

Lattice dynamical investigations of Raman and infrared wavenumbers of scheelite structured silicates



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ABSTRACT

Lattice dynamical investigations have been made for $MSiO_4$ ($M=Zr, Hf, U$) silicates having space group $I4_1/a$ and symmetry C_{4h}^6 by calculating Raman and infrared wavenumbers. Wilson's GF matrix method has been used with normal coordinate analysis to compute the zone center phonons. The model involves four stretching and six bending force constants for the calculation of wavenumbers. The calculated zone center frequencies show satisfactory agreement with the available experimental results. All the infrared wavenumbers have been computed for $HfSiO_4$ and $USiO_4$ in the present study. A complete assignment of modes for the calculated Raman and infrared frequencies has also been made. An appropriate assignment of infrared modes of $HfSiO_4$ and $USiO_4$ has been made by using theoretical calculations. Evaluation for potential energy distribution for each mode has been made to determine the role of force constants for Raman and infrared wavenumbers.

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1. Introduction

The orthosilicate compounds with composition $MSiO_4$ ($M=Zr, Hf, U$) have gained considerable attention due to extensive range of physical and chemical properties [1, 2]. $ZrSiO_4$ is a ubiquitous accessory mineral that accommodates radioactive elements e.g. uranium and thorium and is an excellent geochronological material for quantitative dating [3]. It acts as a host material by retaining actinides in its structure and shows good potential for immobilization of nuclear materials [4]. Many useful physical and chemical properties of $ZrSiO_4$ make it suitable to be used as a functional material in metallurgical and electronic industry. $ZrSiO_4$ and $HfSiO_4$ with high melting point, low thermal expansion, structural and chemical stability are also found suitable to be used as a high quality refractory material [5]. These minerals have good optical quality, large refractive index and dielectric constant and hence they are a promising material as a gate dielectric in place of conventional SiO_2 [6–8]. $HfSiO_4$ having low compressibility may be used in toughened oxide ceramic compounds [9]. Also, $HfSiO_4$, $ThSiO_4$ and $USiO_4$ emerge to be suitable for fission reactor applications being the materials with effective resistance to radiation. Thus it becomes quite imperative to focus on these orthosilicates towards research related to materials, earth sciences and radioactive waste disposal.

At ambient pressure, these compounds crystallize in zircon phase (space group $I4_1/amd$). The phase transition from zircon to scheelite phase (space group $I4_1/a$) occurs at high pressure [10]. In particular, several studies have been performed both experimentally and theoretically for the zircon phase [11–14], however not much efforts have been paid to the scheelite phase of these materials. The comprehensive study of the scheelite structured silicates is very important since it leads to the understanding of material bonding and phase transitions. Using Raman spectroscopy and XRD, Knittle et al. [15] and Gucsik et al. [16] have reported the vibrational modes of scheelite phase of $ZrSiO_4$ but the band positions and number of bands obtained in their studies are inconsistent. Smirnov et al. [17] have investigated the zone center phonons of $ZrSiO_4$ based on DFT calculations but the mode assignment is incompatible with the earlier studies [15–16]. Manoun et al. [18] determined the Raman spectra of synthetic $HfSiO_4$ which undergoes a change from zircon to scheelite phase at a pressure of 19.6 GPa. Eleven out of thirteen frequencies have been observed in Raman spectra of scheelite structured $HfSiO_4$. Bauer et al. [19] have studied the Raman spectra of $USiO_4$ for pressures upto 35 GPa and observed a phase transition from zircon to scheelite type structure at 15 GPa. The vibrational properties of $USiO_4$ and the phase stability have also been reported by Zhang et al. [20] by X ray diffraction and infrared measurements at high pressure.

The detailed study of the vibrational modes of these scheelites is still lacking in the literature. Neither the complete Raman nor infrared spectra of $HfSiO_4$ and $USiO_4$ have been reported so far to

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the best of our knowledge. Knowledge of these modes is very essential for the investigation of inter and intramolecular interactions using vibrational spectroscopic methods. Therefore in this paper, an attempt has been made to investigate the zone center phonons and mode assignment of $MSiO_4$ ($M = Zr, Hf, U$) using normal coordinate analysis involving four stretching and six bending force constants. All infrared modes in $HfSiO_4$ and $USiO_4$ have been assigned for the first time. GF matrix method has been applied to the minerals under consideration and the results thus obtained are compared with the experimental results. The calculated zone center frequencies are found to be in good agreement with the observed results. The calculation for potential energy distribution is also made for each mode which gives the dominant contribution of various force constants.

