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High-pressure phase transitions and pressure-induced amorphization in $LiVO_3$

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Abstract. Lithium metavanadate ($LiVO_3$) single crystals have been studied by Raman spectroscopy under high pressure up to 200 kbar. Three phase transitions were observed and they are believed to be a series of transitions involving the breaking up of the infinite VO_4^- chains into VO_3^- ions of average symmetry C_{3v}. On decompression, the $LiVO_3$ transforms into an amorphous phase instead of reverting to the ambient crystalline phase, similarly to what has been observed for α-$NaVO_3$. The difference in the behaviours between $LiVO_3$ and α-$NaVO_3$ on compression has been explained by the different sizes of the Li^+ and Na^+ ions. The restoration of the virgin crystalline phase and the relinking of the VO_4^- chains were observed after heating the reclaimed samples.

1. Introduction

Studies of amorphization are currently attracting considerable attention and information on precursor phase transitions is of direct relevance. Metavanadates are important materials for these studies as they are members of the pyroxene family and thus, by implication, such studies may be of geophysical interest. In our early studies [1, 2], it was shown that α-$NaVO_3$ undergoes a crystalline–amorphous phase transition at ~ 60 kbar, which is the lowest amorphization pressure reported for ionic crystals. High-pressure experiments have been performed on many of the metavanadate samples, such as $CsVO_3$, NH_4VO_3, $RbVO_3$, and KVO_3 [3–6]. All these materials undergo phase transitions and some of the high-pressure phases are disordered or partially disordered, but only $NaVO_3$ shows clear evidence of pressure-induced amorphization.

The structure of $LiVO_3$ is similar to that of $NaVO_3$. They are both monoclinic while the structures of most of the other metavanadates are orthorhombic. The structure of $LiVO_3$ has been extensively studied [7–12]. $LiVO_3$ is ferroelectric at room temperature and it transforms to paraelectric at 410 °C [13]. No low-temperature work or high-pressure study has been reported on $LiVO_3$.

2. Experimental details

$LiVO_3$ was prepared by heating the stoichiometric proportions of Li_2CO_3 and V_2O_5 in a ceramic crucible to 800 °C for 1 h after it had been well ground to give a uniform mixture. It was then cooled slowly at a rate of 3 °C h^{-1} to room temperature. The crystals obtained were brownish in colour. Raman spectra recorded for $LiVO_3$ crystals were very different from the starting materials, confirming the reaction was complete.

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A gasketed diamond anvil cell was used to generate the high pressures. The gaskets used were stainless steel of thickness 200 μm with a hole of 200 μm in diameter and were predented before the samples were loaded. A small single-crystal sample and a ruby chip were loaded into a gasket hole together with a 4:1 mixture of methanol:ethanol, which acts as a quasihydrostatic pressure-transmitting medium. The pressure was calibrated by the ruby-fluorescence technique. 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

$LiVO_3$ is monoclinic, of space group $C2/c$ (C_{2h}^6) with the following parameters: $a = 10.158$, $b = 8.4175$, $c = 5.8853$ Å; $\beta = 110.48°$; $V = 471.1$ Å^3, $Z = 8$ [7, 8]. It belongs to the pyroxene family, characterized by infinite VO_3^- chains, formed by VO_4 tetrahedra sharing corners in the c direction. There are two types of Li atom, Li(1) and Li(2). The Li(1) atoms form Li–O edge-sharing chains of octahedra, which also extend in the c direction. The Li(1)–O chains are linked to the VO_3^- chains by sharing corners with the V–O chains. The highly distorted Li(2) sites lie between the octahedral and the tetrahedral chains and provide additional linkage for the two chains.

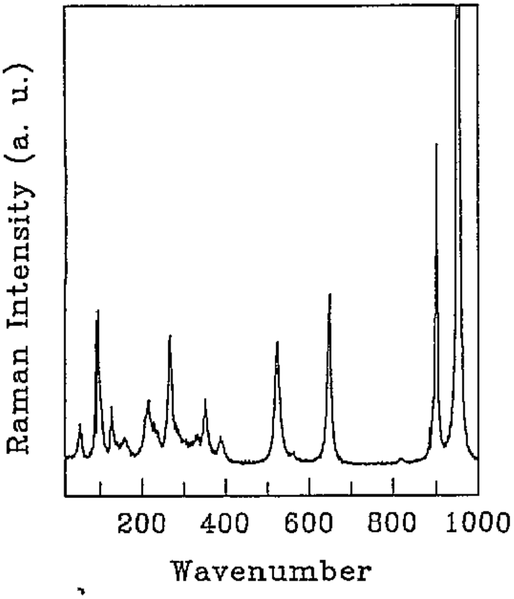

Figure 1. The Raman spectrum of $LiVO_3$ under ambient conditions.

