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Far-infrared optical properties of YVO_4 single crystal

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Abstract. Near-normal incident infrared reflectivity spectra of a (001) YVO_4 single crystal have been measured at different temperatures in the frequency region between 100 and 6000 cm^{-1}. The reflectivity spectra are analyzed with the factorized form of the dielectric function, and the dielectric properties and optical conductivity of the YVO_4 crystal are obtained. From the TO/LO splitting, effective charges at different temperatures are calculated to study the ionicity of YVO_4. The internal modes of the VO_4^{3-} ion and the external modes of the $Y(VO_4)$ lattice are compared with SiO_4^{4-} in zircon and with other rare-earth vanadates.

PACS. 77.22.Ch Permittivity (dielectric function) – 78.20.-e Optical properties of bulk materials and thin films – 63.20.-e Phonons in crystal lattices

1 Introduction

The yttrium vanadate (YVO_4) single crystal is a very important laser-host material [1–5] and an excellent birefringent optical crystal newly developed. It has large birefringence and a very wide transparency range from the visible to the infrared. Hence, it is an ideal candidate for optical polarizing components, [6,7] which makes it widely used in fiber-optic application. Compared with other well-known birefringent crystals such as calcite ($CaCO_3$) or rutile (TiO_2), YVO_4 has larger hardness, better fabrication property, and in addition, it is water insoluble and easier to obtain in large, high quality crystals at lower cost. Owing to its outstanding physical properties, it is an excellent synthetic substitute for conventional crystals in many applications including fiber-optic isolators and circulators, beam displacers and polarizers, etc.

The YVO_4 crystal with space group I41/amd has a zircon-type structure as shown in Figure 1 of [8]. The V^{5+} ions are located at the center of distorted O-ion tetrahedra. The Y^{3+} ions, in the D_{2d} site symmetry, are eightfold coordinated to oxygen ions and reside between isolated VO_4 tetrahedral units. A unit cell with lattice constants $a = b = 0.712$ nm and $c = 0.629$ nm contains two chemical formula of YVO_4. Under high pressure, the structure undergoes a transition into a scheelite phase and the internal structural parameters change [8].

There have been several reports on the Raman spectra of YVO_4, which are mainly focused on the structural phase transition and the effect of rare earth ions doping on it [8–10]. However, little work was done on the infrared optical and structural properties at low temperatures due to the fact that up to now the interest on YVO_4 was focused on the design of high power laser and opto-communication devices operating at room temperature. It is of great interest to explore its physical properties at low temperature in order to extend its application to temperatures lower than room temperature. It has been reported that several rare earth vanadates with zircon-type structure undergo a Jahn-Teller distortion at low temperatures to an orthorhombic phase [11]. However, no indication of a Jahn-Teller distortion in YVO_4 has been observed at low temperatures. Nevertheless, a local short-range distortion cannot be excluded. Infrared spectroscopy is a powerful tool to provide insight into dynamical processes related to phonons, charge carriers, spins, and their coupling processes. Precise information on optical properties such as dielectric response to electromagnetic waves low frequency is of essential importance and much desired. In this paper we report on the detailed optical properties of YVO_4 at different temperatures, from 300 down to 10 K. Effective ion charges are calculated to study the ionicity in YVO_4.

2 Experiment

A single crystal of YVO_4 was grown by Hefei Kejing Materials Technology Co. Ltd. with the Czochralski growth method. A rectangular piece ($10 \times 10 \times 0.5\,mm^3$) was cut and one-side polished with the surface parallel to the (001) plane. The crystal was transparent to visible light. Near-normal incidence measurements (with an incidence angle of about 8°) were performed with the electric field perpendicular to the crystallographic c-axis (i.e., $E \parallel ab$).

