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Investigation of the phase stability of LuVO₄ at high pressure using powder x-ray diffraction measurements and lattice dynamical calculations

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Abstract

High pressure angle dispersive x-ray diffraction measurements are carried out on LuVO₄ in a diamond anvil cell up to 33 GPa at the Elettra synchrotron radiation source. The measurements show that LuVO₄ undergoes a zircon to scheelite structure phase transition with a volume change of about 11% at about 8 GPa. A second transition to a monoclinic fergusonite structure occurs above 16 GPa. The data are also recorded while releasing the pressure, and indicate that the scheelite phase is metastable under ambient conditions. The equations of state and changes in internal structural parameters are reported for various phases of LuVO₄. Lattice dynamical calculations based on a transferable interatomic potential were also performed and the results support the stability of the scheelite structure at high pressures. The calculated structure, equation of state and bulk modulus for all the phases are in fair agreement with the experimental observations.

1. Introduction

Insulating RVO₄ (R—rare earth) compounds with zircon type structure [1] have isolated VO₄ tetrahedra, which surround the R atom to form RO₈ dodecahedra. VO₄ and RO₈ extend parallel to the *c*-axis and are chain joined laterally by edge-sharing RO₈. R ions are expected to retain much of the non-interacting ionic character due to the absence of mediation by conduction electrons. These rare earth vanadates are of considerable theoretical and technological interest [2]. All of them possess the same zircon structure but with the population of the 4f sub-shell changing monotonically (with

the exception of CeVO₄). The series allows study of the interesting changes in covalent effects on 4f occupancy. When doped with suitable ions they serve as excellent host materials for laser application. The comparable crystal field splitting and Hund's correlation energy that can flip the ionic spin, the metal–insulator transition resulting from the lifting of orbital degeneracy by a Jahn–Taylor (J–T) type mechanism, charge ordering or inhibition of electron hopping by antiferromagnetic ordering or band broadening etc are expected to yield a rich variety in the high pressure behaviour. In fact the 4f spin–lattice coupling can be recognized through the contrasting behaviour of PrVO₄ and LuVO₄. A strong coupling may lead to a cooperative J–T transition to lower symmetry and ordering of R spins. Strong anomalies in the temperature dependence of the lattice parameters and/or elastic constants in RVO₄

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Table 1. The structural parameters of the various phases of LuVO₄ as obtained from the Rietveld refinements of the experimental data and model calculations.

(a) Structural parameters of zircon LuVO ₄ at ambient pressure, space group $I4_1/amd$, $Z = 4$ (residuals [23] $R_{wp} = 12.2\%$, $R_p = 9.1\%$, $R(F^2) = 29.2\%$, 96 reflections)							
		Expt.			Calc.		
a (Å)			7.0266(3)			6.791	
c (Å)			6.2329(4)			6.432	
	Site	x	y	z	x	y	z
Lu	4a	0	0.75	0.125	0	0.25	0.125
V	4b	0	0.25	0.375	0	0.25	0.375
O	16h	0	0.439(6)	0.201(6)	0	0.427	0.219
(b) Structural parameters of scheelite LuVO ₄ at 12.9 GPa, space group $I4_1a$, $Z = 4$ (residuals $R_{wp} = 4.7\%$, $R_p = 3.6\%$, $R(F^2) = 14.9\%$, 108 reflections)							
		Expt.			Calc.		
a (Å)			4.8949(7)			4.864	
c (Å)			10.6841(31)			10.799	
	Site	x	y	z	x	y	z
Lu	4a	0	0.25	0.625	0	0.25	0.625
V	4b	0	0.25	0.125	0	0.25	0.125
O	16h	0.270(8)	0.606(3)	0.546(6)	0.259	0.611	0.552
(c) Structural parameters of fergusonite LuVO ₄ at 32.9 GPa, space group $I2/a$, $Z = 4$ (residuals $R_{wp} = 1.7\%$, $R_p = 1.3\%$, $R(F^2) = 4.6\%$, 161 reflections)							
		Expt.					
a (Å)			4.878(3)				
b (Å)			10.360(6)				
c (Å)			4.689(4)				
β (deg)			94.59(4)				
	Site	x	y	z			
Lu	4e	0.25	0.626(3)	0			
V	4e	0.25	0.129(7)	0			
O1	8f	0.905(18)	0.955(11)	0.226(20)			
O2	8f	0.453(11)	0.213(6)	0.767(40)			

(R—Pr, Nd, Tb, Dy, Ho, Tm, Yb) are due to such a quadrupole–lattice strain coupling [3].