The Raman spectrum of $LiVO_3$ at ambient pressure is shown in figure 1. Like other alkali-metal vanadates, the spectrum consists of some very intense Raman peaks. A total of

Table 1. Observed Raman bands in the ambient-conditions phase, their assignments, and their pressure dependences.

Frequency (cm^{-1})	Intensity	Assignment	$d\omega/dp$ (cm^{-1} $kbar^{-1}$)	$(1/\omega)(d\omega/dp) \times 100$ ($kbar^{-1}$)
54.7	m		−0.17	−0.32
95.8	s		0.3	0.31
102.2	sh	lattice	0.25	0.24
127.5	m	modes	0.35	0.27
160.0	w		0.29	0.18
214.3	m	δVOV	0.52	0.24
231.3	sh	ρ_r, ρ_t, ρ_w and	0.47	0.20
267.3	m	chain deformations	0.15	0.06
301.4	br		1.67	0.55
326.0	w			
352.4	m	δVO_2	0.49	0.14
388.5	m			
524.6	s	VOV	0.64	0.12
559.9	w	stretch		
648.9	s		0.67	0.10
820.6	w	VO_2		
902.4	s	stretch	0.23	0.03
954.0	vs		0.3	0.03

18 bands were observed (see also the spectrum at 0.8 kbar in figure 2) and their frequencies are listed in table 1, together with the assignment and the pressure dependence of the frequencies in the ambient-pressure phase. The assignment and classification of the bands follow that of Seetharaman *et al* [14] for α-$NaVO_3$. The spectrum of $LiVO_3$ clearly resembles that of α-$NaVO_3$ [1], especially in the spectral regions involving the VOV and VO_2 chain-stretching vibrations, reflecting their structural similarity. For example, the four strongest Raman-active bands above 500 cm^{-1} were found at 523.7, 648.3, 901.8, and 953.5 cm^{-1} for $LiVO_3$, while those for $NaVO_3$ were observed at 507.9, 634.2, 917.8, and 955.1 cm^{-1}, with the band of highest frequency being by far the strongest in both cases.

Figure 2 shows the representative high-pressure Raman spectra and the respective phase for pressure up to 197 kbar. When the single-crystal sample is scanned in two perpendicular orientations, the spectra obtained are generally the same but the band at 301 cm^{-1} is much stronger in one direction. This orientation was chosen in order to enhance the broad band at 301 cm^{-1}. The intensities of all bands decrease drastically with increasing pressure. The intensity drop from 0 to 31 kbar is approximately tenfold for the bands due to the V–O–V antisymmetric stretch at $\sim$ 670 cm^{-1} and the VO_3 symmetric stretch at $\sim$ 960 cm^{-1}, indicating the onset of a phase transition.

The band at 54 cm^{-1} is a soft mode. Its frequency decreases continuously with pressure from 54 cm^{-1} at ambient pressure to about 51 cm^{-1} at 31.2 kbar (see table 1 and figure 3). Above this pressure, its intensity becomes too weak to be detected, due to the continued decrease in the intensities mentioned above. The same band also softens at low temperature [15]. All the other bands show the expected frequency increase under compression, with the frequency of the broad band at 301 cm^{-1} increasing abnormally fast.

