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Lattice vibrations of AVO_4 crystals (A = Lu, Yb, Dy, Tb, Ce)

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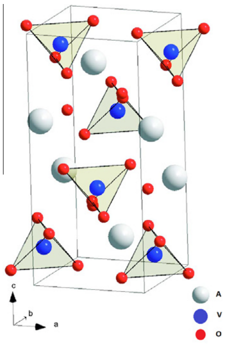
HIGHLIGHTS

- Normal coordinate analysis performed to calculate Raman and IR wavenumbers of AVO_4 (A = Lu, Yb, Dy, Tb, Ce) in scheelite structure.
- An appropriate assignment of infrared modes has been made for the first time for these materials.
- Good agreement has been obtained between the calculated and experimental values.
- Contribution of each force constant toward frequencies has also been determined.

GRAPHICAL ABSTRACT



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ABSTRACT

A short range force constant model has been applied using normal coordinates to investigate the Raman and the infrared wavenumbers in rare earth AVO_4 compounds (A = Lu, Yb, Dy, Tb, Ce) having space group $I4_1/a$ and symmetry C_{4h}^6. The calculation of zone center phonons has been made by using four stretching and five bending force constants. The calculated Raman and infrared wavenumbers are in very good agreement with the observed ones. The present calculations interpret reasonably the mode assignment of 779 cm^{-1} as E_g mode and 853 cm^{-1} as A_g mode in case of $LuVO_4$, which were assigned differently in earlier observation. The potential energy distribution has also been investigated for determining the significance of contribution from each force constant toward the Raman and the infrared wavenumbers.

Introduction

The rare earth orthovanadates AVO_4 (A = rare earth ion) have been investigated recently because of their several applications due to their optical, magnetic and electronic properties. There are many applications of these materials in the fields such as cathodoluminescent, thermophosphors, optical polarizers, scintillators, phosphors, lithium ion batteries, birefringent and nuclear waste storage materials [1–4].

The Rare earth orthovanadates crystallize in a tetragonal zircon-type structure [space group (SG): $I4_1/amd$] at ambient conditions. With the increase in pressure there is irreversible phase transition from zircon structure to scheelite structure [space group C_{4h}^6 ($I4_1/a$)] and this scheelite-phase is metastable at ambient pressure and it does not go back to the zircon phase on release of pressure. Zircon phase consist of a chain of alternating edge-sharing VO_4 tetrahedra and AO_8 dodecahedra extending parallel to the *c*-axis. The chains are joined by edge sharing AO_8 dodecahedra along the *a*-axis. With the increase in pressure, the covalent bond V–O remains undistorted while the volume of AO_8 dodecahedra gets reduced. It has been noticed that phase transition pressure depends on the radius of A cation in AVO_4. With the increase in radius of A cation (r_a) phase transition pressure decreases i.e. compound having A cation of smaller radius is more stable in zircon phase [5]. The details of transition in AVO_4 are given below for various rare-earth ions.

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For $LuVO_4$, above 8GPa fraction of zircon phase decreases and scheelite phase increases. At about 16 GPa there is complete phase transition from zircon phase to scheelite phase, which remains stable up to 21.1 GPa. On further increasing temperature there is second transition, from scheelite structure to monoclinic fergusonite-type structure [6].

In case of $YbVO_4$, zircon structure is stable up to 5.2 GPa. At around 5.9 GPa pressure, zircon and scheelite phase co-exist up to about 13 GPa. Pure scheelite phase appear at about 13.5 GPa. Transition from scheelite to monoclinic fergusonite-type structure, occurs above 13.8 GPa [7].

For $DyVO_4$ and $TbVO_4$, zircon to scheelite transformation occurs at about 6.6 GPa and 6.5 GPa respectively. These materials remain stable in scheelite structure up to about 30 GPa [8].

$CeVO_4$ shows distinctive behavior in phase transition because of large size of Ce cation. This compound crystallizes in zircon phase at ambient conditions. At about 5.5 GPa there occur phase transition from zircon to monazite phase under quasi-hydrostatic conditions and up to 12 GPa monazite phase remain stable. Panchal et al. [9] stated in their paper that, zircon type $CeVO_4$ transform to scheelite phase at about 4GPa and at a temperature of around 600 °C. Hence transformation from zircon structure to scheelite structure occurs at ambient temperature under non-hydrostatic compression [9,10]. For these AVO_4 compounds zircon to scheelite transition is reversible and scheelite phase is quenchable at ambient conditions [9].

Vibrational studies have been used to give the information about the displacements of the atoms or ions, some of which are related to the polarization of the material and Raman scattering is a useful tool to study the phase transition and to detect change in local order involving significant variations in the anion–cation bond forces. Therefore, the Raman and infrared phonons must be studied experimentally as well as theoretically.

In the present work we have considered the AVO_4 (A = Lu, Yb, Dy, Tb, Ce) compounds with scheelite structure for the investigation of their Raman and infrared frequencies.