Several zircon type materials transform [4–10] to a pressure quenchable scheelite type with approximate 10% volume reduction due to more efficient polyhedral packing when pressurized well above the equilibrium transition pressure. The transition is characterized by accompanying change in the electronic structure and lattice disorder. Among the vanadates, only YVO₄ has been investigated under pressure [10]. Under pressure, in YVO₄, the internal mode frequencies of the VO₄ tetrahedra decrease and the optical absorption edge shifts (by 1.1 eV) to lower energy due to electronic structure change dominantly occurring in VO₄. The oxygen displacement is highly anisotropic with the maximum amplitude perpendicular to the edge shared between VO₄ and RO₈. It exhibits a zircon to scheelite type phase transition at 8.5 GPa. On further increase of pressure to 26.5 GPa, the scheelite phase undergoes another pressure-driven phase transition. A possible structure candidate is the monoclinic fergusonite structure. The fergusonite structure has also been identified as the first high pressure phase of scheelite structure compounds [11] YLiF₄, BaWO₄, PbWO₄ etc. Molecular dynamics simulations have recently been employed to successfully identify the mechanism [12] of the scheelite to fergusonite phase transition in YLiF₄.

Here we report the results of investigations of high pressure phase stability of LuVO₄ using synchrotron-based x-ray diffraction and lattice dynamical calculations. We observe a zircon to scheelite phase transition above 8 GPa. The electrical resistance was also measured across this transition to look for any electronic structure change. Scheelite phase transforms to monoclinic fergusonite structure near 16 GPa. Results of lattice dynamical calculations that identify the stability region of scheelite structure in LuVO₄ are also presented. The details of measurements and the lattice dynamics calculations are given respectively in sections 2 and 3. The results and discussion, and conclusions are presented in sections 4 and 5, respectively.

2. Experimental details

LuVO₄ was prepared by heating appropriate amounts of dried Lu₂O₃ (Indian Rare Earth Ltd 99%) and V₂O₅ (Alfa 99%) at 800 °C for 18 h; this was followed by remixing and heating in pellet form, at 975–1000 °C for 24 h. Samples obtained after the second heat treatment were characterized by powder x-ray diffraction. The cell constants and atomic coordinates refined from the data recorded at ambient pressure for the zircon phase of LuVO₄ are in close agreement (table 1) with the reported data¹.

Angle dispersive x-ray diffraction (ADXRD) measurements were carried out at the powder x-ray diffraction beam line of ELETTRA Synchrotron source, Trieste, Italy. For high pressure measurements, fine powdered samples of LuVO₄ were loaded in a Mao–Bell type diamond anvil cell (DAC). A pair of diamond anvils with culet diameter of about 400 μm was used in the DAC. A hardened steel gasket with a central hole of diameter of 100 μm and thickness 50 μm contained the sample and the x-ray beam was collimated by an 80 μm diameter pinhole. A methanol–ethanol (4:1) mixture was used as the pressure transmitting medium. The pressure was determined *in situ* by using platinum powder mixed with the sample as pressure calibrant and the estimated error in pressure is 0.2 GPa. The wavelength of the x-rays employed and the sample to image plate distance were respectively calibrated employing Si and Pd diffraction patterns. X-ray powder patterns at various pressures were collected employing x-rays of wavelength 0.648 Å. Images of the powder diffraction rings were collected on a MAR345 image plate detector and read with a resolution of 100 × 100 pixel size. Typical exposure times of 20–30 min were employed for measurements at high pressures. The powder images thus obtained were integrated using the program FIT2D [13] to yield intensity versus 2θ plots. The powder patterns so obtained were further corrected for the absorption by the diamonds. Since the data were unaffected by any texture effects, multi-phase Rietveld refinement was carried out at all pressures to extract the lattice parameters. Patterns were collected up to the highest pressure of 33 GPa.