2. Crystal structure and symmetry

Zircon structured silicates $MSiO_4$ ($M = Zr, Hf, U$) undergo a transformation in phase from zircon to scheelite at high pressure [15–16, 18–20]. Hence the researchers are feverishly in the direction to study this high pressure scheelite structure due to their possible geophysical implications. The scheelite phase is a body centered tetragonal having space group $I4_1/a$ and symmetry C_{4h} . The M and Si atoms are situated at S_4 sites and oxygen atoms occupy C_1 sites. At S_4 sites, one occupied by Si and the other with M are coordinated with four and eight oxygen atoms to form SiO_4 tetrahedra and MO_8 dodecahedra as given in Fig. 1. In scheelite phase, each SiO_4 tetrahedron shares the corners of neighboring four MO_8 dodecahedra and is shown in Fig. 1. It is reported in the literature that radius of M cation influences the phase transition pressure i.e. it decreases with the increase in the radius of cation [21]. For $ZrSiO_4$, there is a complete phase transition at 38.6 GPa [15]. However, the scheelite phase appears at 19.6 GPa [18] for $HfSiO_4$ and at 15 GPa [19] for $USiO_4$ respectively. The primitive unit cell contains two formula units. Hence there are twelve atoms per unit cell giving rise to thirty six zone center frequencies. The site symmetry and atomic coordinates of $MSiO_4$ ($M = Zr, Hf, U$) are given in Table 1. Factor group analysis is found to be very valuable to understand the number and symmetry of internal and external vibrational modes in these scheelite structures. Hence a detailed assignment of vibrational modes according to group theoretical

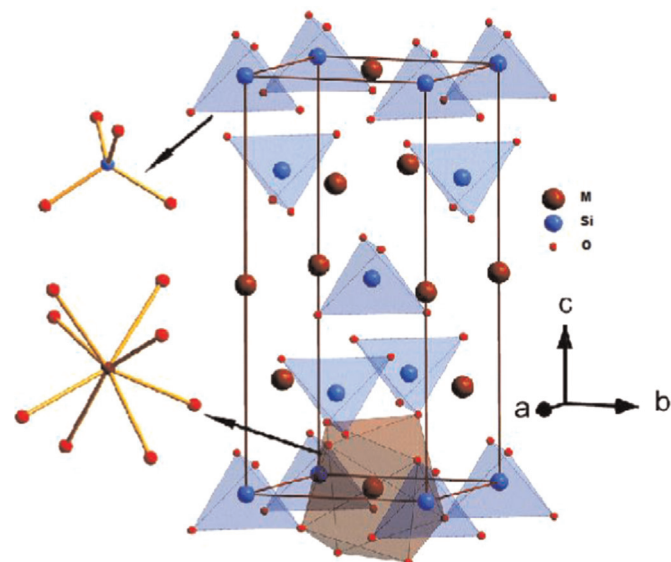


Fig. 1. Crystal structure of $MSiO_4$ ($M = Zr, Hf, U$) in its scheelite phase. MO_8 and SiO_4 units are shown in brown and blue shades.

analysis is made in the present study. The total number of zone center phonons is

$$\Gamma_{\text{total}} = 3A_g + 5B_g + 5E_g + 5A_u + 3B_u + 5E_u$$

Here, Raman active modes are $3A_g$, $5B_g$ and $5E_g$ while infrared active modes are $4A_u$ and $4E_u$. Out of thirty six zone center phonons, $1A_u$ and $1E_u$ are acoustical in nature and $3B_u$ are inactive modes. The letters A and B represent non degenerate modes whereas E denotes doubly degenerate mode. The subscripts g and u indicate even and odd parity of inversion in centrosymmetric crystals. Therefore active optical modes are given as

$$\Gamma_{\text{optical}} = 3A_g + 5B_g + 5E_g + 4A_u + 4E_u$$

3. Theory

Lattice dynamical calculations have been made through Wilson's GF matrix method [22] using normal coordinate analysis. This method introduces the concept of internal coordinates which makes the problem more logical. Changes in interatomic distances or in the angle between chemical bonds, or both, can be used to provide a set of $3N-3$ internal coordinates. The zone center frequencies are determined in terms of kinetic and potential energies of the system. The Kinetic energy T is dependent on geometrical arrangement of the atoms and their masses m_{ij} , whereas the potential energy V which originate due to interactions within the molecule, is defined in terms of force constants F_{ij} . Their expressions in terms of internal coordinates S (bond stretching and angle deformation) are given below:

$$T = \frac{1}{2} \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} (G^{-1})_{ij} \dot{S}_i \dot{S}_j$$

$$V = \frac{1}{2} \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} F_{ij} \dot{S}_i \dot{S}_j$$

where G^{-1} stands for the inverse of the G matrix which is describing the kinetic energies in terms of mass-weighted Cartesian displacements and $\dot{S} = \frac{dS}{dt}$

Eigen value equation for calculation of normal frequencies is given by

$$|FG - E\lambda| = 0$$

where F represents the potential energy matrix, G is a matrix involving kinetic energies, E is a unit matrix and λ is related with frequency ν and is given by

$$\lambda = 4\pi^2 c^2 \nu^2$$

The matrix F was formulated by using short range force constant model involving four stretching force constants K_i and six bending force constants H_i . The short range forces are those which are significant upto certain neighbors and their magnitude generally decreases after the second neighbor interaction. The bending forces have been included in our calculations because the stretching forces only are not sufficient to explain the transverse vibrations. Short range forces between nearest neighbors Si–O, M–O, O–O and bending forces between O–M–O and O–Si–O have been used in the study to calculate PED (potential energy distribution). Lattice parameters, atomic coordinates (given in Table 1), masses of the atoms, symmetry coordinates and the experimentally observed Raman and infrared frequencies [16, 18–20] are the input parameters used in the calculations. We have optimized the force constants so as to make the vibrational frequencies in good agreement with the observed Raman and

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