Pressure-Induced Structural Behavior of Orthorhombic Mn₃(VO₄)₂: Raman Spectroscopic and X-ray Diffraction Investigations

Swayam Kesari, Alka B. Garg, Oliver Clemens, Boby Joseph, and Rekha Rao*

ABSTRACT: The effect of high pressure on the structure of orthorhombic Mn₃(VO₄)₂ is investigated using in situ Raman spectroscopy and X-ray powder diffraction up to high pressures of 26.2 and 23.4 GPa, respectively. The study demonstrates a pressure-induced structural phase transition starting at 10 GPa, with the coexistence of phases in the range of 10–20 GPa. The sluggish first-order phase transition is complete by 20 GPa. Importantly, the new phase could be recovered at ambient conditions. Raman spectra of the recovered new phase indicate increased distortion and as a consequence the lowering of the local symmetry of the VO₄ tetrahedra. This behavior is different from that reported for isostructural compounds Zn₃(VO₄)₂ and Ni₃(VO₄)₂ where both show stable structures, although almost similar anisotropic compression of the unit cell is observed. The transition observed in orthorhombic Mn₃(VO₄)₂ could be due to the internal charge transfer between the cations, which favors the structural transition at lower pressures and the eventual recovery of the new phase even upon pressure release in comparison to other isostructural compounds. The experimental equation of state parameters obtained for orthorhombic Mn₃(VO₄)₂ match excellently with empirically calculated values reported earlier.

INTRODUCTION

Searching novel materials with new phases/polymorphs having desired properties under different thermodynamic conditions is a topic of recent interest because of their useful technological applications and for understanding basic principles. Since vanadium shows multiple oxidation states, it forms different stoichiometric oxides, showing a wide range of applications. When vanadium forms oxide compounds in combination with other magnetic ions, the vacant d-orbitals in the vanadium atom serve as magnetic linking groups resulting in interesting coupling behavior.

Orthovanadates of family Aₓ(VO₄)₂, having Kagomé staircase structures show interesting magnetic transitions for A = Ni, Co, Mn. They have potential applications as electrodes in lithium ion batteries when A = Ni, Co, Zn. For A = Mg, Zn, Ni, Co, Mn, the family Aₓ(VO₄)₂ of compounds commonly adopts an orthorhombic structure with the Cmca space group at ambient conditions. There exists another vanadate within the Aₓ(VO₄)₂ family, namely, Cuₓ(VO₄)₂, which crystallizes in a triclinic structure at ambient conditions but has a high-temperature polymorph of orthorhombic structure (space group Cmca). Similarly, Mnₓ(VO₄)₂ is also reported to exist in a tetragonal structure (space group I42d), which is a high-temperature phase (which can be stabilized at ambient temperature via quenching or substitution of Mn²⁺ by 2 Li⁺) called ht-Mnₓ(VO₄)₂ as against the thermodynamically stable low-temperature orthorhombic phase, which is commonly called lt-Mnₓ(VO₄)₂. 14