For measuring electrical resistance up to 10 GPa a Bridgman anvil set-up was employed. Details are given elsewhere [14].

3. Lattice dynamic calculations

Within the quasi-harmonic approximation, lattice dynamic calculations are carried out to derive the dynamical matrix, which is diagonalized, to obtain the phonon frequencies, dispersion, and polarization vectors. The dynamical matrix, which comprises mainly the force constants between various pairs of atoms, can in principle be computed using quantum-mechanical first-principles techniques. However, because of the complex structure involving several atoms in the unit cell, an atomistic approach based on empirical interatomic potentials is used here. The interatomic potentials [15, 16] consist of Coulombic and short ranged Born–Mayer type interaction terms, van der Waals interactions, and the V–O bond-stretching potential. The polarizability of the oxygen atoms is introduced in the framework of the shell model [17]. The empirical parameters are optimized to reproduce the minimum enthalpy for ambient structure. Further, the potential parameters satisfy the condition of dynamic equilibrium and also the computed long wavelength phonon modes [18] are close to their measured values. The same procedure was earlier adopted for ZrSiO₄, and resulted [19] in a consistent description of high pressure phase transitions, thermodynamic properties and inelastic neutron scattering data. The potential that we have developed reproduces the ambient structure (table 1) of the zircon phase of LuVO₄.

The stability of a crystalline phase is largely determined by the minimization of the Gibbs free energy [20]. In the quasi-harmonic approximation, the Gibbs free energy of *n*th phase is given by

$$G_n = \Phi_n + PV_n - TS_n$$

where Φ_n , V_n and S_n refer to the internal energy, lattice volume and the vibrational entropy of the *n*th phase. By minimizing the Gibbs free energy with respect to the structure variables (lattice parameters and atomic positions), while keeping the space group unchanged, the optimum crystal structure and volume at a fixed pressure and zero temperature can be obtained. The free energy changes due to internal energy and volume are predominant in pressure-driven transitions over changes due to vibrational entropy. However we have also included the vibrational contributions in the phase diagram, by calculating the phonon frequencies. For this the phonon modes over the entire Brillouin zone were calculated on a 4 × 4 × 4 mesh throughout the irreducible Brillouin zone to obtain the phonon density of states $g(E)$ and used to derive the Gibbs free energy. The phase diagram is then obtained [20] by comparing the Gibbs free energies in various phases. Computations have been carried out at pressure intervals of 2 GPa. The Gibbs free energy has been calculated as a function of pressure for zircon and scheelite phases of LuVO₄. The calculations were performed using the latest version of the program DISPR [21] developed at Trombay.

4. Results and discussion

4.1. X-ray diffraction measurements at high pressures

The typical angle dispersive x-ray diffraction data collected for LuVO₄ at different pressures are shown in figures 1 and 2. X-ray patterns could be indexed to the zircon structure (space group $I4_1/amd$) up to 8 GPa. Beyond 8 GPa a few broad diffraction peaks that can be indexed to the scheelite phase appear even though the peaks of the zircon phase persist. This indicates a gradual transition to the scheelite (space group $I4_1/a$) phase as in several materials [8, 10] with ambient zircon structure. As the pressure is further increased, the intensity of diffraction peaks corresponding to the zircon phase goes down whereas the diffraction peaks corresponding to scheelite phase build up in intensity. Beyond 12.9 GPa, the diffraction patterns could be indexed with pure scheelite phase. The diffraction lines of the scheelite phase are also very broad as has been observed for several materials that transform [8, 10] to this phase under pressure. The transition is a first-order reconstructive transformation and involves extensive rearrangement of the crystal structure and an approximate volume decrease of 11%. Because of this, the rate at which the transformation occurs is slow, and the zircon and scheelite phases coexist over a large pressure range (8–13 GPa) as has also been observed [10] for YVO₄.

