Pressure-induced amorphization and decomposition in ZrV_2O_7: A Raman spectroscopic study

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In situ high-pressure Raman spectroscopic studies on ZrV_2O_7 suggest growth of disorder in the high-pressure orthorhombic phase, inferred from the excessive broadening of Raman peaks, and the sample gradually turns amorphous above 4 GPa. The samples pressure cycled from 10 GPa exhibit irreversible amorphization. On the other hand, the spectrum of the sample pressure cycled from 4 GPa is found to have all the characteristic peaks of V_2O_5 indicating a possible decomposition of the compound into a mixture of simple oxides. A partial decomposition is indeed confirmed from the x-ray-diffraction pattern of the recovered sample. A large decrease of the intensity of the VO_4 tetrahedral stretching modes is consistent with the possible coordination change of vanadium, from fourfold in ZrV_2O_7 to fivefold in V_2O_5. Nucleation of nano-/poorly crystallized grains of the daughter phase even *at ambient temperature* is understood as due to the existence of the fivefold coordinated crystalline phase, V_2O_5.

I. INTRODUCTION

Pressure-induced solid-state decomposition of compounds into mixtures of dense-packed daughter phases, reported in many systems such as Fe_2SiO_4,[1] $CuGeO_3$,[2] Mg_2SiO_4,[3] $Bi_4(GeO_4)_3$,[4] $Zr(WO_4)_2$,[5] $Sc_2(MoO_4)_3$,[6] $Zr(MoO_4)_2$,[7] CO_2,[8] and $KHSO_4$,[9] has been found to occur only at elevated temperature, except in $KHSO_4$. This is because the nucleation and growth of macroscopic phases of the daughter compounds require considerable atomic diffusion that is possible only at elevated temperature. Consequently, at ambient temperature, these compounds invariably exhibit pressure-induced amorphization (PIA) as the decomposition is kinetically hindered.[10] $KHSO_4$ decomposes at ambient temperature as one of the daughter compounds, H_2SO_4, happened to be liquid.[9] The report of the specific volume of the $Zr(WO_4)_2$ in the pressure-amorphized state being the same as that for a mixture of ZrO_2 and $2WO_3$ strongly suggested that the pressure-amorphized state is a precursor to decomposition.[11] Here, we report the evidence of pressure-induced solid-state decomposition occurring at ambient temperature in ZrV_2O_7, a network structure that exhibits negative thermal expansion above 373 K.

Several network structures such as $Zr(WO_4)_2$,[12] $Zr(MoO_4)_2$,[13] $Sc_2(MoO_4)_3$,[6] $Sc_2(WO_4)_3$,[14] $Lu_2(WO_4)_3$,[15] and $Y_2(WO_4)_3$ (Ref. 16) that exhibit negative thermal expansion (NTE) are found to undergo amorphization at high pressure. Although a correlation between the NTE and PIA has often been mentioned,[14,15,17–19] another network structure $Al_2(WO_4)_3$ that shows positive thermal expansion also undergoes PIA.[20] In this context, it is of interest to examine other similar network structures such as ZrV_2O_7 (Refs. 21 and 22) and HfV_2O_7 (Ref. 23) that exhibit PIA. The high-temperature cubic phase of ZrV_2O_7 bears structural similarities with the cubic $Zr(WO_4)_2$ and exhibits NTE.[24] Instead of separated pairs of WO_4 ions, here, two VO_4 tetrahedra share an oxygen atom at a common vertex to form V_2O_7 structural unit. Consequently, the main difference with respect to zirconium tungstate is that all the corners of the polyhedra are

