.4(*m*)	νVO$_2$ symmetric	0.46	0.05
955.1(*vs*)		0.49	0.05

gions, especially that involving the chain exterior, δVO$_2$, which should be sensitive to the repacking of the lattice or the change of cation coordination number, essentially do not change except for the expected frequency increase on compression. The main effect of pressure therefore is on the O-V-O bridging angles and the V-O bridging bonds. The large percentage frequency increase with pressure for some of the corresponding bands also indicates major changes involving these motions (Table I). Above 60 kbar, the chains have been deformed so much that it is no longer energetically favorable to have infinite chains. This is evident from the appearance of the broad bands at 61 kbar. We speculate the strong peak at 807 cm^{-1} as due to individual VO$_3^-$ ions rather than broken chains formed by several VO$_3^-$ ions. Aqueous solutions of metavanades have been shown to have infinite VO$_3^-$ chains[13,15] or form (VO$_3$)$_n^{n-}$ ions.[16] In neither case do they have strong bands at the 800-cm^{-1} region. The strongest peak is always above 900 cm^{-1}. The broad band at 917 cm^{-1} is therefore assigned to the skeleton vibrations of the broken chains. We assign the weak shoulder at the lower side of the 800-cm^{-1} band to the ν_3 asymmetric vibration of the VO$_3^-$ ion and the very broad band at about 300 cm^{-1} to the ν_4 deformation (the 800-cm^{-1} band belongs to the symmetric vibration ν_1). At 61 kbar, therefore, we have a mixture of three phases, the original α phase as indicated by the sharp bands, a phase with broken chains, and another new phase (very probably amorphous) with VO$_3^-$ ions. There is a very broad background at the lattice region below 200 cm^{-1}, which we take as additional indication that the mixed phase is highly disordered.

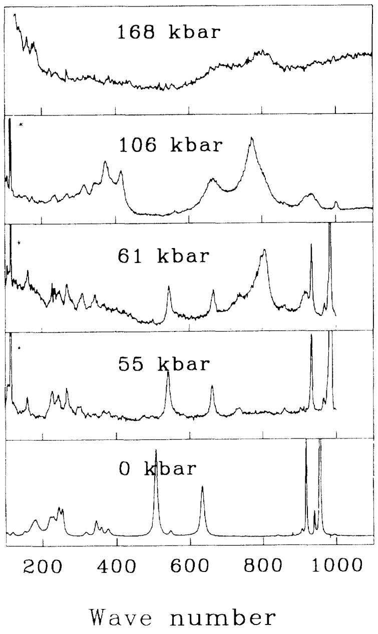

FIG. 1. Raman spectra under high pressure. The spectra at 0 and 55 kbar belong to α phase. A mixture of α and amorphous phases exists at 61 and 106 kbar, and the spectra at 168 kbar is of pure amorphous phase. * denotes plasma line.

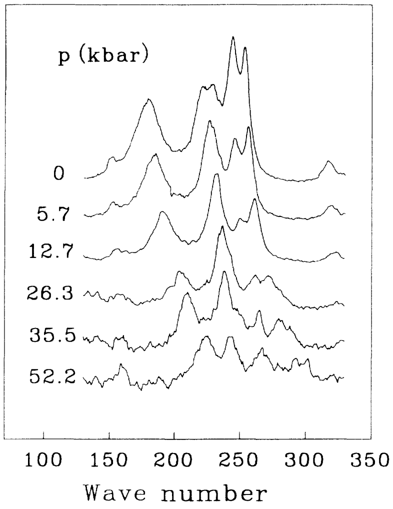

FIG. 2. Raman spectra showing gradual deformation of the VO$_3^-$ chain before the crystalline-amorphous transition.

As the pressure is increased further, the sharp peaks belonging to the α phase decrease and disappear above 135 kbar. At the same pressure the broad peak at 917 cm^{-1} becomes vanishingly small and the overall intensity of the lattice peaks also decreases, implying increased degrees of amorphization. The sample may be completely amorphous with individual VO$_3^-$ ions above 135 kbar.

Detailed analysis of the 800-cm^{-1} region shows that there are several bands overlapping at 61 kbar, but there is only one band at 774 cm^{-1} at 106 kbar. It is reasonable to suggest that the chains of corner-linked tetrahedral VO$_4$ break and become VO$_3^-$ in two steps: First the chains break but with most of the bond angles unchanged, then the O-V-O bond rearrange to form

VO_3^- ions with averaged C_{3v} symmetry. So that just above the crystalline-amorphous transition pressure, the spectra appear more complex.

To further prove that the high-pressure phase is indeed amorphous, we recorded Raman spectra of $NaVO_3$ in the aqueous solution and also melt quenched at different temperatures (Fig. 3 and Table II). Although VO_3^- chains still exist in aqueous solutions,[15] they should be highly disordered in the directions perpendicular to the chains. This is supported by the very broad δVO_2 band at 508 cm^{-1}, which should be very sensitive to the environment since it involves the vibrations of the single bonded oxygen atoms. The spectra of the melt quenched samples resemble that of the α phase but with wider bandwidths. The bands are wider for the sample quenched from higher temperature, confirming that they are somewhat disordered. Table II lists the full width at half maximum (FWHM) for some representative bands in these samples. We clearly see that the FWHM of the high-pressure phase is comparable to that of the δVO_2 in solution but is much larger than all other peaks.

