Solid State Communications 149 (2009) 1637–1640

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Ab initio vibrational and dielectric properties of YVO_4

R. Vali *

School of Physics, Damghan University of Basic Sciences, P.O. Box 36715/364, Damghan, Iran

ARTICLE INFO

Article history:
Received 19 March 2009
Received in revised form
19 June 2009
Accepted 22 June 2009 by J. R. Chelikowsky
Available online 1 July 2009

PACS:
63.20.-e
78.30.-j
77.22.-d

Keywords:
A. YVO_4
D. Phonons
D. IR reflectivity spectra

ABSTRACT

For the yttrium orthovanadate YVO_4 with a tetragonal zircon-type structure, the first complete set of Raman-active and IR-active phonon modes has been calculated using *ab initio* density functional perturbation theory. The calculated IR reflectivity spectra are in good agreement with available experimental data. We report the calculated frequencies of three Raman-active modes that could not be detected experimentally and a new assignment of the experimental Raman data. The contributions of each IR-active phonon modes to static dielectric tensor have been determined.

1. Introduction

YVO_4 is among the most important laser host materials, due to its good thermal, mechanical and optical properties. It is an optically positive crystal with wide transparency region and has a high birefringence which is also very useful for many applications including light isolators, light circulators and polarizers [1]. The structure of single crystal YVO_4 has been studied [2] using angle dispersive powder diffraction technique. It has been observed that at ambient conditions YVO_4 has a tetragonal zircon-type structure.

The Raman and infrared spectra of the YVO_4 have been studied experimentally by Miller et al. [3]. They have observed nine Raman-active modes and six infrared-active modes. However, three Raman-active modes and one infrared-active mode could not be observed in their experiment. Recently, Bi et al. [4] have measured the infrared reflectivity spectra of a (001) YVO_4 single crystal and have determined the frequency of IR-active modes with E_u symmetry. They have also estimated the effective charges of ions in YVO_4, from LO–TO splitting and by the use of the method of Scott [5].

In this paper, we present the first complete set of calculated Raman-active and IR-active vibrational modes (including LO–TO splitting) for zircon-type YVO_4. We report the calculated frequencies of three Raman-active modes that could not be detected experimentally and a new assignment of the experimental Raman data. We also find that the calculated infrared reflectivity spectra are in good agreement with available experimental data. The Born effective charge tensors have been determined and compared with the previous results of Bi et al. [4]. We find that the Born effective charges of Y and O are anomalously large and that of the V is anomalously small. The contributions of each IR-active phonon modes to static dielectric tensor have been determined. The paper is organized as follows. Section 2 describes the technical details of calculations. Section 3 presents the results including the structural parameters, zone-center frequencies, Born effective charge tensors, dielectric permittivity tensors, and IR reflectivity spectra.

2. Technical details

The calculations were performed according to the density functional theory scheme [6] within the local density approximation [7] and using a conjugate-gradient pseudopotential plane-wave method thanks to the ABINIT code [8]. We used norm-conserving pseudopotentials [9,10], with Y (4s, 4p, 4d, 5s), V (3s, 3p, 3d, 4s), and O (2s, 2p) levels treated as valence states. The exchange-correlation energy is evaluated using Ceperley–Alder electron gas data [11]. Convergency was reached for an energy cutoff of 100 Ha for the plane-wave expansion and a $4 \times 4 \times 4$ k-point mesh for the Brillouin zone integration.

The structural optimization has been performed using the Broyden–Fletcher-Goldfarb—Shanno minimization [12], modified to take into account the total energy as well as the gradients. The relaxation was terminated when the residual forces on each atom

* Tel.: +98 0232 5233054; fax: +98 0232 5244787.
E-mail address: vali@dubs.ac.ir.

0038-1098/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ssc.2009.06.036

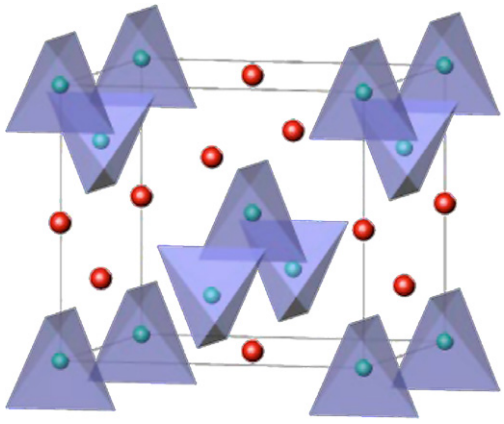

Fig. 1. (Color online) The zircon-type crystal structure of YVO_4 [2].

Table 1
Calculated structural parameters of YVO_4 compared to the experimental values [2].

	Calculated	Experimental
Lattice constants (Å)		
a	7.031	7.1224
c	6.211	6.2913
Internal parameters		
u	0.9355	0.9325
v	0.8006	0.8010

were less than 0.01 eV/Å. The Born effective charge tensors, phonon frequencies, IR reflectivity, and dielectric tensors were computed by density functional perturbation theory according to the scheme presented in Refs. [13,14].

3. Results

The zircon-type YVO_4 has a conventional unit cell which is body-centered tetragonal (space group $I41/amd$) and contains four formula units. A primitive cell containing only two formula units can be defined. As presented in Fig. 1, zircon-type YVO_4 consists of alternating VO_4 tetrahedra and YO_8 units, sharing edges to form chains parallel to the c direction [2].