In Scheelite phase of $LuVO_4$, only Raman modes had been studied experimentally by Rao et al. [11]. Garg et al. [7] had obtained eleven out of 13 Raman wavenumbers for $YbVO_4$ experimentally. Raman modes of $DyVO_4$ and $TbVO_4$ had been studied experimentally by Duclos et al. [8]. Panchal et al. [9] had studied $CeVO_4$ compound experimentally as well as theoretically by using DFT (density-functional theory).

No experimental and theoretical results are available for the infrared modes of these rare earth orthovanadates ($LuVO_4$, $YbVO_4$, $DyVO_4$, $TbVO_4$, $CeVO_4$) with scheelite phase. Also no theoretical results of Raman frequencies are there for scheelite phase of $LuVO_4$, $YbVO_4$, $DyVO_4$ and $TbVO_4$. Hence in this paper an attempt has been made to calculate both Raman and infrared mode frequencies theoretically by using normal coordinate analysis with four stretching and five bending force constants. A very good agreement has been obtained between the present calculated results and the experimentally observed results. Further in case of $CeVO_4$ our theoretically calculated values of Raman modes are far better than the theoretical results obtained by Panchal et al. by using DFT technique [9]. For determining the contribution from each force constant towards the Raman and the infrared modes, the potential energy distribution (PED) has also been investigated.

Structure

At high pressure rare earth orthovanadates AVO_4 (A = Lu, Yb, Dy, Tb, Ce) crystallize in the tetragonal scheelite structure [space group C^6_{4h} ($I4_1/a$), $Z = 4$]. The scheelite phase consists of VO_4 tetrahedra aligned along the *a*-axis and AO_8 dodecahedra are interspersed between the VO_4 tetrahedra along the *c*-axis. Its structure is shown in Fig. 1. Lattice parameter and position co-ordinates are taken from the work of Mittal et al. [12], Garg et al. [7], Duclos et al. [8] and Panchal et al. [9].

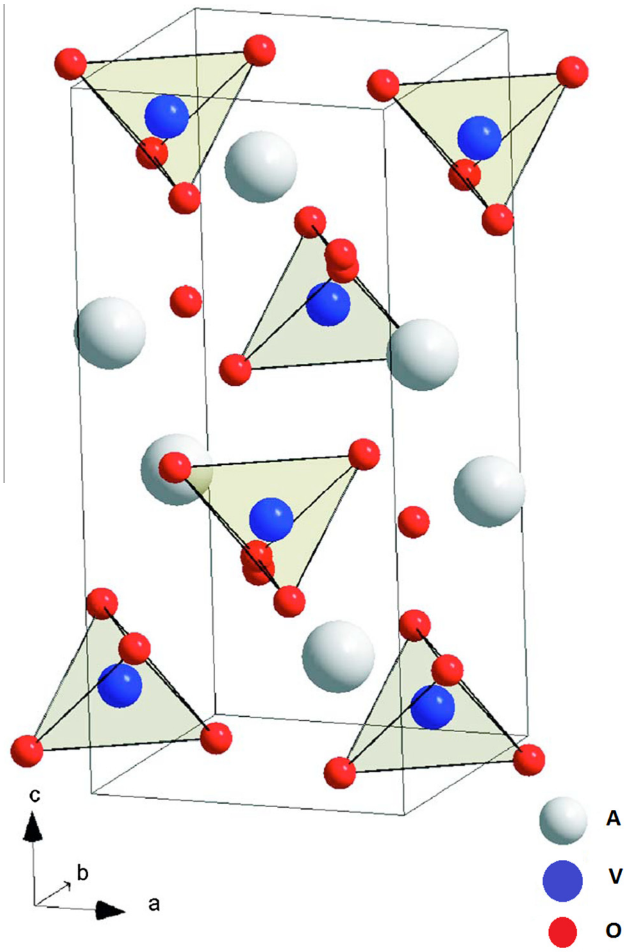

Fig. 1. Crystal structure of AVO_4 (A = Lu, Yb, Dy, Tb, Ce) crystals in their scheelite structure.

From group theory calculations the total number of zone center phonon modes present for each species is

$$\Gamma^{total} = 3A_g + 5E_g + 5B_g + 5A_u + 5E_u + 3B_u$$

Out of these normal modes $1A_u + 1E_u$ are acoustical. $3B_u$ are silent modes So the active optical modes are given as

$$\Gamma^{optical} = 3A_g + 5E_g + 5B_g + 4A_u + 4E_u$$

where $3A_g$, $5B_g$ and $5E_g$ modes are Raman active and $4A_u$ and $4E_u$ modes are infrared active. The A and B modes are nondegenerate, whereas E modes are doubly degenerate.

Theory

The determination of the frequency of normal vibrations involves the kinetic and potential energies of the system. It is necessary to solve the secular equation (Containing kinetic and potential energy matrix) to determine the normal vibrations frequency. Wilson developed the *GF* matrix method to solve the secular equation which is also known as normal coordinate analysis [13]. If the potential energy matrix is represented by *F* and the kinetic energy