corner linked, leaving no nonbridging (terminal) oxygen atoms.[25] At room temperature, the structure is a $3 \times 3 \times 3$ supercell of the high-temperature phase and exhibits positive thermal expansion. Recently, powder x-ray-diffraction studies of a related compound HfV_2O_7 at high pressure revealed that the diffraction intensities corresponding to the parent phase become weak over the pressure range 3.3–4.0 GPa along with the appearance of a new set of peaks; however, the transformation was rather incomplete leading to a gradual loss of long-range order.[23] Earlier, high-pressure x-ray powder-diffraction studies of ZrV_2O_7 have shown that above 1.4 GPa, the compound exhibits transition to an orthorhombic structure,[21] and subsequently becomes amorphous above 4 GPa. The high-pressure phases have not been examined using Raman spectroscopy, which is a useful technique for probing disorder of structural units and for identifying presence of different chemical compositions, even if the transformation is only partial.[9] In this work, we report the results of *in situ* high-pressure Raman spectroscopic study of ZrV_2O_7, synthesized using solid-state reaction method. The Raman spectra of the samples recovered after pressure cycling to different pressures are compared with those of the starting sample and V_2O_5. X-ray-diffraction pattern of the sample recovered after pressure cycling to 4 GPa is analyzed for possible presence of decomposition products such as V_2O_5 and ZrO_2. The occurrence of pressure-induced decomposition in this system at ambient temperature is discussed in terms of existence of crystalline phases with higher coordination number.

II. EXPERIMENTAL DETAILS

Zirconium vanadate was synthesized by solid-state reaction method using stoichiometric mixture of ZrO_2 (purity 99.99%) and V_2O_5 (99.8%). The mixture was initially calcined at 700 °C for 72 h with several intermittent grinding. Final calcination was carried out at 750 °C for 24 h. The x-ray-diffraction pattern was recorded using STOE diffractometer using Cu Kα radiation. Raman-scattering measure-
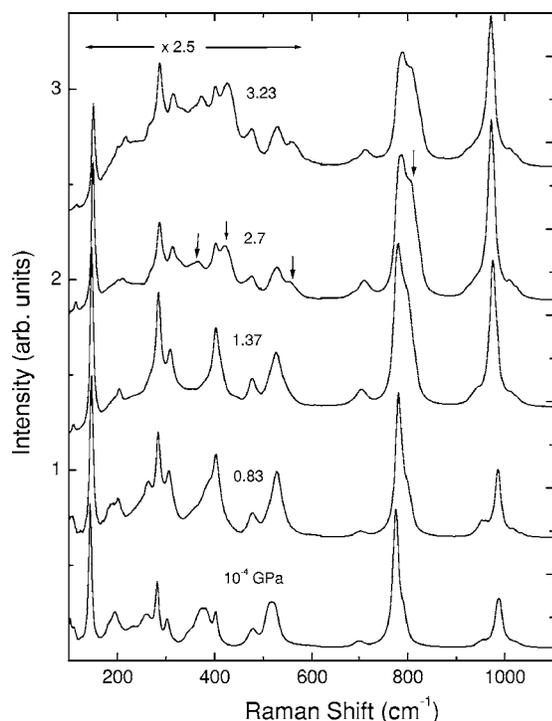
FIG. 1. Raman spectra of ZrV_2O_7 at various pressures. Intensities in the range $100-620$ cm^{-1} have a scale factor of 2.5 and vertically shifted. Arrows indicate the modes that gain in intensity in the orthorhombic phase above 1.4 GPa.

FIG. 2. (a),(b) Pressure dependence of mode frequencies in ZrV_2O_7. The solid lines are linear fit to the data. Many new modes appear and some of the modes corresponding to the cubic phase decrease in intensity and could not be observed above the phase-transition pressure of 1.4 GPa. Arrows indicate transition pressures corresponding to the orthorhombic and amorphous phases.

ments at high pressure were carried out using a diamond-anvil cell (DAC), Diacell Products, UK, Model B-05. A 4:1 methanol-ethanol mixture was used as pressure transmitting medium. The pressure inside the cell was measured using the standard ruby fluorescence technique. Raman spectrum of polycrystalline ZrV_2O_7 from inside the DAC was excited using 532 nm line of power $\sim$15 mW. Scattered light was analyzed using a homebuilt 0.9 m single monochromator, coupled with a super notch filter and detected by a cooled charge coupled device (Andor Technology). The entrance slit is kept at 50 μm, which gives a spectral bandpass of 3 cm^{-1}.