The strong (112) reflection for the scheelite phase develops a shoulder above 16 GPa indicating another phase transition. Similar splitting of the (112) peak is also observed in high pressure diffraction studies [10] of YVO₄, BaWO₄ and

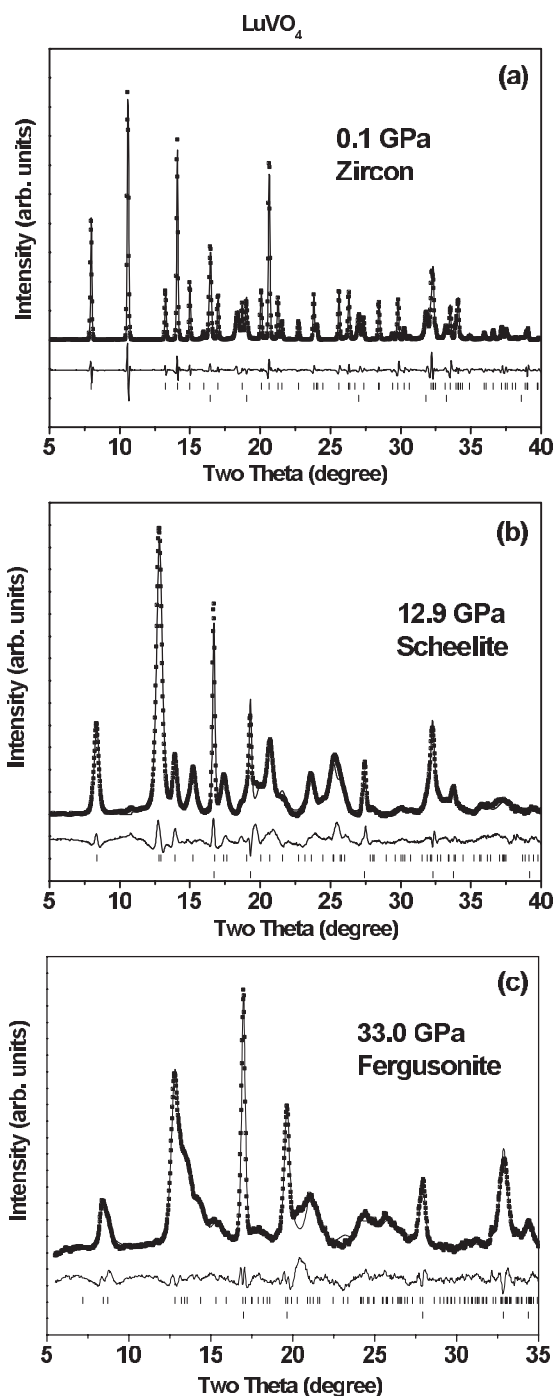


Figure 1. Rietveld refinement of angle dispersive x-ray diffraction patterns of zircon, scheelite and fergusonite phases. The upper and lower ticks correspond to the sample and pressure calibrant (Pt) respectively. X-ray wavelength = 0.648 Å. The polynomial-fitted background has been subtracted from the data.

PbWO_4 also show [11] a scheelite to monoclinic fergusonite ($I2/a$, $Z = 4$) structural phase transition at high pressure. For LuVO_4 also the new pattern gets indexed to this post-scheelite phase. There is a negligible volume change during this transition and hence it should be of displacive type with small atomic movements. This being a continuous second-order transition, it is observed to be fully reversible with

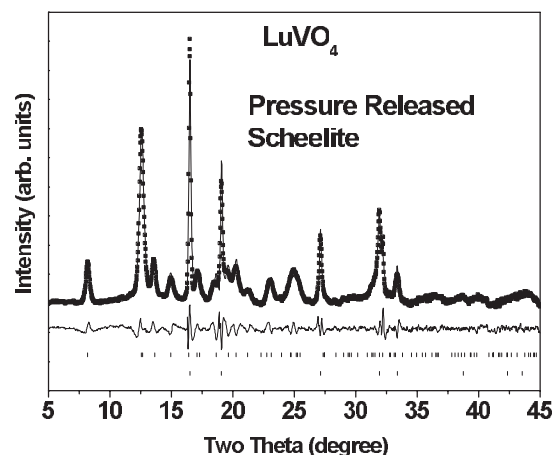


Figure 2. Rietveld refinement of angle dispersive x-ray diffraction patterns of LuVO_4 obtained on release of complete pressure. Upper and lower ticks correspond to the scheelite phase and pressure calibrant (Pt) respectively. X-ray wavelength = 0.648 Å. The polynomial-fitted background has been subtracted from the data.

negligible hysteresis, as expected. We further note that the scheelite phase does not revert to the zircon phase even after the pressure is fully released.