There exist some structural studies on the series of compounds LiₓMn₃₋ₓ(VO₄)₂ that report that its structure changes from tetragonal (described by space group I42d) to orthorhombic structure (described by space group Cmcm) when x is above 0.4. 15 Our earlier investigation of the structural stability of the tetragonal compound Li₀.2Mn₂.9(VO₄)₂ at high pressures using Raman spectroscopy and powder X-ray diffraction (XRD) revealed highly anisotropic compression of the lattice, followed by an irreversible transition to a disordered unidentified crystalline phase above 13 GPa. 16 In the literature, only two members, Zn₃(VO₄)₂ and Ni₃(VO₄)₂, of the orthorhombic Aₓ(VO₄)₂ have been studied under high pressure. Both are reported to be stable up to 15 and 23 GPa, respectively, with both exhibiting anisotropic compressibility, even though it is less pronounced than that of the tetragonal compound Li₀.2Mn₂.9(VO₄)₂. 16 The triclinic
form of Cu3(VO4)2 has been recently reported to decompose under pressure at a moderate pressure of 1.35 GPa to CuO and V2O5. As mentioned earlier, the compound Mn3(VO4)2 exists in two polymorphs, and it is interesting to study both under high pressure for possible new phases in comparison to isostructural compounds Zn3(VO4)2 and Ni3(VO4)2. Apart from the basic research interest, knowledge of high-pressure structural transitions and fundamental properties such as bulk modulus is essential for technological applications. It is reported that in this class of compounds A3(VO4)2, compressibility is decided by that of AO6 octahedra. The VO4 tetrahedra are supposed to be more rigid than the AO6 octahedra, and the bulk modulus in this family of compounds is given by an empirical formula containing average A−O distance and charge on A ion as parameters. Therefore, initial structural parameters such as bond lengths and octahedral distortions of AO6 play an important role in deciding the stability of the compound at high pressures. Here, we report the results of vibrational and structural investigations on lt-Mn3(VO4)2 at high pressures carried out using in situ Raman spectroscopic and powder XRD measurements up to 26.2 and 23.4 GPa, respectively. For high-pressure Raman measurements, a few grains of lt-Mn3(VO4)2, ruby (pressure marker), and a pressure-transmitting medium (16:3:1 methanol–ethanol–water mixture) were loaded inside a diamond anvil cell (Diaccell B-05). The pressure calibration is performed with the ruby fluorescence method with error less than ±0.2 at 10

![Figure 1. Structure of orthorhombic A3(VO4)2 in two orientations.](image-url)
and less than ± 1 GPa at 25 GPa in the present experiment as measured from the full width at half-maximum of the ruby R1 line and from its position at different locations in the sample chamber in the diamond anvil cell. The pressure-transmitting medium 16:3:1 methanol–ethanol–water mixture remains hydrostatic up to 10.5 GPa, then quasi-hydrostatic up to 20 GPa, and becomes nonhydrostatic above 20 GPa.22−23

The angle dispersive powder X-ray diffraction (ADXRD) measurements at various pressures were recorded at the Xpress beamline of Elettra Synchrotron Source, Trieste, Italy. A Mao−Bell-type diamond anvil cell was used for pressure generation, and the sample with a few grains of platinum as in situ pressure marker, along with the 16:3:1 methanol–ethanol–water mixture as a pressure-transmitting medium, was loaded inside a 100 μm hole of a stainless steel gasket. The pressure was calibrated using the equation of state of platinum with an accuracy of 0.1 GPa.24 An X-ray beam of wavelength 0.4957 Å collimated to 80 μm was used to collect the powder diffraction data on a MAR345 image plate area detector with a resolution of 100 μm × 100 μm pixel size. Typically, data were collected for an exposure time of 30 s at each pressure point. The sample-to-detector distance along with various detector orientation parameters was refined with FIT2D software25 using the diffraction pattern of CeO2. The same software was used to convert two-dimensional diffraction rings from the sample to standard one-dimensional intensity vs 2θ plots. The structural refinement of the diffraction peaks from the sample and further data analysis was performed with GSAS software.26 Initially, the background of the XRD pattern was fitted with a Chebyshev polynomial function, followed by modeling the shape of Bragg peaks with the pseudo-Voigt function. Due to the presence of texture in the patterns, the Le Bail analysis method27 available in GSAS software was used to obtain the structural details at various pressures.

