Phase transitions in $Sc_2(WO_4)_3$ under high pressure

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High-pressure x-ray diffraction and Raman scattering studies on scandium tungstate $[Sc_2(WO_4)_3]$ show that it transforms to a monoclinic phase at ~0.6±0.3 GPa. The high-pressure phase has $P2_1/a$ symmetry and is related to the initial orthorhombic phase through cell doubling along the *c* axis. The compound undergoes another phase transition at ~1.6 GPa, accompanied by a volume reduction of ~8%. At ~6.5 GPa, the diffraction pattern and Raman spectra of $Sc_2(WO_4)_3$ indicate the emergence of a disordered crystalline state which evolves into an amorphous phase beyond ~14 GPa. The structural changes are found to be reversible up to ~1.6 GPa. However, transformation to the amorphous state is found to be irreversible, though our results suggest some structural relaxation on release of pressure.

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I. INTRODUCTION

Scandium tungstate belongs to the family of framework compounds, which are comprised of a three-dimensional network of corner-linked polyhedra. Hinged polyhedra in this open framework structure are responsible for several phase transformations that take place in these compounds under different thermodynamic conditions.¹⁻¹³ In addition, due to the highly charged hexavalent W⁺⁶ ion and weak Sc-O interaction, $Sc_2(WO_4)_3$ exhibits the highest ionic conductivity in the $A_2(WO_4)_3$ compounds (where A=Al, Sc, Lu, Yb, Tm, Er, and Y), which makes it very suitable for making gas sensors.⁴ It also has applications as an ideal host lattice for tunable Cr³⁺ solid-state lasers.¹⁴ Similar to a large number of molybdates and tungstates of such transition metals as scandium, hafnium, zirconium, etc.,^{6,12,13} it also exhibits negative thermal expansion (NTE), i.e., its volume decreases on increase of temperature (from 10 to 1050 K). This property is very useful to help design materials with the appropriately tuned thermal expansion, which may be required in several applications such as making electronic components, printed circuit boards, cookware, etc.¹⁵

While some NTE materials such as $Al_2(WO_4)_3$, $Sc_2(MoO_4)_3$, etc.^{1,2,9} have been shown to undergo several pressure-induced phase transitions prior to becoming amorphous at high pressures, some others, such as $Y_2(WO_4)_3$ and $Lu_2(WO_4)_3$,^{16,17} are known to amorphize directly from their initial structure. It has also been suggested that pressure-induced amorphization in these materials may be related to the transverse modes causing NTE.¹³ Also, whereas some of these compounds show a displacive orthorhombic to monoclinic (ferroelastic) phase transition at low temperatures, some others do not show such a transition even up to 10 K.^{5,6,15}

Earlier x-ray-diffraction studies on recovered samples of $Sc_2(WO_4)_3$ have shown that it amorphizes partially when pressurized to 4 GPa, but amorphizes completely and irreversibly when pressurized to ~8 GPa.³ Subsequently, the same authors carried out high-pressure electrical resistance measurements on $Sc_2(WO_4)_3$ at 400 °C and attributed the

increase in ion conductivity at 2.9 GPa to the onset of disorder.⁴ In addition, recent Raman scattering studies have shown that $Sc_2(WO_4)_3$ undergoes a pressure-induced crystal to crystal (*c*-*c*) phase transition at ~0.45 GPa.¹ These studies also support an irreversible phase transition to a highly disordered phase at ~7 GPa. Isostructural $Sc_2(MOO_4)_3$ is also known to undergo crystal to crystal phase transitions at ~0.29 GPa and ~2.7 GPa and crystal to amorphous transition beyond ~3.7 GPa.⁹ But, so far no x-ray-diffraction study at high pressures has been carried out to determine the structures across the phase transitions in $Sc_2(WO_4)_3$. Hence to determine the high-pressure phase transitions and the structure of the new phases, we have carried out x-ray-diffraction and Raman spectroscopy studies on $Sc_2(WO_4)_3$ up to pressures of ~26 GPa and ~20 GPa, respectively.