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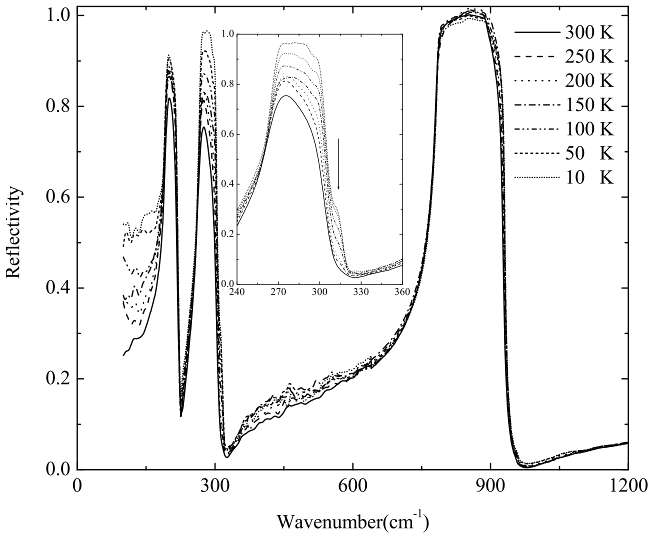


Fig. 1. Experimental FIR reflectivity spectra of YVO_4 crystal at various temperatures. The inset shows enlarged reflectivity spectra from 240 cm^{-1} to 360 cm^{-1}. The arrow indicates the shoulder.

All the reflectivity spectra were taken on a BOMEM DA8 FT-IR spectrometer in the range 100–6000 cm^{-1} with a resolution of 4 cm^{-1}. The sample was mounted in an optical cryostat in vacuum and the temperature was varied from 300 K down to 10 K with an accuracy of 0.02 K. A DTGS detector was utilized in the far-infrared range of 100–700 cm^{-1}, and a liquid-nitrogen cooled mercury cadmium telluride detector was employed in the mid-infrared range of 450–6000 cm^{-1}. To obtain the absolute reflectivity, the reflectance of an evaporated golden mirror was taken at each temperature as reference. The overall experimental accuracy is estimated to be around 2%.

3 Results and discussion

The reflectivity spectra of the YVO_4 single crystal are shown in Figure 1 at several representative temperatures. The reflectivity of YVO_4 is typical that for an insulator. Within the reststrahlen bands, the reflectivity increases slightly with decreasing temperature. This is due to the fact that anharmonic thermal motion weaken with decreasing temperature so that the oscillation strength of the vibrational modes increases. The sharp features in the reflectivity at low frequency are due to the unscreened infrared-active optical phonon modes, while above the highest observed lattice-vibration frequency the reflectivity is flat and featureless up to the highest measured frequency. Three modes can easily be identified at all temperatures. There is also a fourth peak as a shoulder on the second reflectivity band, which is more evident at low temperatures. Therefore, the number of the observed phonon peaks is four and in the following, four oscillators are utilized to make the fits.

Because YVO_4 is insulating and does not have a metallic contribution, the Lyddane-Sachs-Teller (LST) relation offers a reasonable model to analyze the reflectivity spectra. In the following, the mode frequencies are obtained from damped harmonic oscillators fitted to the reflectance spectra with a complex dielectric function $\varepsilon(\omega)$ in the factorized form (generalized LST relation) [12–16]

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \varepsilon_\infty \prod_{j=1}^{n} \frac{\omega_{jLO}^2 - \omega^2 + i\gamma_{jLO}\omega}{\omega_{jTO}^2 - \omega^2 + i\gamma_{jTO}\omega}, \tag{1}$$

where ε_∞ is the high-frequency dielectric constant, ω_{jTO} and ω_{jLO} are the transverse and longitudinal eigenfrequencies of the j-th optical phonon mode, γ_{jTO} and γ_{jLO} their corresponding damping constants. Using this dielectric function, all the reflectivity spectra were fitted with the well-known Fresnel formula:

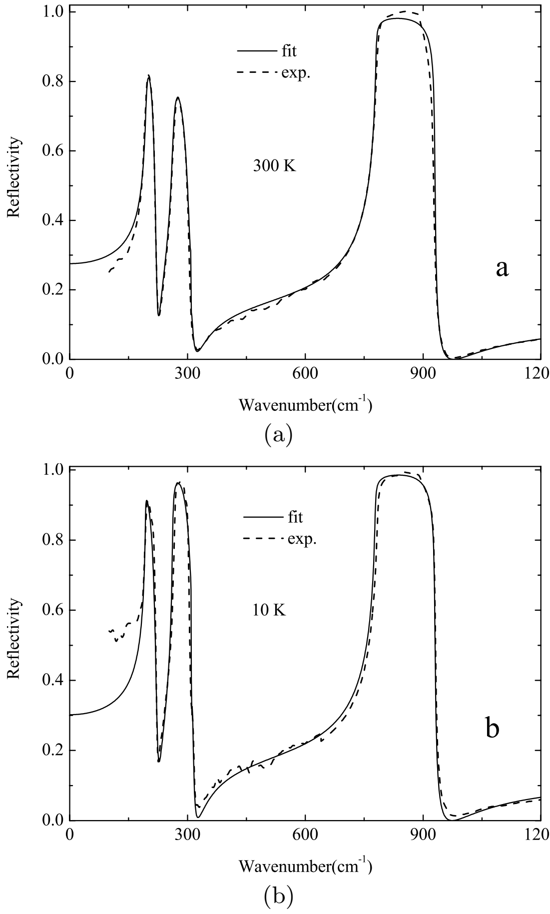
$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2 . \tag{2}$$

Based on equations (1) and (2), a fit of $R(\omega)$ to the observed reflectivity spectra can be obtained with a proper choice of the model parameters ω_{jLO}, ω_{jTO}, γ_{jLO}, γ_{jTO} and ε_∞. Adjustment of the parameters is made by trial and error fitting of equation (2) to the experimental spectra. This method yields not only $\varepsilon(\omega)$ but also the model parameters which characterize the infrared active phonons.

Shown in Figure 2 are the fitting results. Dashed lines indicate the experimental FIR reflectivity spectra and solid lines are the fitting results. It can be seen that a satisfactory agreement is obtained. A small deviation of the calculated curves from the experimental data is seen, especially in the low frequency region. The most probable reason for this discrepancy are multiple reflections which have been neglected in our fitting procedure. However, the neglect of multiple reflections should not affect the following analysis. The fitting parameters at several representative temperatures are listed in Table 1.

From a group-theory analysis [17], it is well known that compounds with I41/amd-D_{4h}^{19} structure symmetry with two chemical formulas in the primitive cell should have the Brillouin-zone center modes at the Γ point with $\Gamma(k=0) = 2A_{1g} + 5E_g + 4B_{1g} + 1B_{2g} + 4A_{2u} + 5E_u + 1A_{2g} + 1A_{1u} + 1B_{1u} + 2B_{2u}$.
Among these modes, the A_{2u} and E_u symmetry representations show dipole moments oriented along and perpendicular to the c directions, respectively. Moreover, four of all five E_u modes are infrared active. Since the electric field of the incident light in our measurements is perpendicular to the c axis, only $4E_u$ modes will contribute to the spectra. Therefore, we tentatively assign the four vibrational modes to the $4E_u$ modes.

From the fitting parameters derived above, the model in-plane dielectric functions $\varepsilon(\omega)$ of the YVO_4 crystal can be calculated using equation (1) [19]. Shown in Figures 3a, 3b are representative results for the real part $\varepsilon_1(\omega)$ (dash-dotted lines) and imaginary part $\varepsilon_2(\omega)$ (solid lines) of $\varepsilon(\omega)$ obtained at 300 K and 10 K. The frequencies of the maxima in $\varepsilon_2(\omega)$ roughly correspond to those of transverse



(a)

(b)

Fig. 2. Representative experimental and fitted reflectivity spectra of YVO_4 at 300 K (a) and 10 K (b). The dashed lines indicate experimental data and the solid lines are the fitting results.

Table 1. The parameters of the oscillator model obtained from the fit to the observed reflectivity spectra of YVO_4 single crystal at different temperatures. The frequencies are in cm^{-1}.