RESULTS AND DISCUSSION

Vibrational Properties at Ambient Conditions. The crystal structure of A3(VO4)2 in the orthorhombic Cmca space group is depicted in Figure 1, which contains AO6 octahedra and VO4 tetrahedra in which each octahedron shares its edge with the three adjacent octahedra and forms layers perpendicular to the [010] direction, and these layers are interconnected by isolated VO4 tetrahedra.17 The unit cell contains two formula units in which the A-atoms reside at two crystallographically distinct (A1 at 4a, A2 at 8e) Wyckoff sites, while the vanadium atoms reside at the 8f site and the oxygen atoms reside at 8f and 16g sites.14 Therefore, there are 78 zone center phonons, of which optic modes transform as Γoptic = 10A′g + 8B1g + 7B2g + 11B3g + 8A1 + 12B1u + 11B2u + 8B3u. Among them, A′g, B1g, B2g, and B3g are Raman active modes; all Ag modes are optically inactive; and the remaining modes are IR-active. Hence, there is a maximum of 36 symmetry-allowed Raman modes at ambient conditions for the orthorhombic Cmca structure.28

Figure 2 represents the Raman spectra of orthorhombic lt-Mn3(VO4)2, Co3(VO4)2, and Ni3(VO4)2 at ambient conditions. All of the observed Raman spectra match with the reported data,16,28,29 and their assignments suggest that the modes in the range of 500−900 cm−1 are predominantly due to the V−O stretching and are mixed with some A−O stretching/bending modes. The modes in the range of 200−500 cm−1 are bending modes. The modes below 200 cm−1 are rigid motions of VO4 tetrahedra and A−O6 octahedra. Major

**Figure 2.** Raman spectra of orthorhombic lt-Mn3(VO4)2, Co3(VO4)2, and Ni3(VO4)2 at ambient conditions.

Raman modes of lt-Mn3(VO4)2 are assigned in accordance with our earlier polarized Raman studies on Ni3(VO4)2.38 and, accordingly, the V−O symmetric stretching modes (A′g-symmetry) in lt-Mn3(VO4)2 are at 645, 811, and 793 cm−1 in the high-frequency region due to the symmetric stretching of short and long V−O bonds (all three bond lengths are given in Figure 1 taken from the literature24,25). The asymmetries in the Raman spectra at around 686 and 783 cm−1 are the asymmetric V−O stretching modes (B2g-symmetry). Similarly, the symmetric (A′g) and asymmetric (B2g) bending and external modes can be assigned in comparison to that of Ni3(VO4)2. The most intense modes in lt-Mn3(VO4)2, Co3(VO4)2, and Ni3(VO4)2 at ambient conditions appear at around 811, 815, and 826 cm−1, respectively. As shown in Table 1, which compares the reported structural details of the three compounds, all of the three compounds have almost similar average V−O bond lengths.16,14 It appears that the most intense symmetric stretching frequency depends predominantly on the radius of the ion A3+ and the tetrahedral distortion, similar to what has been reported for AV2O6.30

Accordingly, the lowest-size Ni2+ (0.69 Å)-containing compound has a large frequency of stretching mode. It may be noted that the unit cell volume also increases from Ni to Mn obeying Vegard’s law. While indicators such as elongation and variance in angles have been used extensively in the literature to describe the distortion in polyhedra,31 we have used the parameter distortion index calculated from bond lengths from the literature, which is compared with Raman data in AV2O6 and tungstate double perovskites.30,32 For VO4 tetrahedra, the distortion index is calculated from

$$\Delta_{1d} = \frac{1}{4} \sum_{n=1}^{4} \left( \frac{a−d}{d} \right)$$

and

$$\Delta_{2d} = \frac{1}{4} \sum_{n=1}^{6} \left( \frac{a−d}{d} \right)^2$$

where d and (d) represent the bond length and average bond length for the corresponding V−O/A−O bonds. We have calculated these distortion indices using the bond lengths reported in the literature24,25 and are given in Table 1. Figure 3 shows the variation of Raman mode frequency of the highest-intensity V−O symmetric stretching mode of lt-Mn3(VO4)2, Co3(VO4)2, and Ni3(VO4)2 with (a) VO4 tetrahedral distortion index (Δ1d) and (b) Shannon radius of cation A3+ (Mn2+, Co2+, Ni2+). Similar to the family of AV2O6, where the V−O frequency corresponding to the symmetric stretching increases with tetrahedral distortion of VO4 octahedra, we have found an increase in Raman frequency with an increase in VO4 tetrahedral distortion.
Table 1. Comparison of Various Structural Parameters of lt-Mn₃(VO₄)₂, Co₃(VO₄)₂, and Ni₃(VO₄)₂ at Ambient Conditions