II. EXPERIMENTAL

Polycrystalline scandium tungstate was prepared by the conventional solid-state reaction of Sc₂O₃ and WO₃ respectively. The x-ray-diffraction pattern of the ambient phase could be indexed in the orthorhombic space group Pnca with the cell parameters a=9.65(2) Å, b=13.3(1) Å, and c =9.56(2) Å, which agree well with the earlier studies.¹⁵ The high-pressure experiments were carried out using Mao-Belltype diamond anvil cells. A finely ground sample of $Sc_2(WO_4)_3$ was loaded in a ~100 μ m hole of tungsten (xray studies) or steel (Raman studies) gaskets, preindented to a thickness of $\sim 70 \ \mu m$. Methanol-ethanol mixture in the ratio of 4:1 was used as a pressure-transmitting medium in both studies. In the Raman experiments, ruby was used as a pressure marker,¹⁸ whereas for the x-ray-diffraction experiments both ruby and copper were used as pressure markers in different experimental runs. For x-ray-diffraction studies using Cu as a pressure calibrant, a standard equation of state of copper¹⁹ was used for the pressure estimation in the diamond anvil cell.

Unpolarized Raman data were collected using a CCDbased single-stage spectrograph in the 45° geometry. The



FIG. 1. (Color online) Structure of $Sc_2(WO_4)_3$ at ambient conditions as viewed down the *a* axis. The solid line indicates the unit cell in the orthorhombic phase. O, W, and Sc represent oxygen, tungsten, and scandium atoms, respectively. Other symbols (a-g) are explained in the text.

532 nm line of a solid state diode laser with <1 mW power was used as an excitation source. An appropriate super-notch filter was used to block the Rayleigh scattering. As a result, the Raman modes below 100 cm⁻¹ could not be recorded. However, several modes between 100 and 1100 cm⁻¹ were recorded as a function of pressure. In the increasing pressure cycle, Raman spectra were recorded in finer pressure steps up to 6 GPa, and beyond that the pressure was raised in coarser steps until 20 GPa. Reasonably good quality Raman data could be obtained with typical collection times of 60-100 s.

Angle dispersive x-ray-diffraction studies were carried out at the Elletra Synchrotron Source employing monochromatic x rays of wavelength 0.6957 Å (calibrated with a LaB₆ NIST standard). The x rays were collimated to 90 μ m, and the two-dimensional patterns were collected on a MAR345 imaging plate. One set of experiments at high pressures were also carried out with the molybdenum x-ray source (λ =0.71069 Å) in our laboratory. For this, data at each pressure were accumulated for ~20 h each. These images were integrated to one-dimensional diffraction patterns using the software FIT2D.²⁰ Le Bail analysis was carried out to determine the cell parameters, using the GSAS software.²¹ Rietveld analysis was also carried out for the initial and first highpressure phase, with the same software.

III. RESULTS AND DISCUSSION

 $Sc_2(WO_4)_3$ crystallizes in the orthorhombic space group *Pnca* with four formula units per crystallographic unit cell. It is made up of corner-shared WO₄ tetrahedron and ScO₆ octahedron, i.e., each octahedron shares its corners with six tetrahedra and each tetrahedron shares its corners with four octahedra. In this structure, W atoms occupy two crystallographically distinct sites whereas the Sc atoms occupy a single site. As shown in Fig. 1, one W atom (W1) is on a general position (8*d*) and the other (W2) occupies a site on a twofold axis (4*c*). The WO₄ tetrahedron at the twofold axis is closer to a regular tetrahedron with an average angle of 109.6°, whereas the second tetrahedron at the general position is more distorted with an average angle of 110.2°. The

structure of $Sc_2(WO_4)_3$ can be viewed as layers of interlinked corner-shared octahedra and tetrahedra stacked parallel to the *ac* plane, as displayed in Fig. 1. These layers are linked through oxygen atoms O3.