At $\sim$ 40 kbar, the spectrum shows an abrupt change with an almost completely new set of bands, indicating a first-order phase transition. There are more peaks in this new phase (which we shall call phase II) than in the ambient-pressure phase I, and nearly all the bands

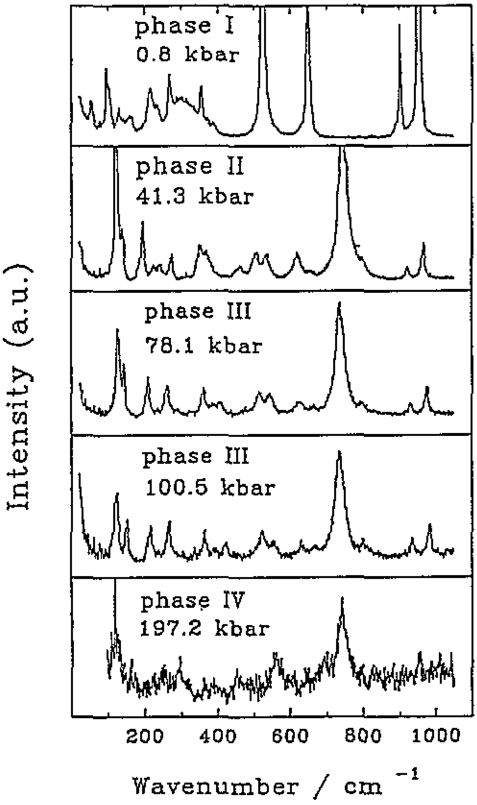

Figure 2. High-pressure Raman spectra of $LiVO_3$ in different phases in sequence of increasing pressure.

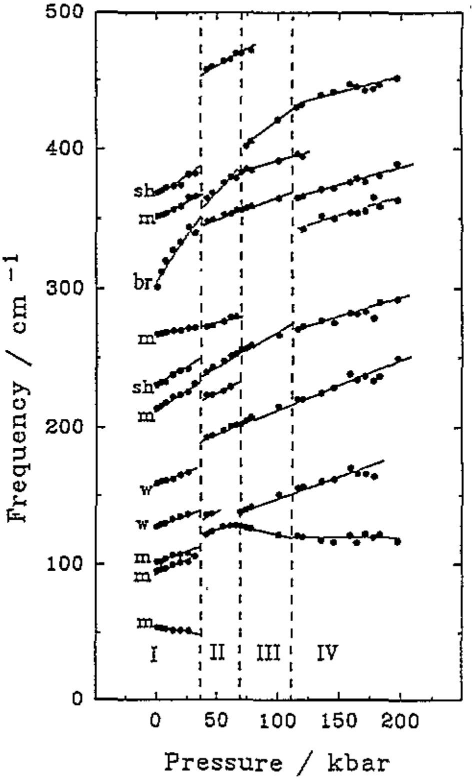

Figure 3. A Raman-frequency-versus-pressure plot for the bands below 500 cm^{-1} in different phases.

show frequency discontinuities at the transition. Under the microscope, the crystal, which was initially transparent in phase I. gradually turned opaque in phase II. The continuous change in the transparency of the crystal agrees well with the incessant decrease in the intensity.

It is noteworthy that a first-order phase transition also occurs for α-$NaVO_3$ at a similar pressure of 43 kbar [16], but the phase transition in α-$NaVO_3$ is preceded by continuous changes of chain-deformation vibrations, probably changes in the V–O–V angles, whereas the transition for $LiVO_3$ is initiated by a soft mode at 54 cm^{-1} and no distinct spectral changes in the chain-deformation region were detected. We suggest that the different mechanisms for the two transitions are due to the different sizes of their cations. The Li^+ ion is much smaller than Na^+, so it should be easier for the V–O chains to rearrange themselves under compression in $LiVO_3$ because of the smaller space the Li^+ ions occupy.

The bands at 797.4 and 732 cm^{-1} are very similar to the strong bands of α-$NaVO_3$ observed in the high-pressure crystalline phase [1,2], and they have been attributed to the breaking of the chains. Thus, we also expect the breaking up of the vanadate chains into possibly VO_3^- for $LiVO_3$ and we assign these two bands as the ν_1 and ν_3 vibrational modes of the VO_3^- ion.