III. RESULTS AND DISCUSSION

X-ray-diffraction pattern confirmed the formation of a single-phase material and it could be fitted to a cubic unit cell with a lattice parameter of 8.774(3) Å, in good agreement with the reported value of 8.777 Å.[24] Figure 1 shows the evolution of Raman spectrum of ZrV_2O_7 at high pressures. The lowest-frequency mode observed in the present studies appears around 144 cm^{-1}. In the spectral range $180-580$ cm^{-1}, there are several overlapping Raman bands and could be fitted to 11 distinct bands at ambient conditions using Lorentzian line-shape function. The high-frequency range between 680 and 1100 cm^{-1} was fitted to five bands centered around 699, 775, 792, 987, and 1020 cm^{-1} at ambient conditions. Around 1.4 GPa, the pressure corresponding to the reported cubic-orthorhombic transition,[21] intensities of some of the bands such as those around 260 and 383 cm^{-1} reduce while new modes around 365, 418, and 545 cm^{-1}

grow in intensity. In the high-frequency region, there is a noticeable change in the relative intensities of the 775 and 987 cm^{-1} bands (Fig. 1). These spectral changes are gradual unlike in ZrW_2O_8 (Ref. 1) wherein the Raman spectrum changes abruptly across the cubic-orthorhombic transition. It may be recalled that in the case of ZrW_2O_8, this transition involves tilting of the WO_4 tetrahedra[26] off the threefold axis together with the inversion of one-third of the W_2O_8 units. This transition is also accompanied by a volume change of about 5%.[26] However, in ZrV_2O_7, x-ray-diffraction studies[21] showed that the volume discontinuity across this transition is rather small, about 0.88%.[27] This is perhaps the reason for less pronounced discontinuities in the phonon spectrum as compared to zirconium tungstate. Figure 2 shows the pressure dependence of mode frequencies in ZrV_2O_7. One can see that most of the mode frequencies increase with increasing pressure. The V-O stretching band around 987 cm^{-1} and the weak sideband at 1020 cm^{-1} decrease in frequency with an increase in pressure and can be understood as due to an increase in V-O bond length evolving toward a higher coordination. A few modes in the tetrahedral V-O bending mode region between 400 and 550 cm^{-1} are found to be weakly dependent on pressure. In particular, the mode at 476 cm^{-1} has a weak negative slope of -1.3 cm^{-1}/GPa in the cubic phase, implying softening of O-V-O bending force constants. Some of the modes show significant changes in the pressure dependence of mode frequencies across cubic-orthorhombic phase transition at 1.4 GPa, as may be noted from Fig. 2. There is a continuous evolution of Raman intensities in the orthorhombic phase (Fig. 1). At pressures around 3.9 GPa, most of the Raman bands corresponding to the parent phase disappear abruptly, consistent with the reported amorphization pressure.[21] Figure 3 shows the typical Raman spectra at
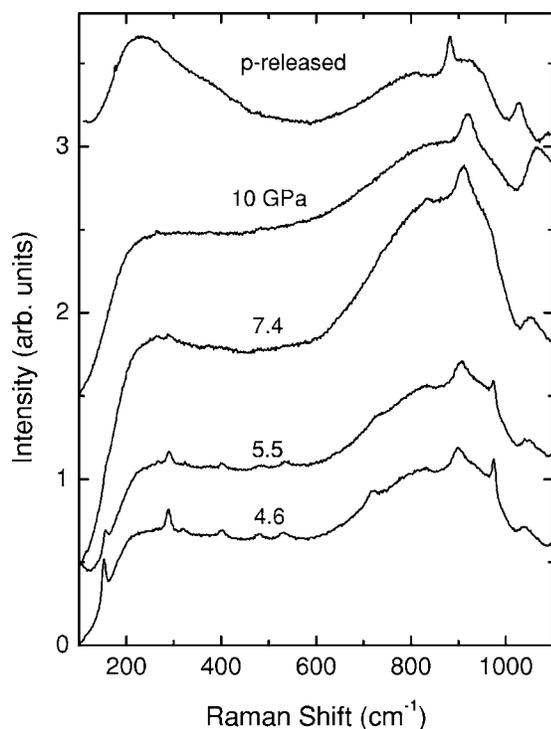
FIG. 3. Raman spectrum of ZrV_2O_7 at various pressures in the amorphous phase above 4 GPa.