In the orthorhombic structure, there are 68 atoms in the unit cell which lead to 201 vibrational modes. Since $Sc_2(WO_4)_3$ is isostructural to scandium molybdate and aluminium tungstate, similar mode classification has been retained for this compound.^{5,9} The unpolarized Raman spectra at room temperature is shown in Fig. 2. The vibrational modes below 300 cm^{-1} are identified to be the lattice modes. The modes in the band centered around $\sim 350 \text{ cm}^{-1}$ are the WO₄ bending modes and the modes at \sim 820 and $\sim 1020 \text{ cm}^{-1}$ are the antisymmetric and symmetric stretch modes of the WO₄ tetrahedra. The number of the observed modes is less than expected because the predicted splitting is too small to be resolved with unpolarized Raman spectra.⁹ However, we observed most of the modes recorded by Hanuza et al.⁵ in aluminium tungstate above 200 cm⁻¹. We also note that the symmetric stretch band of $Sc_2(WO_4)_3$ is found at $\sim 1020 \text{ cm}^{-1}$, quite close to the corresponding mode for $Al_2(WO_4)_3$ (~1030 cm⁻¹) while differing slightly from that of $Sc_2(MoO_4)_3$ at ~980 cm⁻¹. This supports the earlier suggestion that the frequency of the symmetric stretch mode is sensitive to the size of the cations in these compounds.²²

Background subtracted Raman spectra of scandium tungstate at different pressures are shown in Fig. 2. Figures 2(b) and 2(c) show that at ~0.5 GPa the bending modes of the WO₄ tetrahedra at ~350 cm⁻¹ and the antisymmetric modes at ~820 cm⁻¹ broaden significantly, perhaps due to the appearance of a few new modes around the earlier modes.²³ In addition, as shown in Fig. 2(c), the weaker symmetric stretch mode at ~1006 cm⁻¹ shows a relative increase in the intensity. These changes are suggestive of a subtle phase transformation as similar changes in the Raman spectra were also observed in the low-pressure phase transition of Al₂(WO₄)₃ and Sc₂(MOO₄)₃.^{2,9,11}

On further increasing the pressure, at ~ 1.6 GPa we observed an intensity reversal of the symmetric stretch modes at 1000 and 1027 cm^{-1} as shown in Fig. 2(c). In addition, the antisymmetric stretch modes at $\sim 830 \text{ cm}^{-1}$ showed broadening. These changes are quite subtle. At ~ 3 GPa [Fig. 2(a)] we also observed the shifting of the symmetric stretch band towards lower wave numbers. These two features together indicate that structural changes, if any, initiated at ~ 1.6 GPa may be completed by \sim 3 GPa. In fact, x-ray-diffraction results presented below support such a possibility. Similar spectral changes observed earlier in aluminium tungstate and scandium molybdate at \sim 2.8 GPa have also been identified with a phase transition to a lower symmetry phase.^{2,9,11} On release of pressure from 1.6 GPa, the initial Raman spectra reappear, as shown in Fig. 3. This indicates that up to this pressure the changes in the structure are reversible. At still higher pressures, ≥ 6 GPa, we observed that all the modes became very broad, suggesting an increasing structural disorder. By ~11 GPa, various Raman modes merged into broadbands centered at 473 and 955 cm⁻¹. However, even at 20 GPa, the Raman spectrum continued to have a clearly identifiable higher-frequency band $\sim 882 \text{ cm}^{-1}$. In contrast,



FIG. 2. Background subtracted Raman modes of $Sc_2(WO_4)_3$ at different pressures. (a) Overall variations in the Raman spectra with pressure. (b) and (c) The Raman spectra at low pressures in the range 200–600 cm⁻¹ and 700–1100 cm⁻¹ respectively.

the band at 500 cm⁻¹ became too broad to be clearly identified. On release from 20 GPa (Fig. 3), we observed that the broadband at \sim 882 cm⁻¹ splits into two (at \sim 950 and 802 cm⁻¹), suggesting some kind of structural relaxation while still retaining a highly disordered structure.

The existence of these bands close to the bending and stretching modes of WO₄ suggests that despite severe deformations, in some sense the polyhedral nature remains. Moreover, as in the amorphous phase of several other compounds of this family,^{1,9,16} the centroid of the high-frequency band is at somewhat lower frequencies than at the ambient conditions. These results suggest that, in general, in the amorphous phase of these compounds the W-O force constants decrease with pressure, probably caused by an irreversible approach of some nonbonded oxygen atoms close to WO₄, resulting in an effective increase in W-O coordination. We also note here that generally the existence of some nontransforming unit makes the amorphization reversible.²⁴ Therefore, the observed irreversibility in the Raman spectrum implies that WO₄ tetrahedra not only deform, but the structural changes are significantly large to hinder reversal of deformations on retrieval.