Phase II is likely to be a mixture of a stable phase and a metastable phase as the spectrum shows a continuous change from 41.3 kbar to 70.0 kbar. Initially, there are 17

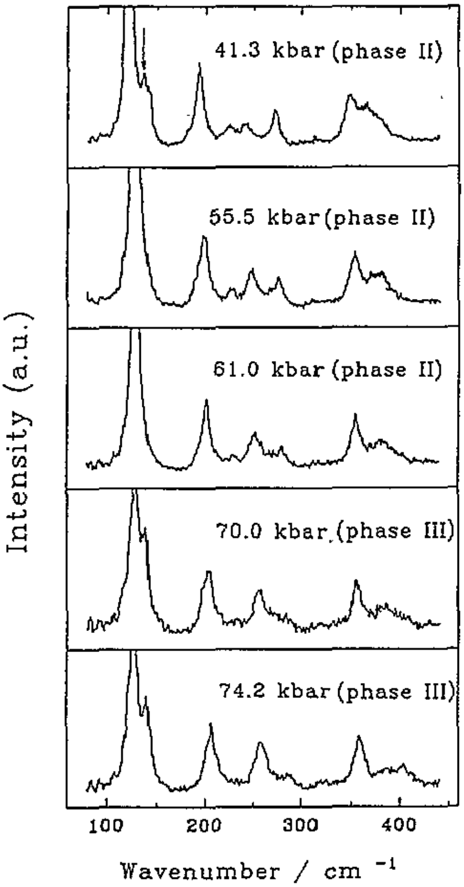

Figure 4. Raman spectra showing the intensity changes of the bands in the 200–300 cm^{-1} region and the splitting of the lattice band at 129 cm^{-1} during the phase II/III transition.

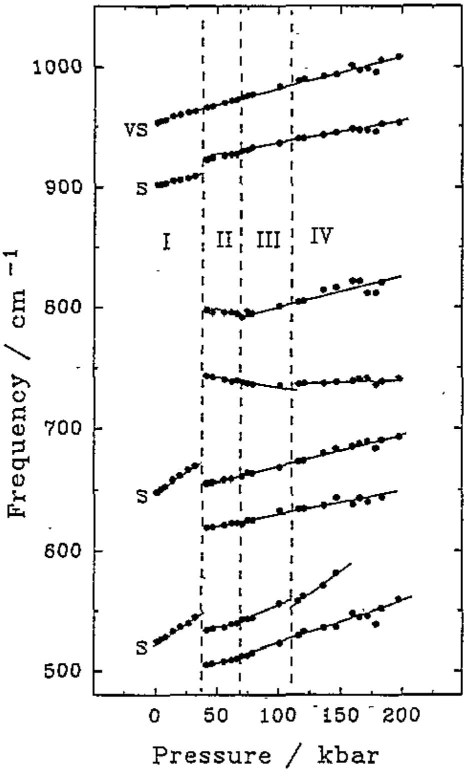

Figure 5. A Raman-freqency-versus-pressure plot for the bands above 500 cm^{-1} in different phases.

peaks in this phase but, as the pressure increases to 55.5 kbar, the lattice band at ~ 136 cm^{-1} disappears (see the band marked by an arrow in figure 4). In the same pressure range, some other spectral changes were also observed in the chain-deformation regions between 200 and 450 cm^{-1}. For example, the bands at 227, 276, and 458 cm^{-1} show a decrease in their intensities while the band at 247 cm^{-1} shows an increase in its intensity, which resembles the high-pressure behaviour of $NaVO_3$ in the ambient-pressure phase. The frequencies of the two bands at 743.4 and 797.4 cm^{-1}, which are associated with the VO_3^- ions, soften with pressure in phase II (figure 5). Note that the band at 797.4 cm^{-1} appears only as a weak shoulder in figure 2, but a spectrum recorded by rotating the sample by 90° showed that this peak is about half as strong as that at 743.4 cm^{-1}.

At 70 kbar, the bands at ~ 227 cm^{-1} and ~ 276 cm^{-1} disappear and the band at 129 cm^{-1} in the lattice region shows a distinct split into two components, one at 126.7 cm^{-1} and the other at 140 cm^{-1}. At this pressure, a new band is also observed at 386.1 cm^{-1} while the band at ~ 470 cm^{-1} is no longer significant. We propose another phase transition (phase II to phase III), probably second order, on account of the appearance of new peaks and the disappearance of some bands. There is no clear frequency discontinuity in the frequency-against-pressure plot for any of the bands during the II/III transitions, but some bands show distinct changes in the gradients of the ω–P plots (figures 3 and 5).