Rietveld refinement of the diffraction patterns of the zircon, scheelite and fergusonite polymorphs was carried out employing the computer programs FULLPROF [22] and GSAS [23] to extract the structural parameters. The parameters which were refined are overall intensity, scaling factor, Chebyshev polynomial background, lattice constants, pseudo-Voigt profile function parameters and atomic fractional coordinates. The Q range of the data does not allow us to extract information about the isotropic temperature factors. These values were kept fixed in the refinement at values predicted from our lattice dynamical calculations. Multi-phase refinement was carried out to take care of pressure calibrant and multi-phase regions of the sample. The result of the refinements for a zircon phase pattern collected at ambient pressure, scheelite phase at 12.9 GPa, monoclinic fergusonite phase at 33 GPa and metastable scheelite phase (pressure released) are shown in figures 1 and 2. The R factors of the refinements shown in figure 1 are given in table 1. At higher pressures, the R factors are very small and do not seem to convey the quality or the goodness of fit. However, it may be noted that the refinements yield meaningful structures [24] and the problem may be due to the general increase in background and reduced counts at the peaks after the transition to the scheelite phase, a condition that can yield low R factors [24].

The lattice parameters and unit cell volumes during increasing pressure are shown in figures 3 and 4 respectively. The data taken (for the scheelite phase) during the pressure release are also plotted (figure 4). It can be seen that for the zircon phase the compressibility along the a -axis is higher than that along the c -axis, while for the scheelite phase the compressibility along the a -axis is smaller than that along the c -axis. For the zircon phase, the structure unit can be considered as a chain of alternating edge-sharing VO_4 tetrahedra and LuO_8 dodecahedra extending parallel to