FIG. 4. Raman spectrum of ZrV_2O_7: (a) as synthesized, (b) at 3 GPa in p-reducing cycle after reaching 4 GPa, (c) at ambient after p released from 4 GPa, and (d) pure V_2O_5. # indicates spectrum recorded in the p-reducing cycle. Arrows in (a) represent the peaks that are unique to ZrV_2O_7 and are absent or drastically reduced in intensity in the pressure-cycled compound. In curve (b), ∗ indicate the position of Raman peaks corresponding to t-ZrO_2.

pressures above 4 GPa. A very broad band (full width at half maximum more than 300 cm^{-1}) centered around 800 cm^{-1} is observed in the high-frequency region. A few sharp features can be seen riding on the broad background, which become too weak to be observed upon further pressurization up to 10 GPa. The pressure-released spectrum resembles that of the amorphous phase of the compound.

In a few other pressure runs, in which the pressure was reduced from about 4 to 5 GPa, Raman spectrum showed features of a relatively ordered phase upon reducing the pressure. Figure 4 shows the Raman spectrum of the compound in which the pressure is reduced from about 4 GPa, that is, just above the amorphization pressure. Upon reducing the pressure from 4 GPa, one can see that the lower-frequency region of the spectrum showed relatively narrow peaks, while the higher-frequency region exhibited broad bands. It is found that while the spectrum of the pressure-cycled sample has some bands matching with those of the parent compound, there are also some differences. The bands around 260, 345, and 370 cm^{-1} in curve (a) are not observed in (c) and a very large reduction in the intensity of the 775 cm^{-1} mode is noted in the high-frequency region. In fact, the spectrum in the range 100–740 cm^{-1} closely resembles that of V_2O_5,[28] which is also shown in Fig. 4 for the sake of comparison. The peaks in the low- and high-frequency regions appear to be riding over a background similar to that found for the amorphized sample.

In the context of catalysis, V_2O_5-ZrO_2 system has been extensively studied using spectroscopic technique.[29] Formation of ZrV_2O_7 from the mixture of ZrO_2 and V_2O_5 at temperatures above 873 K is characterized by the appearance of the modes at 260, 370, and 775 cm^{-1}.[29] In the present work,

it is the same set of modes that disappear/reduce drastically in intensity in the pressure-cycled samples. The broad feature centered around 790 cm^{-1} [curve (b), Fig. 4] that has been identified to be due to Zr-O-V vibrations[29] suggests that these linkages are highly disordered. The overall matching of the spectrum of the pressure-cycled sample with that of V_2O_5 suggests decomposition of ZrV_2O_7 into V_2O_5 and possibly ZrO_2. It may be pointed out that in V_2O_5, the highest-frequency mode (V-O stretching) at 996 cm^{-1} has a typical width of 6 cm^{-1} at ambient conditions. On the other hand, in ZrV_2O_7, this peak appears at 987 cm^{-1} and has a larger width of ∼18 cm^{-1}. The sharp band observed at 996 cm^{-1} in the pressure-cycled sample has a narrow linewidth (8 cm^{-1}) compared to that in ZrV_2O_7, suggesting that it is indeed due to V_2O_5.