| Parameter          | lt-Mn₃(VO₄)₂ | Co₃(VO₄)₂ | Ni₃(VO₄)₂ |
|--------------------|--------------|-----------|-----------|
| ω (cm⁻¹)           | 811          | 815       | 826       |
| Shannon radii of A^+ (Å) | 0.83(h)      | 0.745(h)  | 0.69(h)   |
| unit cell volume (Å³) | 621.4        | 575.5     | 555.7     |
| density (g/cm³)    | 4.21         | 4.69      | 4.83      |
| V—O1 (Å)          | 1.681        | 1.715     | 1.722     |
| V—O2 (Å)          | 1.784        | 1.810     | 1.813     |
| V—O3 (Å)          | 1.685        | 1.702     | 1.704     |
| V—O4 (Å)          | 1.685        | 1.702     | 1.704     |
| ⟨V—O⟩₁₁           | 2.188        | 2.093     | 2.062     |
| ⟨V—O⟩₁₂           | 2.193        | 2.093     | 2.062     |
| ΔTd (10⁻⁴)         | 7.36         | 4.65      | 2.57      |
| ΔOd (10⁻⁴)         | 5.59         | 4.11      | 2.42      |
| A2—O1 (Å)         | 2.108        | 2.032     | 2.013     |
| A2—O2 (Å)         | 2.206        | 2.107     | 2.064     |
| A2—O3 (Å)         | 2.206        | 2.099     | 2.064     |
| (A2—O)₁₁₂ (Å)     | 2.188        | 2.093     | 2.062     |

“Distortion index for VO₄ tetrahedra is calculated from ΔTd = 1/n Σ d − ⟨d⟩ and for AO₆ octahedra is calculated from ΔOd = 1/n Σ d − ⟨d⟩², where d and ⟨d⟩ represent the bond distance and average bond distance for the corresponding V—O/A—O bonds.

It may be also noted from Table 1 that the octahedral distortion is larger in lt-Mn₃(VO₄)₂ compared to the other two vanadates owing to the larger ionic radius of Mn²⁺. It is interesting to investigate if this distortion facilitates structural transition under pressure. Even in other vanadates such as AV₂O₆, distortion of AO₆ octahedra is less with smaller ions such as Co²⁺ or Ni²⁺ as compared to that in MnV₂O₆. It is also remarkable that among the three vanadates being compared, lt-Mn₃(VO₄)₂ has the lowest density and hence is more likely to show structural transitions to denser phases under pressure.

