Thermodynamic Properties and Equation of State of Zircon $ZrSiO_4$

R. Mittal, S.L. Chaplot, N. Choudhury and C.K. Loong*

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Solid State Physics Division, Bhabha Atomic Research Centre
Trombay, Mumbai 400 085, INDIA

*IPNS, Argonne National Laboratory, Illinois 60439, U.S.A.

Abstract

The silicate mineral zircon is a host material for radioactive materials in the earth's crust. Lattice dynamical calculations have been carried out to understand its thermodynamic properties and high pressure behaviour. The calculated phonon density of states, variation of phonon frequencies with pressure and equation of state are in good agreement with the available experimental data. One of the zone centre optic mode involving SiO_4 rotations becomes soft at 47 GPa.

1. Introduction :

The silicate mineral zircon $ZrSiO_4$ is a host mineral for radioactive elements uranium and thorium in the earth's crust and is a natural candidate for usage as a nuclear waste storage material. The elastic constants /1/, long wavelength Raman and infrared modes /2/, specific heat /3/, equation of state /4/ and pressure variation of Raman modes /5/ have been reported for zircon. X-ray diffraction, shock wave and Raman spectroscopic studies /5/ suggest that zircon undergoes a zircon to scheelite type phase transition at high pressure and temperature. Scheelite (space group $I4_1/a$, $Z=2$) is closely related to zircon structure (space group $I4_1/amd$, $Z=2$) and is about 10% more dense than zircon. We have calculated the lattice dynamics of zircon to provide a microscopic understanding of the thermodynamic properties including the equation of state.

2. Lattice dynamical calculations :

The lattice dynamical calculations have been carried out in rigid ion model using the following interatomic potentials /6/:

$$V(r) = \frac{e^2}{4\pi\epsilon_0} \left\{ \frac{Z(k)Z(k')}{r} \right\} + a \exp \left\{ \frac{-br}{R(k)+R(k')} \right\} - \frac{C}{r^6} \quad (1)$$

Where $Z(k)$ and $R(k)$ are respectively, the fractional charge and fractional radius parameter associated with the atom k . $Z(k)$, $R(k)$ and C are empirical parameters, $a=1822$ eV and $b=12.364$ are constants. The first and second terms in eq. (1) are Coulombic and Born Mayer type interactions respectively while the third term is a van der Waals interaction between oxygen atoms only. The parameters of the potential are chosen such that they produce the minimum energy structure close to that

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determined by the diffraction experiments. The radii and charge parameters used in our calculations are given in Table 1. The parameter C is $100 \text{ eV \AA}^6$. Using these potentials, the structures corresponding to minimum free energy are derived as a function of pressure at $T=0$ and are used for lattice dynamical calculations of the various vibrational and thermodynamic properties of zircon.

3. Results and discussion :

The calculated phonon density of states shown in Fig. 1 is in fair agreement with the phonon density of states measured (to be published) at $P=0$ at Argonne National Laboratory. The calculated equation of state including variation of lattice parameters of zircon with pressure are shown in Fig. 2. The calculations have been carried out upto 25 GPa while the experimental data /5/ is available only upto 5 GPa. The bulk modulus and its pressure derivative, and linear compressibilities for lattice parameters calculated from the model are given in Table 2 along with the experimental data. The bulk modulus and its pressure derivative are larger in comparison of those of garnets and olivines. The calculated elastic constants at different pressures are given in Table 3 which shows that C_{66} decreases with increase of pressure. Calculations shows that C_{66} approaches zero at a pressure of about 70 GPa.

The pressure variation of the Raman frequencies is available only for only four modes and that is compared with the model calculations in Fig. 3. The pressure shifts of the observed /5/ Raman modes, for SiO_4 antisymmetric stretch, SiO_4 symmetric stretch, SiO_4 bending and a lattice mode are 4.8 ± 0.2 , 4.1 ± 0.2 , 1.1 ± 0.1 and $3.2 \pm 0.3 \text{ cm}^{-1}/\text{GPa}$ respectively while the calculated values are 5.14, 4.96, 1.65 and 3.24.

At ambient pressure, the phonon density of states extends upto 130 meV. The calculated partial densities of states for the Zr, Si and O atoms are shown in Fig. 1. The translational motions of Zr atoms contribute in the 0-50 meV range while the vibrations of Si and oxygen atoms extend in the full energy range of 0-130 meV. As pressure is increased the peaks in the partial densities of states of Zr, Si and O become broader and shift towards higher energy side. The band gap in the partial density of state of Si around 80 meV increases and a peak at 60 meV in the partial density of state of O vanishes around 47 GPa. At 47 GPa, the compression of Zr-O (4.3%) and Si-O (3.94%) bonds result in the extension of phonon density of states upto 160 meV. At this pressure the motion of Zr atoms contribute in 0-80 meV range (Fig. 1) while the Si and oxygen atoms contribute in the entire 0-160 meV range.

The calculations also shows that a zone centre optically inactive B_{1u} mode involving SiO_4 rotations about the c axis become soft at 47 GPa (Fig. 4) indicating the onset of dynamical instabilities in zircon at high pressure. Experimental data at

this pressure do not exist.

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Figure captions :

- Fig. 1 Calculated pressure variation of the total phonon density of states and the partial density of states for the Zr,Si and O atoms.
- Fig. 2 Equation of state for zircon.
- Fig. 3 Variation of Raman active modes with pressure. At $P=0$, the assignments /2/ of the modes shown by filled and open circles are E_g and A_{1g} respectively.
- Fig. 4 Calculated pressure variation of the phonon branch including the zone centre optically active B_{1u} mode

Table 1 : Potential parameters in zircon

	Zr	Si	O
charge (q_i)	3.40	2.56	-1.49
radii (A^0)	1.88	1.14	1.91

Table 2 : Bulk modulus, its pressure derivative and linear compressibilities of zircon

	Expt./1/	Expt./2/	Calc.
B (GPa)	225	243	247
dB/dP	6.50		6.86
$K_a(GPa^{-1}) \times 10^{-3}$	1.72	1.60	1.45
$K_c(GPa^{-1}) \times 10^{-3}$	0.99	0.95	1.16

Table 3 : Pressure variation of elastic constants of zircon

Elastic constant	Expt./1/ P= 0.0	Calc.		
	(in 10^{11} dynes/cm ²)	P=0.0	P=30 GPa	P=46 GPa
C ₁₁	42.44	46.70	65.71	74.36
C ₃₃	48.96	47.75	64.40	72.10
C ₄₄	11.33	9.64	10.92	11.05
C ₆₆	4.82	3.49	1.88	0.75
C ₁₂	6.92	6.44	13.42	17.30
C ₁₃	15.02	12.83	20.07	24.25

Fig 1

Fig. 4

Fig. 2

Fig. 3