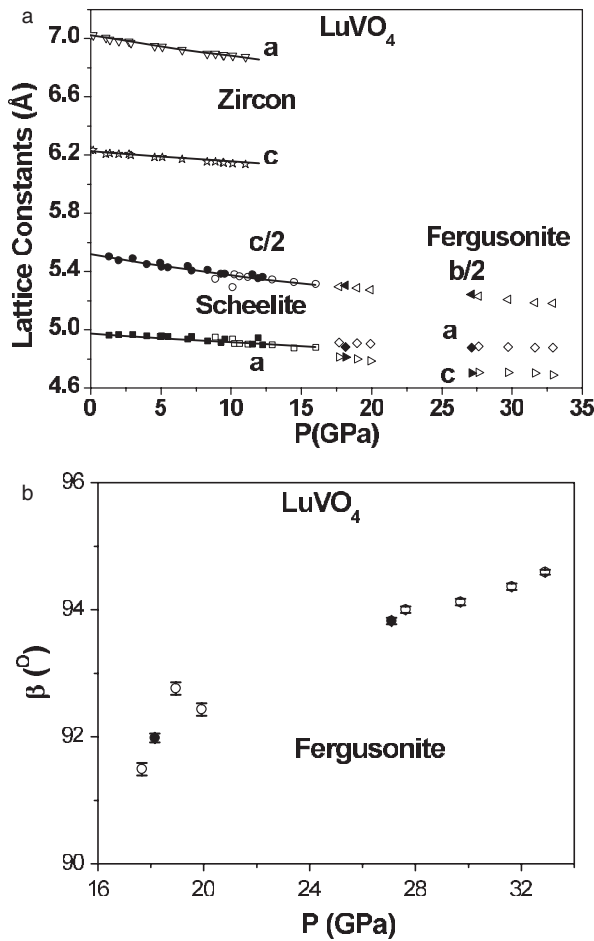


Figure 3. (a) Pressure dependence of the lattice parameters for various phases of LuVO₄. The values from our model calculations have been scaled at $P = 0$ GPa with that determined from a fit to the experimental data and this is shown by solid lines to indicate the pressure variation. The fitted experimental values for the zircon phase are $a_0 = 7.026$ Å, $c_0 = 6.228$ Å and for the scheelite phase are $a_0 = 4.973$ Å, $c_0 = 11.037$ Å. (b) The variation of the monoclinic angle with pressure in the fergusonite phase. The open and closed symbols correspond to the pressure loading and unloading cycles respectively.

the c -axis, with the chain joined along the a -axis by edge-sharing LuO₈ dodecahedra. The scheelite phase consists of VO₄ tetrahedra aligned along the a -axis, whereas along the c -axis LuO₈ dodecahedra are interspersed between the VO₄ tetrahedra. On application of pressure, because of the covalent nature, the V–O bonds remain undistorted while the volume of LuO₈ dodecahedra is reduced. This results in a smaller compressibility along a -axis in the scheelite phase in comparison with the zircon phase. The pressure dependence of the interatomic distances in the zircon and scheelite phases is shown in figure 5. The calculation from the interatomic potential reproduces the observed variation fairly well.

At ambient pressure the difference in volume of zircon and scheelite polymorphs of LuVO₄ is about 11%. Similar change in volume was observed in previous high pressure studies [8, 10] of YVO₄ and ZrSiO₄. The pressure–volume

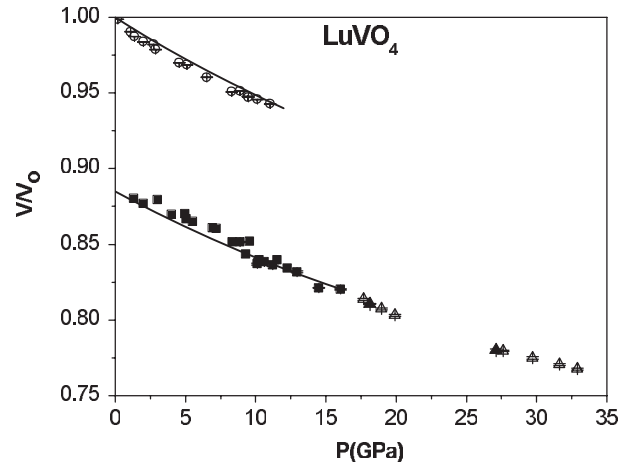


Figure 4. Pressure dependence of the volume for various phases of LuVO₄. Open and closed symbols correspond to the pressure loading and unloading cycles respectively. The solid line corresponds to the computed values (and not a fit to data) from the lattice dynamical calculations that have been normalized by the fitted volume of the zircon phase at $P = 0$, $V_0 = 307.44$ Å³.