Temp.	ε_∞		E_u Modes			
$T = 300$ K	4.0	ω_{TO}	195	263	309	780
		γ_{TO}	6	10	1.6	3
		ω_{LO}	222	309	311	930
		γ_{LO}	10	1	17	3
$T = 100$ K	4.2	ω_{TO}	193	263	310	779
		γ_{TO}	3	6	1.7	3
		ω_{LO}	222	309.8	315	930
		γ_{LO}	10.5	1	13	3
$T = 10$ K	4.3	ω_{TO}	193	262	310.3	778
		γ_{TO}	1.8	2.8	1.7	3
		ω_{LO}	222	310	315	930
		γ_{LO}	12	1	8	3

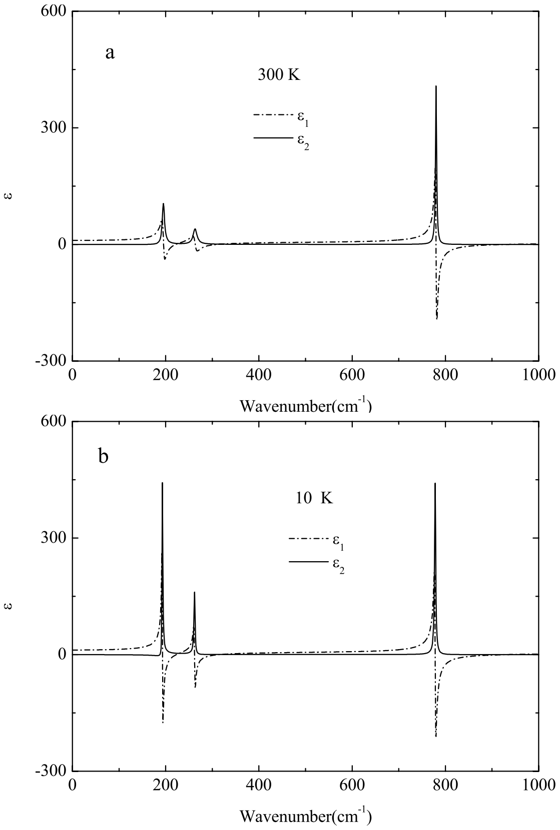


Fig. 3. The real part $\varepsilon_1(\omega)$ (dash-dotted lines) and imaginary part $\varepsilon_2(\omega)$ (solid lines) of the in-plane component of the dielectric tensor of YVO_4 single crystal, which are calculated from the fits of reflectivity spectra with the oscillator model. (a) and (b) correspond to representative results at 300 K and 10 K, respectively.

optical phonons ω_{TO}. At room temperature, the frequencies of the four modes named $E_u(1)$, to $E_u(4)$ are centered at 195, 263, 311 and 780 cm^{-1}, respectively. It is convenient to separate the modes into internal ones, consisting of the internal motions of the tetrahedral VO_4 group, and external ones which involve translations and rotations of the VO_4 tetrahedron as a whole with respect to the Y ion. The external modes involving essentially motion of the relatively massive VO_4 group ought to generally lie at lower frequencies than the internal modes. Hence, the two reflection bands at 195 cm^{-1} and 263 cm^{-1} are assigned to the translation and rotation external modes expected from group theory considerations. The other two correspond to the internal modes, with the 310 cm^{-1} mode produced by the vibrations between oxygen ions and the 780 cm^{-1} mode by the vibration between the V cation and the O anions. With decreasing temperature, the frequencies of the phonon modes deviate a little from those at room temperature. But the intensity of the imaginary part $\varepsilon_2(\omega)$ is greatly enhanced for the two external modes. In contrast, the internal mode of highest frequency remains nearly unchanged. The different temperature dependences are due to the tightly bound VO_4 tetrahedron in YVO_4. A simplified structure of YVO_4 can be considered as being composed of two sublattices of Y ions and VO_4 "molecules", the vibration between the two sublattices being sensitive to the anharmonic thermal motion. The 310 cm^{-1} mode is hardly resolved owing to its low oscillation strength. This can be attributed to the fact that oxygen ions indirectly connect through intermediate V cations and no bonds