The Y and V atoms are located at (0, 3/4, 1/8) and (0, 1/4, 3/8) on the 4a and 4b Wyckoff sites, respectively. The O atoms occupy the 16h Wyckoff sites (0, u, v), where u and v are internal parameters. The calculated and experimental [2] structural parameters are summarized in Table 1. The calculated lattice constants a and c, as well as the internal parameters u and v are found to be in very good agreement with their corresponding experimental values [2].

The theoretical group analysis predicts the following irreducible representations of vibrational zone-center modes: $2A_{1g} + 5E_g + 4B_{1g} + 1B_{2g} + 4A_{2u} + 5E_u + 1A_{2g} + 1A_{1u} + 1B_{1u} + 2B_{2u}$. Of which, the following modes are IR-active: $3A_{2u}$ which are polarized along the crystalline c axis (z direction) and $4E_u$ modes whose vibrational motions are in the x–y plane perpendicular to c axis. The following modes are Raman-active: $2A_{1g} + 5E_g + 4B_{1g} + 1B_{2g}$, while, $1A_{2g} + 1A_{1u} + 1B_{1u} + 2B_{2u}$ modes are inactive. There are also three translational modes: $A_{2u} + E_u$. The E_g and E_u modes are twofold degenerate.

Table 2 summarizes the calculated frequencies of the IR-active modes, while panels (A) and (B) of Fig. 2 display the calculated IR reflectivity spectra (without damping) at normal incidence, respectively, on the [001] and [100] surfaces of a YVO_4 single crystal.

The calculated IR reflectivity of panel (B) can be compared with the experimental one [4], shown in the bottom panel of Fig. 2. As can be seen from panel (B), there are four phonon peaks corresponding to $4E_u$ modes. From experimental reflectivity, three modes can easily be identified. There is also another peak as a shoulder on the second reflectivity band, which is evident in the inset of the bottom panel of Fig. 2.

Table 2
Comparison of the calculated and experimental frequencies (cm^{-1}) of the IR-active modes of YVO_4 (in cm^{-1}). The experimental values are taken from Ref. [4] (For E_u mode in first column), and from Ref. [3] (second column).

Mode	Calculated	Experimental	
E_u (TO1)	199.5	193	196
E_u (LO1)	216.6	222	
E_u (TO2)	271.1	262	261
E_u (LO2)	275.1	310	
E_u (TO3)	310.2	310.3	
E_u (LO3)	331.3	315	
E_u (TO4)	825.1	778	788
E_u (LO4)	856.0	930	
A_{2u} (TO1)	249.4		310
A_{2u} (LO1)	255.8		
A_{2u} (TO2)	456.5		455
A_{2u} (LO2)	461.0		
A_{2u} (TO3)	856.0		803
A_{2u} (LO3)	865.2		

The calculated frequencies of the $4E_u$ modes named $E_u(1)$ to $E_u(4)$ are reported in Table 2, together with the experimental values. Measurements of E_u modes reported independently by Miller et al. [3] and Bi et al. [4]. In Table 2, good agreement is observed between our calculations and the experimental data of Bi et al. In Ref. [3], Miller et al. have observed a weak band with E_u symmetry at 310 cm^{-1}, and they have attributed it to anharmonic effect. However, our calculation supports the interpretation of Ref. [4] that this band is due to the fundamental lattice vibration. Furthermore, our calculations do not give any frequency of A_{2u} symmetry close to the frequency of 310 cm^{-1}, experimentally observed by Miller et al. [3]. Instead, we identify an A_{2u} mode at 249.4 cm^{-1}. In fact, as can be seen from Panel (A) of Fig. 2, there are three modes with polarization along the c axis, corresponding to $3A_{2u}$ modes. The calculated frequencies of these modes named $A_{2u}(1)$ to $A_{2u}(3)$ are at 249.4, 456.5 and 856.0 cm^{-1}, respectively.

For IR-active modes there are LO–TO splitting due to the coupling of the atomic displacement with the long-range electric field by means of the Born effective charge tensors. In Table 2 the calculated frequencies of the LO phonon modes are compared with the available experimental data.

The calculated Born effective charge tensors of Y, V and O atoms are reported in Table 3. Due to the high local site symmetry of Y and V atoms, their Born effective charge tensors are diagonal and have only two components: $Z^*_{\parallel}$ and $Z^*_{\perp}$ along and perpendicular to the c axis, respectively. Previously, the effective charge of the ions in the YVO_4 has been estimated by Bi et al. [4], using the method of Scott [5] and by taking into account only two E_u modes ($E_u(1)$ and $E_u(2)$). In this way they have obtained $Z^*_Y = +2.538$, $Z^*_V = 3.793$, and $Z^*_O = -1.583$, for direction perpendicular to the c axis, which are in disagreement with our results. The main reason of the differences is that the result of Scott's method would be exact, within the rigid-ion model approximation; if all LO and TO frequencies had been taken into account. As can be seen from Table 2, other E_u modes also have considerable LO–TO splitting and thus cannot be eliminated in computing of the effective charges, through Scott's method. Furthermore, YVO_4, has high birefringence and thus the Born effective charge will be different along and perpendicular to the c axis.

We note that $Z^*_{\parallel}$ for Y is anomalously large compared to the nominal ionic charge of the yttrium ion Z $= +3$. The other component of the yttrium Born effective charge ($Z^*_{\perp}$) is also large compared to the nominal ionic charge, although the effect is not