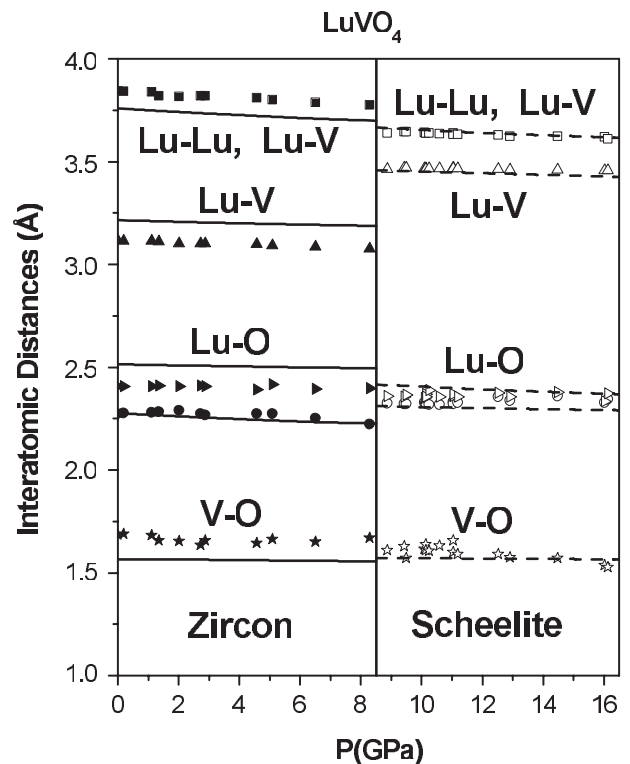


Figure 5. Pressure dependence of interatomic distances in LuVO₄. The solid and dashed lines correspond to the calculation from the interatomic potential in the zircon and scheelite phases respectively.

data were fitted with a Birch equation of state [25] in order to determine the bulk modulus B at zero pressure and its pressure derivative B' . The parameters obtained are $B = 147$ GPa, $B' = 4.3$ for the zircon phase and $B = 194$ GPa, $B' = 5.3$ for scheelite phase. The values for the scheelite phase are obtained by fitting to the pressure unloading data from 12 GPa.

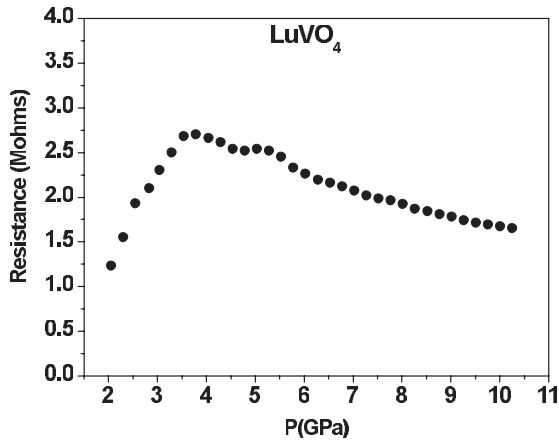


Figure 6. Electrical resistance as a function of pressure for the zircon phase of LuVO₄.

4.2. Electrical resistance measurements

The results of electrical resistance measurements on the zircon phase of LuVO₄ up to 10 GPa are shown in figure 6. There is an initial increase in resistance with pressure indicative of an increase in band gap with pressure. However across the region of structural transition, there is no discontinuous change in resistance. Thus there is no change in band gap due to the structural transition. The absence of any major electronic rearrangement implies that computations based on empirical potentials should reproduce the measured structural behaviour.

4.3. Raman and infrared modes, crystal structure and phase stability from lattice dynamical calculations

In the following, we compare the results for computed Raman and infrared modes, phase stability, structural parameters and pressure–volume relations with measurements.

The comparison between the calculated and experimental [18] long wavelength Raman and infrared modes for LuVO₄ in the zircon phase is shown in figure 7. The average deviation of our calculations from the experimental data is 5.7%. The large LO–TO splitting for the A_{2u} and E_u modes has been correctly described by our calculation.

The calculated free energies as a function of pressure show that beyond 8 GPa at 300 K, the scheelite phase has a lower free energy, indicating the greater stability of this phase (figure 8). The only measured transition pressure is at 300 K (ELETTRA do not have a facility for varying temperature at high pressure), which is also included in figure 8. The onset of a first-order phase transition from zircon to scheelite phase is well reproduced from our calculations. As expected, the greater stability of scheelite phase at high pressures arises primarily due to its lower volume. The calculated values of the atom position parameters for the polymorphs of LuVO₄ are in fair agreement with the experimental values (table 1).

The scheelite to fergusonite phase transition is of second order, and therefore a free energy crossover as in figure 8 is not expected. However, the calculations for the scheelite phase based on the present interatomic potential do not show