In order to determine the structure of the high-pressure phases, we have carried out x-ray-diffraction studies on scandium tungstate up to pressures of 26 GPa. The diffraction patterns of Sc₂(WO₄)₃ at a few representative pressures are shown in Fig. 4. Some of the indices of the ambient pressure phase (*Pnca*) have been shown in this figure. The diffraction peaks marked with "W" and "Cu" are from the tungsten gasket and copper pressure marker, respectively. The diffraction pattern at ~ 0.7 GPa shows some new, very weak diffraction peaks at $2\theta \sim 2.4^\circ$, 8° , and 12° . This is indicative of the beginning of a phase transition to probably a lowersymmetry phase with a larger unit cell. It is complete only by \sim 1 GPa. This transition is in agreement with our Raman results discussed above. On further increase of pressure at \sim 1.9 GPa, the diffraction pattern showed several changes. The diffraction peaks at 7° and 8° split and the diffraction peaks at $\sim 10^{\circ}$ moved apart. However, these changes were more clearly visible at \sim 3.5 GPa, and have been shown in Fig. 4. These changes imply the presence of a second phase transition between 1.6 and 3.5 GPa. It is worth mentioning here that even in the Raman spectrum an intensity reversal was observed in the WO₄ symmetric stretch modes at \sim 1.6 GPa, and only at \sim 3 GPa did the center of the symmetric stretch band shift toward lower wave numbers. Both of these results taken together suggest that the second phase transition is initiated at \sim 1.6 GPa and is complete only at



FIG. 3. Raman modes of $Sc_2(WO_4)_3$ on release of pressure from 1.6 and 20 GPa.

~3 GPa. This phase continues to exist up to ~4.2 GPa. Beyond this pressure, at about 6.5 GPa the diffraction pattern indicates that $Sc_2(WO_4)_3$ is in a highly disordered structural state. This state grows progressively into an amorphous phase, and at ~26 GPa the diffraction pattern is typical of an amorphous solid. This disorder is inherent to the sample and cannot be attributed to nonhydrostatic stresses, as the split-



FIG. 4. Background subtracted x-ray-diffraction patterns of $Sc_2(WO_4)_3$ at different pressures. The W and Cu represent diffraction lines from the tungsten gasket and copper pressure marker, respectively. Due to a large number of peaks, only some of the indices of the ambient and the high-pressure phases are shown. The gasket peaks at 14.4 GPa, 26 GPa and on release of pressure are broad since these data were collected with the diverging molybde-num $K\alpha$ x rays of the laboratory source.

ting of the R_1 - R_2 ruby line indicates that the sample environment at ~14 GPa is reasonably quasihydrostatic. Earlier, similar behavior has also been observed in Al₂(WO₄)₃, Sc₂(MoO₄)₃, and Y₂(WO₄)₃.^{1,9,16} On release of pressure from ~26 GPa, the amorphous phase is retained, in broad agreement with our Raman results as well as earlier studies.³ In fact, the shifting of the broad hump, at ~14° (indicating the first diffraction peak of the amorphous phase) to lower angles on release of pressure, also indicates the structural relaxation (Fig. 4). However, from the present diffraction data the nature of structural relaxation cannot be determined.

Rietveld analysis of the diffraction pattern at ambient conditions was carried out with the GSAS software.²¹ At ambient conditions, the cell constants and the positional parameters are in good agreement with the earlier reported values.¹⁵ A typical fit to the data at ambient condition is shown in Fig. 5(a) (parameters of goodness of fit are RF²=0.065; R_{wp} =0.026). The diffraction pattern at \sim 0.7 GPa could be refined to the initial orthorhombic phase except for a few weak new diffraction peaks, suggesting the coexistence of two phases. Since the new diffraction peaks are very weak at 0.7 GPa, it is difficult to characterize the new high-pressure phase at this pressure. A Le Bail analysis of the diffraction pattern at ~ 1 GPa shows that it can be fitted to a monoclinic space group with $P2_1/a$ symmetry. This symmetry change is similar to the one observed in the ferroelastic phase transition at low temperature.^{6,9} The cell constants of the new high-pressure phase are found to be $a_{m1}=16.03(2)$ Å, b_{m1} =9.4 Å, c_{m1} =18.6 Å, and β =124.89°(3), and the unit cell can be related to that of the orthorhombic phase by the relations