On decompression the spectra are at large reversible down to 40 kbar with some degree of hysteresis (Fig. 4). But the intensities of all the sharp bands in the 400 cm^{-1} region decrease with reducing pressure, reenforcing our claim that they belong to the α phase or the broken chains. It is interesting to note that the broad band in the lattice region below 200 cm^{-1} reappears around 60 kbar and disappears at lower pressure. Below 40 kbar, the frequency of the broad band at 800 cm^{-1} continues to increase with its intensity decreasing quickly. All the broad bands disappeared below 16 kbar. On either pressure quench or slow release, the samples do not go back to the starting α form. At 0 kbar, there is a weak band at 954.5 cm^{-1}, and it can be assigned to the strongest peak of the α form with confidence. But there are three stronger sharp peaks at 160, 173, and 266 cm^{-1}, which do not belong to either the α or β form. Although the α and β forms are the thermodynamically stable phases, the kinetic energy required to reorient and relink the disordered VO_3^- ions into chains of corner-shared VO_4 tetrahedra is too large at room temperature. The sample transforms to an intermediate phase instead. This intermediate phase may also be amorphous as characterized by the gradual weakening of the broad bands. When the amorphous samples were repressurized up to 100 kbar, only a small peak was detected at 800 cm^{-1} above 45 kbar showing the transition is mainly irreversible on compression as well.

It is important to see if the amorphous samples go back to their stable crystalline phases given enough thermal energy. After heating the sample to 330 °C, the α phase

TABLE II. Bandwidths (FWHM) of some representative bands in different physics forms (cm^{-1}).

	VO_2 symmetric	VO_2 antisymmetric	V-O-V	δVO_2
Melt 1[a]	7.3	7.2	12.4	11.7
Melt 2[b]	9.0	9.8	20.8	19.4
α form	5.4	3.0	11.6	9.9
Solution	26.5			53.4
Amorphous[c]	50.8[d]	50.2[e]		

[a] Melt quenched at 750 °C.
[b] Melt quenched at 900 °C.
[c] Measured at 106 kbar.
[d] Symmetric stretch of VO_3^- at 774 cm^{-1}.
[e] Antisymmetric stretch of VO_3^- at 666 cm^{-1}.

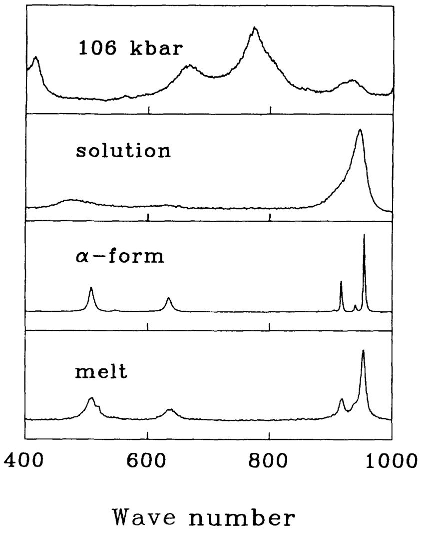

FIG. 3. Comparison of some of the fundamental bands of $NaVO_3$ at different forms. The bandwidths of these bands are listed in Table II. "Melt" indicates melt quenched at 900 °C.

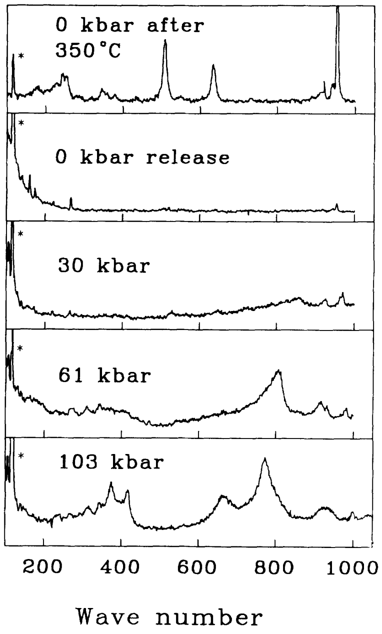

FIG. 4. Raman spectra on decompression. The spectra at 103 and 61 kbar belong to the amorphous phase, and those at 30 and 0 kbar belong to an intermediate phase, probably amorphous as well. The sample reverts back to the α form when heated. * denotes plasma line.

is restored together with a small portion (~5%) of the β phase. In Fig. 4, the scattering of the laser line is much smaller after heating, indicating increased degree of crystallization. We have also used the laser to heat the amorphous samples at ambient pressure and recorded the spectra in the 900-cm^{-1} region which are the V-O vibrational modes of the chains. All the spectra were recorded using 100 mW after they have been subjected to increasing laser power ranging from 100 to 700 mW. Raman peaks appear after the samples are exposed to laser power greater than 200 mW. The Raman bonds get narrower and the frequencies move closer to those of the starting α phase with increasing heating power. They become virtually identical for power higher than 700 mW. This is a clear demonstration of the restoration of the α phase and therefore the relinking of the chains.

It is interesting to note that most materials which undergo crystalline-amorphous transitions have chains formed by corner-linked MO_4 tetrahedra at ambient pressure and room or elevated temperature. It is worthwhile to study other similar materials with corner-linked polyhedra. X-ray diffraction, Raman, and IR spectroscopy are the established techniques in determining pressure-induced amorphous transitions. Raman spectroscopy is more advantageous over IR since it requires less sample preparation and its peaks are usually sharper. We are currently studying NH_4VO_3, and its Raman bands also disappear at about 60 kbar. Therefore NH_4VO_3 may be in a glassy state as well under high pressure like SiO_2, which also has vanishingly weak Raman signals.

We have also studied the β form up to 104 kbar.[17] Two crystalline-amorphous transitions are observed—one at 14 kbar involving major structure changes and another at about 44 kbar with only minor spectral changes. No amorphous phases have been observed.

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