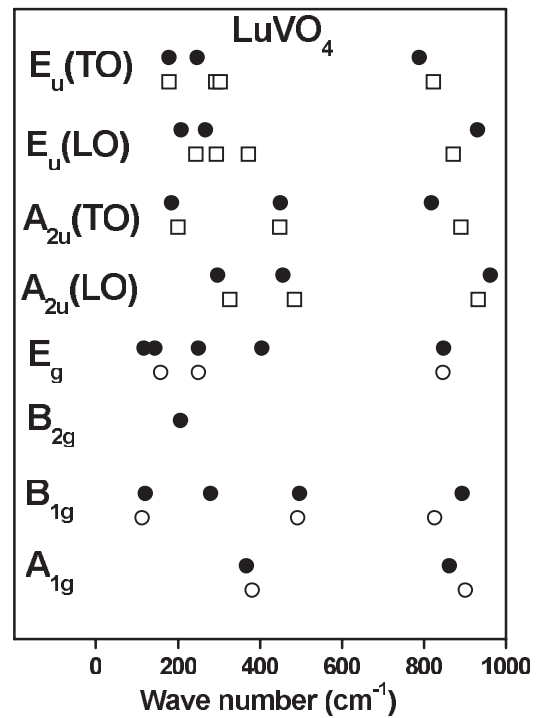


Figure 7. Comparison of the calculated (filled circles) and experimental long wavelength Raman [18a] (open circles) and infrared [18b] modes (open squares) for various group-theoretical representations in cm⁻¹ units (1 cm⁻¹ = 0.124 meV) for LuVO₄ in the zircon phase.

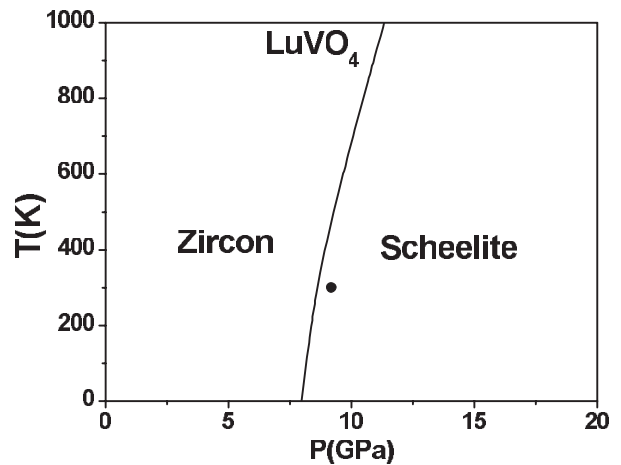


Figure 8. The calculated phase diagram of LuVO₄ as obtained (line) from comparison of the calculated free energies for the zircon and scheelite phases of LuVO₄. The experimentally observed zircon to scheelite phase transition at 300 K is shown by a filled circle.

any soft phonon mode that could lead to the distortion of the scheelite structure up to a pressure of 100 GPa. Recent *ab initio* calculations [11a] for the high pressure phase transformations in BaWO₄, and PbWO₄ also could not reproduce the scheelite to fergusonite phase transition. Though the measured lattice parameter data for LuVO₄ show that the monoclinic distortion of the scheelite structure is small and continuous, the soft *P*–*V* relation of the fergusonite phase implies bond reconstruction.

The crystal structures of the zircon and scheelite phases of LuVO₄ at different pressures, as calculated by minimization of the free energy, reproduce the anisotropic behaviour of the compression of lattice parameters a and c (figure 3). The computed volume as a function of pressure for LuVO₄ in the zircon and scheelite phases plotted in figure 4 is in reasonable agreement with measurements. The calculated volume change of about 11% from zircon to scheelite phase transition is in good agreement with experimental observation (figure 4).

The bulk modulus and its pressure derivative have been determined by fitting the calculated volume data at different pressures to the Murnaghan equation of state [25]. The calculated values of the bulk modulus and its pressure derivative are $B = 166$ GPa and $B' = 4.8$ for zircon phase and $B = 173$ GPa and $B' = 5.3$ for scheelite phase. These values are in fair agreement with the measurements given in section 4.1.

5. Conclusions

Results of investigation on the structural stability of LuVO₄ up to 33 GPa are reported. The results support the existence of a zircon to scheelite type first-order phase transition in zircon-structured LuVO₄. The lattice dynamical calculations support the experimental observations. The scheelite to monoclinic fergusonite transition is found to take place at about 16 GPa with no evidence of any further structural phase transition up to 33 GPa. The scheelite phase can be pressure quenched.

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