Vibrational Properties at High Pressures. Figure 4a,b depicts the Raman spectra of lt-Mn₃(VO₄)₂ up to 26.2 GPa in the pressure-increasing cycle at a selected pressure in the various regions. All of the modes show hardening behavior. While there is no significant change in low-frequency modes, there is a change in the intensity profile in the V—O stretching region, which is clearly seen in Figure 4b. In the high-frequency region, at a pressure of about 2.5 GPa, the intensity of the weak symmetric stretching (A₂) mode at 793 cm⁻¹ increases and becomes strong under further pressurization, and the simultaneous decrease in the intensity of the highest-frequency mode is observed. At around 9 GPa, the intensity of the weak mode became comparable with the highest stretching mode at 811 cm⁻¹. Above 10 GPa, this weak mode becomes the highest-intensity mode in the Raman spectra. Similar intensity exchange behavior is seen in the Raman spectra of Pr₂Ti₂O₇ across the structural phase transition. Above 15 GPa, a new mode appears at around 875 cm⁻¹ marked with an arrow in Figure 4b. This appearance of a new stretching mode could be related to distortions in VO₄ tetrahedra under high pressure. Polyhedral distortions resulting in lowering of symmetry and additional peaks in Raman spectra are observed in other oxides also. All of the weak modes disappear, followed by the complete disappearance of the entire Raman spectra above 23 GPa. This could be related to changes in the electronic structure induced by high pressure. We pressurized the compound further up to 26.2 GPa, but we could not obtain Raman signals even at higher laser power at the highest pressure achieved. Figure 5 represents the variation of Raman mode frequencies with pressure; all of the modes show gradual hardening behavior up to 23 GPa. We have fitted the variation with a line in the two pressure regions: one below 10 GPa where the intensity exchange behavior is observed and the other above 10 GPa, which may indicate the coexistence of the two-phase region. The pressure dependencies for all of the modes are given in Table 2. We have also explored the compound in the decompression cycle from 26.2 GPa, but we could recover the Raman signal only when pressure was fully released, and the Raman spectra are different compared to ambient Raman spectra as shown in Figure 6. The presence of hysteresis suggests the transition is first order in nature; additional mode beyond the strongest symmetric stretching mode is indicative of lowering of the local symmetry of the VO₄ tetrahedra. The new mode that appears beyond 15 GPa.
when extrapolated to ambient pressure is at 829 cm\(^{-1}\) and matches with the highest-frequency new mode in the pressure released data. The proposed phase transition is at pressures when the medium is quasi-hydrostatic, and we do not have

Figure 4. Raman spectra of lt-Mn\(_3\)(VO\(_4\))\(_2\) at various pressures up to 26.2 GPa in the pressure-increasing cycle (a) in full range and (b) in the V–O stretching region showing the appearance of a new peak indicated by the arrow mark.

Figure 5. Variation of Raman mode frequencies of lt-Mn\(_3\)(VO\(_4\))\(_2\) with pressure. The solid line indicates linear fitting to the data and the change of color in the solid lines demarcates the two phases.

Table 2. Raman Mode Frequency of lt-Mn\(_3\)(VO\(_4\))\(_2\) and Its Pressure Dependence in the Range up to 10 GPa

| Raman mode frequency \(\omega_i\) (cm\(^{-1}\)) | \(\frac{\partial \omega}{\partial P}\) (cm\(^{-1}\)/GPa) | isothermal mode Gruneisen parameter \(\gamma_i = \frac{\omega_i}{\omega} \frac{\partial \omega}{\partial T}\) |
|---|---|---|
| 102.3(1) | 0.4(1) | 0.5(1) |
| 121.9(1) | 1.2(1) | 1.14(9) |
| 148.2(5) | 1.1(2) | 0.9(1) |
| 171.8(2) | 2.7(1) | 1.82(7) |
| 242.3(2) | 1.4(1) | 0.67(5) |
| 252.2(4) | 3.4(2) | 1.56(9) |
| 272.8(8) | 4.5(2) | 1.91(8) |
| 320.3(1) | 1.3(1) | 0.47(4) |
| 327.1(1) | 3.9(4) | 1.4(1) |
| 376.8(2) | 2.0(1) | 0.61(3) |
| 407.2(5) | 3.5(2) | 1.00(6) |
| 435.8(4) | 2.2(1) | 0.58(3) |
| 459.9(8) | 5.5(2) | 0.98(3) |
| 649.9(8) | 4.6(2) | 0.77(3) |
| 782.8(8) | 1.35(2) | 0.20(3) |
| 796.1(3) | 2.0(2) | 0.29(3) |
| 809.2(2) | 2.8(2) | 0.40(3) |

\*The isothermal mode Gruneisen parameters are calculated using zero-pressure bulk modulus \(B_0 = 116\) GPa determined from high-pressure XRD. \*Indicates modes that appear only at high pressures due to lifting of degeneracy.
experimental data under perfectly hydrostatic conditions. Therefore, the role of nonhydrostaticity in bringing about transition above 10 GPa cannot be excluded in the present investigation.