In order to confirm the decomposition of ZrV_2O_7 at high pressure, *ex situ* x-ray-diffraction measurements were also carried out. The compound was subjected to a compressive stress of ∼4.6 GPa in a conventional opposed-anvil apparatus. The Raman spectrum of the sample recovered after pressure release was found to be similar to that of curve (c) in Fig. 4, except for a somewhat larger fraction of ZrV_2O_7, inferred from the intensity of the 775 cm^{-1} mode. Figure 5 shows the x-ray-diffraction patterns of the as-synthesized and pressure-cycled samples. One can see that the recovered pattern has, in addition to the diffraction peaks of ZrV_2O_7, also the peaks corresponding to those of V_2O_5 and tetragonal
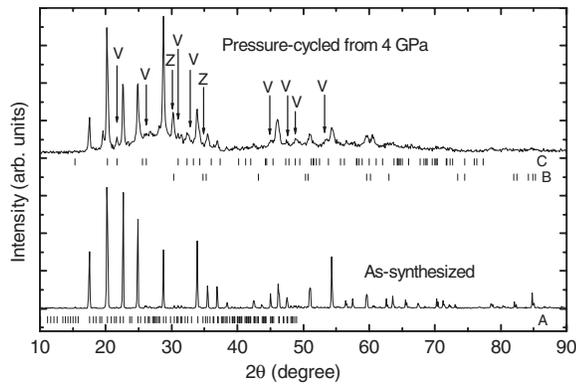
FIG. 5. Powder x-ray-diffraction pattern of ZrV_2O_7 recorded using Cu $K\alpha$ radiation; (a) as synthesized and (b) sample recovered after pressure cycling to about 4.5 GPa. The tick patterns A, B, and C correspond to JCPDS data for ZrV_2O_7 (Ref. [45]: calculated pattern only up to 49°), tetragonal ZrO_2 (Ref. [46]), and V_2O_5 (Ref. [47]), respectively. $3 \times 3 \times 3$ supercell ZrV_2O_7 has a large number of weak (<0.5% intensity) superlattice reflections as evident in the tick pattern. The intense peaks are essentially those of the smaller cubic cell. The peaks labeled as V and Z in the recovered pattern correspond to those of V_2O_5 and tetragonal ZrO_2, respectively. Note that some of the intense peaks such as the one around 2θ $=20.2, 33.9$ can be indexed to both ZrV_2O_7 and V_2O_5.

ZrO_2 (t-ZrO_2), confirming a partial decomposition of ZrV_2O_7. The width of the diffraction lines in the pressure-cycled sample is found to be more compared to that of the as-synthesized sample, suggesting small crystallite sizes of the pressure-cycled sample. In addition, an amorphouslike background centered around 28° also appears to be present. Thus, the pressure-cycled sample appears to be a mixture of the parent compound, V_2O_5, t-ZrO_2, and also amorphous ZrV_2O_7. It may also be pointed out that in the earlier x-ray studies, while the diffraction intensities of the parent phase reduced drastically around 3.9 GPa, new weak peaks were indeed observed even up to 6.4 GPa [Fig. 1(a) in Ref. [21]], suggesting poorly formed crystalline phase, different from that of the parent compound. This is consistent with the present observation, namely, the presence of some crystallinelike Raman peaks even in the amorphous phase at 4.6 GPa (Fig. [3]); frequencies of which are very close to those of V_2O_5, indicating traces of poorly crystallized V_2O_5. Formation of t-ZrO_2 rather than the monoclinic phase in the pressure-cycled sample may be due to the small crystallite size, as the t-ZrO_2 is known to be stable in sizes less than about 30 nm.[30] The weak Raman bands at 262 and 640 cm^{-1} in curve (b) of Fig. [4] closely match with the Raman bands expected for t-ZrO_2.[31] Poorly crystallized ZrO_2 is known to exhibit a broad peak in the range 300–600 cm^{-1} and is attributed to a mixture of monoclinic and tetragonal ZrO_2 phases.[28]

Several reasons have been considered for understanding pressure-induced structural transitions, such as mechanical instability.[32,33] One of them is the repulsive contribution to free energy from nonbonded interactions.[34] This factor is known to be relevant in the temperature-driven transition in ZrV_2O_7; one of the reasons is to avoid certain short O-O distances.[22] Such unfavorable nonbonded distances/