The band at 743.4 cm^{-1} continues to soften in phase III, while the frequency of the band at 797.4 cm^{-1}, which has decreased to 792.3 at 70 kbar, starts to show the expected increase with compression. Another soft mode was observed at 128 cm^{-1} in phase III. The pressure dependence of the bands in the 700 cm^{-1} regions is similar to that of α-$NaVO_3$ in the amorphous phase at pressures above 60 kbar [2]. However, the bands for $LiVO_3$ are much narrower, indicating a periodic structure associated with $LiVO_3$. Again we attribute this difference to the smaller size of the Li^+ ions as compared to that of Na^+, which will allow repacking of the $LiVO_3$ into another structure much more easily. The larger size of the Na^+ ions, on the other hand, hinders the rearrangement of the broken chains into a crystalline structure, and hence results in an amorphous phase.

At pressures above 115 kbar, the frequency of the band at ~ 736 cm^{-1} starts to show an increase while the mode at ~ 120 cm^{-1} continues to soften. Some other changes were also observed in the same pressure range. For example, the band at 259 cm^{-1} is weaker than the band at 207.8 cm^{-1} at 78 kbar but it becomes stronger at about 100 kbar. The band at 359.6 cm^{-1} splits into two bands of similar intensity. Two other bands, at 396.6 cm^{-1} and 558.7 cm^{-1}, show a decrease in their intensities, which disappear at a higher pressure of 136 kbar and 159 kbar respectively. This gradual change is illustrated in figure 6. A second-order phase transition from phase III to phase IV is proposed at ~ 115 kbar.

At higher pressure, there seem to be still some changes in the spectra but, due to the decreased signal-to-noise ratio, they are no longer conclusive. Another problem faced at high pressure is that the pressure becomes non-hydrostatic due to the methanol–ethanol liquid medium used. Stress-related splitting often occurs as a result. There is no drastic change in the spectra till 197 kbar, the highest pressure reached in this work.

The spectra in phases III and IV are simpler than those in phases I and II, and hence are indicative of higher symmetries for III and IV. The second-order phase transitions of II/III and III/IV are expected to be due to the repacking of the VO_3^- ions, as demonstrated by the continuous change and softening of the bands in the 700 cm^{-1} region, into structures with average C_{3v} symmetry for the VO_3^- ions. Note that the bands in the 900 cm^{-1} regions are related to the VO_4^- chains while the bands in the 700 cm^{-1} region are related to the VO_3^- ions. There are small but definite bands in the 900 cm^{-1} region even in phase IV, indicating that there are still some broken VO_4^- chains left at a pressure as high as 200 kbar.

On decompression, the spectra are reversible until 22 kbar, at which pressure the sample transforms to a phase with no Raman-active bands. The Raman bands start to appear again when the sample is repressurized above 36 kbar, as shown in figure 7. The spectra on further pressurization are similar to those obtained in the virgin compression. We speculate that the reclaimed sample is in an amorphous phase and is similar to SiO_2 glass and high-pressure-released α-$NaVO_3$ [1], which also do not have any Raman-active bands. Incidentally, SiO_2 in the crystalline form (α-quartz) is also a well known sample to undergo pressure-induced amorphization and has been extensively studied [17–19].

To demonstrate that an amorphous sample would recrystallize given enough thermal energy, this sample was heated in an oven. Bands with the main features of ambient-phase $LiVO_3$ were restored after the sample was heated to 150 °C. However, the band frequencies are generally lower and the spectrum is considerably different from that of the virgin sample in the low-frequency region as shown in figure 8. It is apparent that there is not sufficient thermal energy at 150 °C for the individual VO_3 ions to relink themselves into the infinite

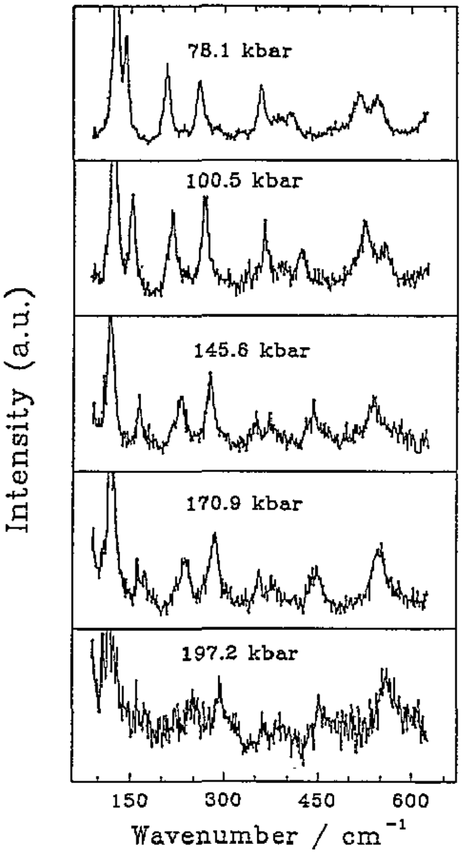

Figure 6. Raman spectra showing changes for the bands below 600 cm^{-1} in sequence of increasing pressure.