It is clear that the compression behavior in lt-Mn₃(VO₄)₂ is different from that reported in Li₀.2Mn₂.9(VO₄)₂ (which is isostructural with tetragonal ht-Mn₃(VO₄)₂). In Li₀.2Mn₂.9(VO₄)₂ there appeared a broad mode at a much lower frequency (750 cm⁻¹), indicative of higher coordination of vanadium further leading to a disordered phase. On the other hand, in orthorhombic lt-Mn₃(VO₄)₂, the changes appear only near the symmetric stretching region more like only distortion of tetrahedra because of the change in different bond lengths. The intensity exchange in the stretching-mode region at around 10 GPa may indicate the beginning of a sluggish structural change. At higher pressures, from the Raman spectroscopic study, it is clear that the lattice structure of orthorhombic lt-Mn₃(VO₄)₂ changes, which is reflected in Raman spectra as a distortion of VO₄ tetrahedra, and it fully transforms into a new structure above 23 GPa. Therefore, we have also investigated the structure of orthorhombic lt-Mn₃(VO₄)₂ using high-pressure XRD, which is discussed in the next section.

**Structural Investigation at High Pressures.** Figure 7 shows the evolution of X-ray diffraction patterns of lt-Mn₃(VO₄)₂ at various pressures. A few patterns collected while unloading the pressure (marked with the letter r) are also shown in the same figure. As seen, in addition to the diffraction peaks from the sample, peaks from platinum used as an in situ pressure marker and stainless steel used as a gasket are also observed. In the first pattern collected at 0.5 GPa, all of the diffraction peaks emanating from the samples could be fitted with the ambient orthorhombic Cmca phase. No major changes were observed in the diffraction patterns collected up to 7.7 GPa, except for the shifting of diffraction peaks to higher angles due to lattice compression. All of the patterns up to 7.7 GPa could be fitted with the ambient orthorhombic phase. In Figure 8, we show the refined pattern at 5.3 and 9.9 GPa. Various residuals of the refinement, i.e., wRₑ and Rₑ, are 1.46% and 1.0% for 5.3 GPa data and 1.43% and 1.0% for 9.9 GPa, respectively. A similar kind of refinement was obtained for the data refined at other pressures. In the subsequent data collected at 9.9 GPa, there is an appearance of an extra diffraction peak at around 15° (2θ) indicated by an arrow in Figure 7. In the data collected at 10.8 GPa, there is another new broad peak at around 13.2° (2θ), suggesting the onset of a structural transition. As the pressure is increased further, till 16.2 GPa, the intensity of the emerging peaks increases while the intensity of diffusion peaks from the ambient phase reduces. This behavior indicates the coexistence of two phases till 16.2 GPa. In the data collected at 20.1 GPa, the intensity of most of the diffusion peaks from the ambient phase decreases below the detection limit of the detector and the patterns consist of broad peaks mainly from the high-pressure phase along with those from the pressure marker and the gasket. This
The trend continues till 23.4 GPa, the highest pressure reached in the present investigations. On pressure release, the diffraction pattern remains similar to the one observed at the highest pressure, except for the shifting of the peaks to lower angles due to lattice decompression. The observations obtained in the high-pressure XRD are consistent with the high-pressure Raman investigations discussed in the previous section. Figure 9 depicts XRD patterns of ambient and pressure-retrieved \( \text{lt-Mn}_3(\text{VO}_4)_2 \), which confirm the structural transition and the presence of the high-pressure phase in the pressure-recovered \( \text{lt-Mn}_3(\text{VO}_4)_2 \) whose diffraction peaks are marked with red arrow. Note that due to the addition of a few weak broad peaks, we could not refine the structure of the high-pressure phase.