$$a_{m1} \approx -b_o + c_o, \tag{1}$$

$$b_{m1} \approx -a_o, \tag{2}$$

$$c_{m1} \approx -2c_o,\tag{3}$$

where m1 and o denote the monoclinic and the orthorhombic phases, respectively. The Rietveld analysis of this phase was also attempted, starting with the fractional coordinates of the low-temperature monoclinic phase of $Sc_2(MoO_4)_3$.⁶ For this phase, the goodness of fit parameters are $RF^2=0.12$, R_{wp} =0.021, and it can be seen in Fig. 5(b) that the discrepancy between the calculated and observed diffraction pattern is not large. This indicates that the structure of the new highpressure phase of $Sc_2(WO_4)_3$ is similar to the high-pressure phase of $Sc_2(MoO_4)_3$. Figure 6 shows the structure of the high pressure monoclinic phase at ~ 1.2 GPa (with the refined coordinates from Rietveld analysis). The ac plane of the monoclinic phase shown in this figure is equivalent to the bc plane of the orthorhombic phase (Fig. 1). The solid lines show the unit cells in the respective phases. It can be seen from Figs. 1 and 6(a) that in the monoclinic phase, the parallelogram formed by the four ScO_6 octahedra at sites a, b, c, and d elongates along the [011] direction of the orthorhombic cell, due to the rotation of the WO_4 tetrahedra at *i*. In



FIG. 5. Fitted profile as well as difference plot shown at different pressures. The dotted line indicates the observed intensities, and the profile fit is shown by the solid line. The difference between the observed and calculated intensities is plotted at the bottom, and vertical bars represent the expected positions of diffraction peaks. (a) ambient pressure, (b) 1 GPa, and (c) 4.2 GPa.



FIG. 6. View of the $Sc_2(WO_4)_3$ structure in the first monoclinic phase $(P2_1/a)$ (a) down the *b* axis (b) down the *c* axis.

addition, in the orthorhombic phase the distance between the scandium atoms at sites a and c (10.69 Å) is equal to the distance between the scandium atoms at sites e and g (i.e., repeat units along the c_o axis), whereas in the monoclinic phase the distance between the scandium atoms at sites a and c (10.44 Å) is not equal to the distance between the scandium atoms at sites e and g (10.71 Å). These unequal distances lead to a doubling of the unit cell along the c_o axis.

Le Bail analysis of the diffraction data at 1.9 GPa can also be carried out with the $P2_1/a$ symmetry. However, the refined cell constants are considerably different from the fits at ~ 1 GPa, implying substantial structural rearrangement, and we shall represent these unit-cell dimensions with the subscript m_2 . At ~1.9 GPa, a_{m2} =13.81 Å, b_{m2} =9.6 Å, c_{m2} =18.26 Å, and β =123.91°. These results show that the b_{m1} axis expands and there is a considerable collapse of the a_{m1} axis. The β angle also decreases slightly. The goodness of fit parameters are found to be $\chi^2 = 0.078$, $R_{wp} = 0.024$, and Fig. 5(c) shows the Le Bail fit of the diffraction pattern at 4.2 GPa. So as to rationalize these observations, we note that, as shown in Fig. 6(b), the layers of tetrahedra and octahedra are connected only by the oxygen atom O3 (as it was in the orthorhombic phase). The observed pressure-induced variation of the fractional coordinates implies increasing bending of WO₄ tetrahedra at the O3 linkages as the pressure is increased from ${\sim}0.6$ GPa. It is likely that the sudden collapse of the a_{m1} axis and increase in the b_{m1} axis, observed at 1.9 GPa, are due to a discontinuous jump in the tetrahedral



FIG. 7. Variation of V/V_0 (a) and lattice parameters (b), (c), and (d) as a function of pressure. The solid circle denotes the orthorhombic phase, ∇ represent the first monoclinic phase, and the unfilled circles show the second monoclinic phase.

deformations beyond some limiting value of bending. However, as the structure of this phase could not be determined due to the limitations of the available data, these suggestions cannot be confirmed.