interpolyhedral angles could also arise under compression. Many of the systems that show negative thermal expansion and a tendency for PIA are also reported to have larger compressibilities, often resulting in short nonbonded distances at moderate pressures. For example, in ZrV_2O_7, the volume reduction even at 4 GPa is about 15%, whereas for TiP_2O_7 and ZrP_2O_7, which do not exhibit PIA, these values are 6% and 8%, respectively.[21] Rapid increase in the repulsive contribution due to nonbonded interactions is quite possibly driving the system to transform into structures of smaller volumes/larger coordination. Decomposition of ZrV_2O_7 at high pressure may be rationalized from the volume change considerations.[4] At ambient conditions, the volume of ZrV_2O_7 per f.u. is 169 $Å^3$, whereas for the monoclinic ZrO_2 and orthorhombic V_2O_5, these values are 35.06 and 89.6 $Å^3$, respectively. The fractional decrease in volume upon decomposition $[V_{ZV} - (V_Z + V_V)]/V_{ZV}$ turns out to be quite large, about 26%. Here, V_{ZV}, V_Z, and V_V denote the volume of zirconium vanadate, m-ZrO_2, and V_2O_5, respectively. The t-ZrO_2 has a slightly smaller volume compared to m-ZrO_2. For ZrV_2O_7, reduction in volume upon compression to 4 GPa, estimated from compressibility data, is only 15% which implies that at 4 GPa, the daughter products would still have volume much smaller compared to the parent compound. Decomposition at high pressure is also favorable from coordination considerations. V_2O_5 has a layered structure made up of edge- and corner-sharing VO_5 square pyramids,[35] whereas in the monoclinic ZrO_2, Zr atoms have sevenfold oxygen coordination.[36] Studies on the evolution of the local structure of ZrW_2O_8 in the high-pressure orthorhombic phase[37] revealed that the W-O bond length increased continuously to accommodate higher W-O coordination. However, decomposition in other tungstates and molybdates does not occur at ambient temperature close to the amorphization pressure because the decomposition products (WO_3 and MoO_3) exist in only sixfold coordinated crystalline phases. On the other hand, existence of a fivefold coordinated crystalline phase of V_2O_5 facilitates its occurrence at ambient temperature in zirconium vanadate. In the present case, the decrease in the frequency of the 987 cm^{-1} mode in ZrV_2O_7 strongly points toward the tendency for increased coordination. In short, the local atomic coordination in ZrV_2O_7 around 4 GPa being favorable for formation of V_2O_5 appears to be the important factor for decomposition.

The question, why decomposition does not proceed further when the pressure is increased beyond 4 GPa, still remains to be understood. While solid-state decomposition at high pressures is as such kinetically hindered at ambient temperature,[10] stability of the new daughter phases under these conditions is another factor, which could be responsible for decomposition not proceeding at much higher pressures. High-pressure behavior of m-ZrO_2 has shown that above 4 GPa, the system undergoes a transition to a new orthorhombic phase.[38] Many vanadium oxide-based systems that have VO_4 structural units, as in the case of $Ca_3(VO_4)_2$,[39] $Sr_3(VO_4)_2$, $Ba_3(VO_4)_2$,[40] $LiVO_3$,[41] etc., have been reported to become disordered/amorphous under the application of pressure due to impeded transition to a sixfold coordinated structure. High-pressure investigations of V_2O_5 by Loa *et*

al.[42] have shown that the compound exhibits a transition to a highly disordered phase around 7 GPa, evolving toward a sixfold coordinated structure. One may expect that decomposition from a point wherein the average V-O coordination is 5 would be easier than from a point where the average coordination is 6. In fact, Suzuki *et al.*[43] have shown that crystallization temperature of the orthorhombic V_2O_5 starting from splat-cooled glassy V_2O_5 increases with increasing pressure. The reason for the irreversibility of amorphous phase when *p* cycled from higher pressures could thus be related to a larger barrier for formation of VO_5-like structural units from VO_6 octahedra. Recently, ultrasonic studies have shown softening of elastic constants of zirconium tungstate at high pressure.[44] This essentially implies instability of the structure against a structural phase transition. As both ZrW_2O_8 and ZrV_2O_7 undergo cubic-orthorhombic transition at high pressure, it is likely that ZrV_2O_7 may also exhibit similar softening. The network structures that exhibit NTE invariably have lots of empty spaces between the polyhedral structural units and consequently are loosely packed and have significantly lower density as compared to the oxides from which they are synthesized. Hence, at high pressure, the decomposition of the network structure into a mixture of dense-packed simple oxides becomes energetically favorable. The present results also support this argument.