The variation of lattice parameters and the unit cell volume with pressure obtained by refinement of X-ray diffraction data for \( \text{lt-Mn}_3(\text{VO}_4)_2 \) is shown in Figure 10a,b. The variation of the unit cell volume shown in Figure 10b and the variation of lattice parameters shown in Figure 10a have been fitted with third-order Birch–Murnaghan equation of state (BM-EOS), which is indicated by continuous curves in Figure 10a,b, and the axial compressibilities and bulk modulus along with pressure derivative of bulk modulus have been estimated. The fitted values of axial compressibilities are \( K_a = 3.1 \times 10^{-3} \text{ GPa}^{-1} \), \( K_b = 2.32 \times 10^{-3} \text{ GPa}^{-1} \), and \( K_c = 2.9 \times 10^{-3} \text{ GPa}^{-1} \). These data clearly show that the compressibility of the three axes varies as \( K_a > K_c > K_b \). Similar anisotropic compression of lattice parameters with pressure is observed for the other isostructural compounds \( \text{Zn}_3(\text{VO}_4)_2 \) and \( \text{Ni}_3(\text{VO}_4)_2 \) (listed in Table 3 for easier comparison)\(^{17,18} \) where the authors predicted that the anisotropic behavior could be due to the nature of the Kagome layered crystal structure. The obtained value of ambient pressure bulk modulus and the pressure derivative of bulk modulus are \( 116(2) \text{ GPa} \) and \( 2.6(5) \), respectively. The bulk modulus obtained from the present experiment shows excellent matching with the empirically estimated value of 115 GPa.\(^{18} \) Experimental bulk modulus is in comparison with the other isostructural members \( \text{Zn}_3(\text{VO}_4)_2 \) (\( B_0 = 115 (2) \text{ GPa}, B'_0 = 5.1(6) \))\(^{17} \) and \( \text{Ni}_3(\text{VO}_4)_2 \) (\( B_0 = 139 (3) \text{ GPa}, B'_0 = 4.4(3) \)).\(^{18} \) We have used this value of bulk modulus for \( \text{lt-Mn}_3(\text{VO}_4)_2 \) (\( B_0 = 116 \text{ GPa} \)) to calculate the isothermal mode Grüneisen parameters listed in Table 2 for all of the observed Raman modes using \( \gamma_T = \frac{B'_0}{\omega_0} \left( \frac{\partial \omega}{\partial p} \right)_T \), which scales the phonon frequency with unit cell volume. The isothermal mode Grüneisen parameters for all of the observed Raman modes are positive.

A remarkable result of this study is the observation of a structural transition, which is completed by 20 GPa. A similar result was also seen in \( \text{Li}_{0.2}\text{Mn}_{2.9}(\text{VO}_4)_2 \) above 13 GPa.\(^{16} \) The absence of any structural transition in isoostructural Zn and Ni compounds within the pressure range explored (up to 15 GPa for Zn and up to 23 GPa for Ni compound) could be due to the lesser octahedral distortion in the ambient structure in these compounds as compared to Mn compounds.
As has been described in ref 8, the band gap in Mn₃(VO₄)₂ corresponds to a charge transfer from Mn²⁺ to V⁵⁺ according to
\[ \text{Mn}^{2+} + \text{V}^{5+} \rightarrow \text{Mn}^{3+} + \text{V}^{4+} \]