The variation of the volume (V/V_0) and the cell constants with pressure is shown in [Fig. 7(a)-7(d), respectively].²⁵ Figure 7(a) shows that there is very little change in the volume (<0.5%) at the first transition. This is consistent with the small volume changes observed in the low-temperature ferroelastic phase transitions from orthorhombic (Pnca) to monoclinic phases $(P2_1/a)$ in this family of compounds.^{5,6} At this pressure, the c_o axis almost doubles and the a_o and b_o axes transform, as given in Eqs. (1) and (2). On further increase of pressure, it was observed that, at ~ 1.9 GPa, there are no significant changes in the c_{m1} axis, but the b_{m1} axis expands while the a_{m1} axis displays a sudden compression. This leads to a volume discontinuity of about 8%, indicating a first-order phase transition. Even in aluminum tungstate and scandium molybdate, a phase transition was observed at \sim 2.7 GPa.^{1,9} However, the structure of this phase has not been determined. The large volume discontinuity across this transition shows that this phase is quite dense and fairly incompressible.

In the context of pressure-induced amorphization observed in $Sc_2(WO_4)_3$, we note that the existence of a pressure-induced amorphous state in ZrW_2O_8 and hence in NTE compounds has been explained in terms of frozen eigenvectors of several transverse modes representing polyhedral orientations, due to the inability to cross the transient point of minimal bent.¹³ Simultaneous softening of several modes has also been invoked to explain the similar behavior in ice.²⁶ In essence, these calculations suggest that the resulting amorphous phase is an assemblage of a large number of incommensurate structures.²⁷ It is worth noting that generally the transformations driven by soft modes are expected to be reversible.²⁸ However, most of the systems where such models have been invoked are the cases of irreversible amorphization, where an amorphous phase slowly emerges over a range of pressure and no mechanism of irreversibility has been proposed. We may speculate that the strains across tiny sized grains of incommensurate structures may be responsible for this behavior, but obviously more work is necessary to settle this issue. Moreover, once a mode corresponding to one q softens, the parent structure should transform to the new structure. Thus the explanation of amorphization based on the mode instability has to be on the basis of branch softening in the resulting phase. Notwithstanding these difficulties, this model is physically appealing and it is possible that even in $Sc_2(WO_4)_3$ a similar mechanism is operative and should encourage more experiments and theoretical calculations to investigate the pressure-induced changes in the acoustic modes. In $Sc_2(WO_4)_3$, the monoclinic phases are a precursor to the amorphous phase, as also observed in aluminium tungstate and scandium molybdate.^{2,9} Though the thermal expansion behavior in the monoclinic phase of $Sc_2(WO_4)_3$ has not been studied, Evans and Mary⁶ have shown that the low-temperature monoclinic phase of scandium molybdate has a positive thermal expansion. If the behavior is the same for the high-pressure phase too (due to the structural similarity), then it is doubtful that in this compound the pressure-induced amorphization is related to negative thermal-expansion behavior. The proposed relation between NTE and pressure-induced amorphization has also been debated in a recent paper.²⁹ Purely structurally, we note that in the higher-density monoclinic phase, the reduced compressibility implies an increase in the repulsive forces between various polyhedra. Hence on further increase of pressure the polyhedra would try to rearrange so as to minimize the free energy. In most cases, the pressure-induced amorphization is due to the inability of the structure to transform to a stabler crystalline phase due to poor kinetics. It is likely that the present case is similar and structural frustration arises from the inability to cross the energy barrier to the higher-pressure ordered phase and the structure locally deforms to minimize the energy.

IV. CONCLUSIONS

High-pressure Raman and x-ray-diffraction studies on scandium tungstate show that this compound undergoes structural phase transitions around $\sim 0.6 \pm 0.3$ GPa and ~ 1.6 GPa. X-ray-diffraction data are consistent with both the phases being monoclinic with $P2_1/a$ space group. In addition, the second monoclinic phase is a much denser phase. At still higher pressures, at ~ 6.5 GPa this compound becomes disordered, which progressively and irreversibly grows into an amorphous phase. The presence of broadbands of the bending modes centered at 473 cm⁻¹ and the asymmetric and symmetric modes centered at 955 cm⁻¹ also indicates that the constituent polyhedra are highly distorted, and the lowering of frequency of the high-frequency band with respect to that at ambient conditions suggests that the effective W—O coordination may be higher at these pressures.

The structural changes up to ~ 1.6 GPa are found to be reversible, which can be rationalized in terms of the monoclinic phase being related to the initial phase through small rotations of the WO₄ tetrahedra, which spring back on release of pressure.

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