IV. SUMMARY AND CONCLUSIONS

Raman spectroscopic studies have been carried out on ZrV_2O_7 up to 10 GPa, confirming irreversible pressure-induced amorphization of the compound above 4 GPa. On the other hand, when the pressure is reduced from just above the amorphization pressure, the Raman spectrum of the pressure-cycled sample shows evidence for decomposition of the compound into V_2O_5 and ZrO_2. Decomposition is also confirmed from the *ex situ* x-ray-diffraction measurements, and the products are identified to be V_2O_5 and tetragonal ZrO_2. These results strongly suggest that in ZrV_2O_7, pressure-induced amorphization is indeed driven by kinetically hindered decomposition. Though pressure-induced solid-state decomposition usually requires elevated temperature, ZrV_2O_7 appears to be unique that a partial decomposition proceeds even at ambient temperature. The decomposition at ambient temperature is believed to have been facilitated by the existence of a fivefold coordinated crystalline phase of the daughter product V_2O_5.

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[1] W. A. Bassett and L. C. Ming, Phys. Earth Planet. Inter. **6**, 154 (1972).

[2] W. Hegenbart, F. Rau, and K. J. Range, Mater. Res. Bull. **16**, 413 (1981).

[3] T. Kato, T. Kubo, H. Morishima, E. Ohtani, A. Suzuki, D. Yamazaki, K. Mibe, T. Kikegawa, and O. Shimomura, Rev. High Pressure Sci. Technol. **7**, 119 (1998).

[4] A. K. Arora, T. Yagi, N. Miyajima, and R. Gopalakrishnan, J. Phys.: Condens. Matter **16**, 8117 (2004).

[5] J. M. G. Amores, U. Amador, E. Moran, and M. A. A. Franco, Int. J. Inorg. Mater. **2**, 123 (2000).

[6] A. K. Arora, T. Yagi, N. Miyajima, and T. A. Mary, J. Appl. Phys. **97**, 013508 (2005).

[7] A. Grzechnik and W. A. Crichton, Solid State Sci. **4**, 1137 (2002).

[8] O. Tschauner, H. K. Mao, and R. J. Hemley, Phys. Rev. Lett. **87**, 075701 (2001).

[9] A. K. Arora and T. Sakuntala, High Press. Res. **17**, 1 (2000).

[10] A. K. Arora, Solid State Commun. **115**, 665 (2000).

[11] A. K. Arora, V. S. Sastry, P. Ch. Sahu, and T. A. Mary, J. Phys.: Condens. Matter **16**, 1025 (2004).

[12] T. R. Ravindran, A. K. Arora, and T. A. Mary, Phys. Rev. Lett. **84**, 3879 (2000).

[13] D. V. S. Muthu, B. Chen, J. M. Wrobel, A. M. K. Anderson, S. Carlson, and M. B. Kruger, Phys. Rev. B **65**, 064101 (2002).

[14] R. A. Secco, H. Liu, N. Imanaka, and G. Adachi, J. Mater. Sci. Lett. **20**, 1339 (2001).

[15] H. Liu, R. A. Secco, N. Imanaka, and G. Adachi, Solid State Commun. **121**, 177 (2002).

[16] S. Karmakar, S. K. Deb, A. K. Tyagi, and S. M. Sharma, J. Solid State Chem. **177**, 4087 (2004).

[17] R. J. Speedy, J. Phys.: Condens. Matter **8**, 10907 (1996).

[18] C. A. Perottoni and J. A. H. da Jornada, Science **280**, 886 (1998).

[19] S. K. Sikka, J. Phys.: Condens. Matter **16**, S1033 (2004).

[20] N. Garg, V. Panchal, A. K. Tyagi, and S. M. Sharma, J. Solid State Chem. **178**, 998 (2005).

[21] S. Carlson and A. M. K. Anderson, J. Appl. Crystallogr. **34**, 7 (2001).

[22] R. L. Withers, J. S. O. Evans, J. Hanson, and A. W. Sleight, J. Solid State Chem. **137**, 161 (1998).