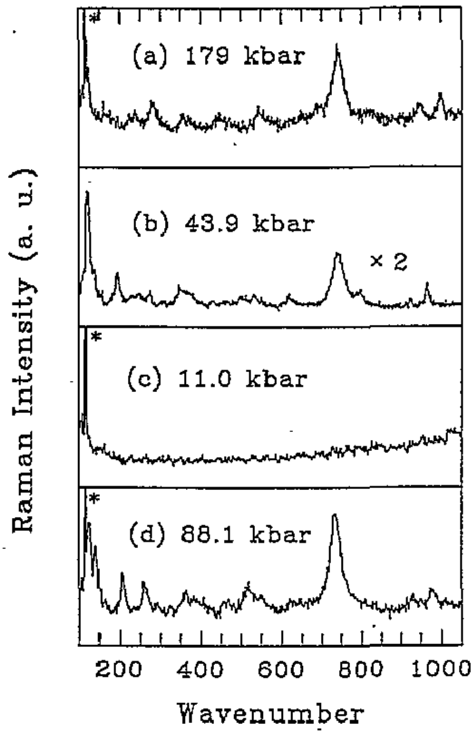

Figure 7. Raman spectra of $LiVO_3$ in sequence of decreasing pressure. Spectrum (a) belongs to phase IV; (b) phase II; (c) an amorphous phase; and (d) is repressurized to 88 kbar and belongs to phase III. * denotes a plasma line.

VO_4 chains and to form 'perfect' crystals. The spectrum recorded after heating to 450 °C is almost identical to that of the virgin sample.

4. Conclusions

Under high pressure up to 197 kbar, three phase transitions have been observed at about 35, 70, and 115 kbar. The first phase is first order and involves a complete change in the Raman spectra. It is believed that the infinite chains along the *c* axis behave similarly as in α-$NaVO_3$ and hence the chains break up into VO_3^- ions. There are no broad bands observed in this case and thus this is not a crystalline–amorphous phase transition. This could be due to the smaller size of Li^+ ions, which allows the broken VO_3^- ions to repack themselves into a crystalline structure. The second and third phase transitions involve only subtle changes and thus are of second order. Phase III and phase IV have fewer bands than phase II and therefore the structures are of higher symmetry.

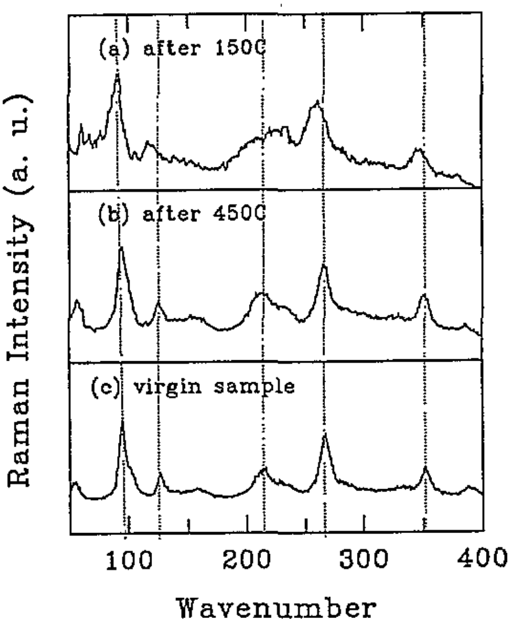

Figure 8. Raman spectra showing the gradual restoration of the VO_4^- chains. Note that the spectrum (b) resembles (c) more than (a).

When the pressure is released, the crystal structure does not have enough energy for the sample to arrange itself into a crystalline structure and, instead, it transforms to an amorphous phase with no Raman-active bands. The stable phase of $LiVO_3$ at ambient conditions was restored after heating the reclaimed sample to 450 °C.

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