The Raman investigation reported in this article clearly indicates significant changes in the vanadium coordination and distortion of the polyhedron. According to the pressure-coordination rule,⁵⁶ increase of pressure tends to increase the coordination number of the cations due to a decrease of the size of the larger, more compressible anions. Since stabilization of V⁴⁺ in tetrahedral coordination is not possible, this might also trigger such an internal charge transition, which might lead to the irreversible charge transformation observed at higher pressures for both modifications of Mn₃(VO₄)₂. This could also be structurally supported from the behavior of Mn⁵⁺ at high pressures, for which it has been reported that the Jahn–Teller (JT) distortion of Mn⁵⁺ decreases substantially under pressure leading to the appearance of new phases in a wide variety of compounds such as in CaMn₂O₄,⁵⁷ GdMnO₃,⁵⁸ Ca₃Mn₂[SiO₄]₂(O₄H₄),⁵⁹ LaMnO₃,⁶⁰ etc. In CaMn₂O₄ and GdMnO₃, the unit cell volume is reduced and the disappearance-suppression of JT distortion in MnO₆ in the high-pressure phase is responsible for the structural phase transition in both.⁵⁷,⁵⁸ In LaMnO₃, an insulator-to-metal phase transition occurred under pressure due to the change of high JT distortion to less JT distortion of MnO₆ octahedra with pressure, although the crystal structure remained unchanged.⁵⁹,⁶⁰ In Ca₃Mn₂[SiO₄]₂(O₄H₄), the JT distortion of MnO₆(OH)₂ octahedra under pressure was suppressed totally and a gradual transition of high-spin to low-spin electronic state of Mn⁵⁺ under high pressure appeared.⁶¹

In lt-Mn₃(VO₄)₂, the distortion in the octahedra at the Mn²⁺ site at ambient conditions is low compared to the above-listed compounds due to Mn being present in the d⁵ high-spin divalent state. Therefore, we hypothesize that the compression could decrease the band gap and favor the internal charge transfer between the cations, which would be favorable for Mn₃(VO₄)₂ in comparison to other A₃(VO₄)₂ compounds, and explain the transition at lower pressures observed here. A pressure-induced band-gap collapse is reported among InVO₄, InNbO₄, and InTaO₄ across their phase transitions.⁶² Since the data do not allow for a detailed structural analysis to display the above-suggested model, it is of interest to investigate this possibility in more detail in a follow-up study by theoretical methods.

### CONCLUSIONS

We have explored the structural stability and vibrational behavior of lt-Mn₃(VO₄)₂ under compression using in situ Raman spectroscopy and synchrotron XRD measurements. The changes in the Raman spectra under pressure suggest that there exists a pressure-induced structural change above 20 GPa. Furthermore, Raman spectroscopy indicates the local structural distortion and symmetry lowering. Changes in XRD indicate pressure-induced crystal structural change at around 10 GPa with coexistence in the range of 10–20 GPa. The compressibility parameters of the orthorhombic phase were analyzed using the third-order Birch–Murnaghan equations of state. Equation of state of lt-Mn₃(VO₄)₂ is obtained, and the bulk modulus obtained is comparable with those reported earlier. Anisotropic reduction is seen in the unit cell parameters that are comparable with those reported for the isostuctural compounds Zn₃(VO₄)₂ and Ni₃(VO₄)₂.

### AUTHOR INFORMATION

**Corresponding Author**

Rekha Rao — Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India; Homi Bhabha

Table 3. Linear Compressibilities and Room-Temperature Equation of State (EOS) Parameters of Zn₃(VO₄)₂, Ni₃(VO₄)₂, Li₄₀.₂Mn₂₉(VO₄)₂, and lt-Mn₃(VO₄)₂

| Compound                      | Orthorhombic Zn₃(VO₄)₂ | Orthorhombic Ni₃(VO₄)₂ | Orthorhombic lt-Mn₃(VO₄)₂ |
|-------------------------------|-------------------------|------------------------|---------------------------|
| K₀ (GPa⁻¹)                    | 2.9(1) × 10⁻³            | 2.7(1) × 10⁻³           | 3.1 × 10⁻³                |
| K₆ (GPa⁻¹)                    | 1.9(1) × 10⁻³            | 1.79(6) × 10⁻³          | 2.3 × 10⁻³                |
| K₆ (GPa⁻¹)                    | 2.7(1) × 10⁻³            | 2.33(5) × 10⁻³          | 2.9 × 10⁻³                |
| V₀ (Å³)                       | 585.0(4)                 | 555.7(2)                | 623.4(2)                  |
| B₀ (GPa)                      | 115(2)                   | 139(3)                  | 116(2)                    |
| B₀’                           | 5.1(6)                   | 4 (fixed)               | 2.6(5)                    |

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