[23] U. L. C. Hemamala, F. El-Ghussein, A. M. Goedken, B. Chen, Ch. Leroux, and M. B. Kruger, Phys. Rev. B **70**, 214114 (2004).

[24] A. K. A. Pryde, K. D. Hammonds, M. T. Dove, V. Heine, J. D. Gale, and M. C. Warren, J. Phys.: Condens. Matter **8**, 10973 (1996).

[25] N. Khosrovani, A. W. Sleight, and T. Vogt, J. Solid State Chem. **132**, 355 (1997).

[26] J. D. Jorgensen, Z. Hu, S. Teslic, D. N. Argyriou, S. Short, J. S. O. Evans, and A. W. Sleight, Phys. Rev. B **59**, 215 (1999).

[27] From the tabulated values of cell parameters at various pressures (Ref. [18]), volumes of ZrV_2O_7 in the cubic phase at 1.38 GPa and the orthorhombic phase at 1.58 GPa were calculated to be 622.0 and 610.5 $Å^3$, respectively. Extrapolated volume of the cubic phase at 1.58 GPa is 615 $Å^3$ and the discontinuity at 1.58 GPa is estimated to be 0.88%.

[28] J. R. Sohn, J. S. Han, and J. S. Lim, Mater. Chem. Phys. **91**, 558 (2005).

[29] L. L. Male, H. G. Niessen, A. T. Bell, and T. D. Tilley, J. Catal. **194**, 431 (2000).

[30] G. Baldinozzi, D. Simeone, D. Gosset, and M. Dutheil, Phys. Rev. Lett. **90**, 216103 (2003).

[31] T. Merle, R. Guinebretiere, A. Mirgorodsky, and P. Quintard, Phys. Rev. B **65**, 144302 (2002).

[32] F. Sciortino, U. Essmann, H. E. Stanley, M. Hemmati, J. Shao, G. H. Wolf, and C. A. Angell, Phys. Rev. E **52**, 6484 (1995).

[33] N. Choudhury and S. L. Chaplot, Phys. Rev. B **73**, 094304 (2006).

[34] S. K. Sikka and S. M. Sharma, Curr. Sci. **63**, 317 (1992).

[35] R. Enjalbert and J. Galy, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **C42**, 1467 (1986).

[36] D. K. Smith and H. W. Newkirk, Acta Crystallogr. **18**, 983 (1965).

[37] T. Varga, A. P. Wilkinson, A. C. Jupe, C. Lind, W. A. Basset, and C.-S. Zha, Phys. Rev. B **72**, 024117 (2005).

[38] O. Ohtaka, H. Fukui, T. Kunisada, T. Fujisawa, K. Funakoshi, W. Utsumi, T. Irifune, K. Kuroda, and K. Kikegawa, Phys. Rev. B **63**, 174108 (2001).

[39] A. Grzechnik, Solid State Chem. **139**, 161 (1998).

[40] A. Grzechnik and P. F. McMillan, J. Solid State Chem. **132**, 156 (1997).

[41] Z. X. Shen, C. W. Ong, M. H. Kuok, and S. H. Tang, J. Phys.: Condens. Matter **7**, 939 (1995).

[42] I. Loa, A. Grzechnik, U. Schwarz, K. Syassen, M. Hanfland, and R. K. Kremer, J. Alloys Compd. **317**, 103 (2001).

[43] T. Suzuki, S. Saito, and W. Arakawa, J. Non-Cryst. Solids **24**, 355 (1977).

[44] C. Pantea, A. Migliori, P. B. Littltwood, Y. Zhao, H. Ledbetter, J. C. Lashley, T. Kimura, J. Van Duijn, and G. R. Kowach, Phys. Rev. B **73**, 214118 (2006).

[45] Powder Diffraction File, Card No. 87-0562, JCPDS (International Center for Diffraction Data, Newton Square, Penyslvania).

[46] Powder Diffraction File, Card No. 50-1089, JCPDS (International Center for Diffraction Data, Newton Square, Penyslvania).

[47] Powder Diffraction File, Card No. 41-1426, JCPDS (International Center for Diffraction Data, Newton Square, Penyslvania).