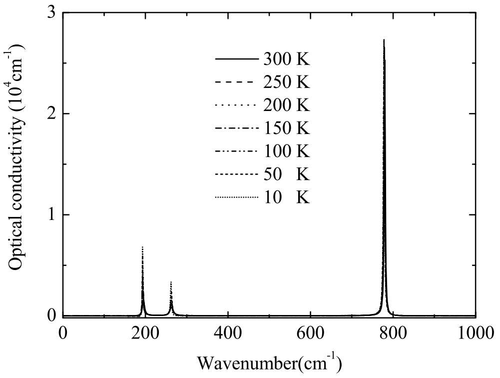


Fig. 4. The real part optical conductivity for temperatures between 10 K and 300 K from 0 to 1000 cm^{-1}.

between them form in the VO_4 tetrahedron, so that the binding force is relatively weak. Our result suggests that there is no distortion in YVO_4 with decreasing temperature.

Shown in Figure 4 is the frequency dependence of the real part of the optical conductivity at different temperatures. According to $\sigma_1(\omega) = (\omega/4\pi)\varepsilon_2(\omega)$, the real part of the frequency dependent optical conductivity $\sigma_1(\omega)$ is obtained. It is seen that no free carrier contribution can be observed except that from the phonons, this agrees well with the fact that YVO_4 is a good insulator.

In the approximation of zero phonon, one can simply obtain the LST relation from equation (1), which connects static optical permittivities ε_0 and high-frequency optical permittivities ε_∞ with transverse and longitudinal phonon frequencies:

$$\frac{\varepsilon_0}{\varepsilon_\infty} = \prod_i \frac{\omega_{iLO}^2}{\omega_{iTO}^2}. \tag{3}$$

From equation (3), static optical permittivities ε_0 of YVO_4 single crystal at different temperatures are also obtained, as shown in Figure 5. It shows that ε_0 increases with decreasing temperature. At room temperature ε_0 is about 10.31.

The effective charges of the ions in YVO_4 can be estimated using the method of Scott [18] and Gervais [20]. The following equations are used to determine Z_k^*, the effective ionic charges (in the Gauss unit system):

$$4\pi^2 \sum_j (\omega_{jLO}^2 - \omega_{jTO}^2) = \frac{4\pi}{V_c} \sum_k \frac{(Z_k^* e)^2}{M_k}, \tag{4}$$

$$Z_Y^* + Z_V^* + 4Z_O^* = 0 \tag{5}$$

where V_c is the unit-cell volume, j and k index the lattice modes, and M_k the mass of the atoms. The summation is over all the ions in the unit cell. On the left-hand side of equation (4), ω_{jTO} and ω_{jLO} are the transverse and longitudinal phonon frequencies of the jth mode which can be obtained from peaks in the imaginary dielectric function and the dielectric loss function, respectively. But there are three unknowns in the above two equations. So another relationship must be provided. As mentioned above, YVO_4 can be treated as a binary system where the Y ions vibrate against the VO_4 tetrahedra and only the two external modes on the left-hand side of equation (4) are included. Consequently, equation (5) evolves into the following form: $Z_Y^* + Z_{VO_4}^* = 0$. This method for obtaining effective charges was proven effective in some titanate compounds [20–22]. The results of the calculation are shown in Table 2, where the effective charges at different temperatures are listed. The data indicate that the bonding in yttrium vanadate is strongly ionic, which suggests little overlap of Y states with oxygen $2p$ levels. Furthermore, the temperature hardly influences the ionicity. But it must be noticed that the YVO_4 crystal is anisotropic with the c axis shorter than the $a = b$ axes. Therefore, there are two sets of Z_k^* for the ions. The values estimated by our measurement are the effective charges in the orientation perpendicular to the c axis. From first-principles study of zircon [23,24], there are two different configurations for oxygen atoms in the tetragonal phase, which will produce different Zr-O bond lengths leading to different Born effective charges along and perpendicular to the tetragonal axis. For YVO_4 with similar lattice symmetry, it is also the case. It will be of great interest to perform first-principle calculations of YVO_4 to study this property.

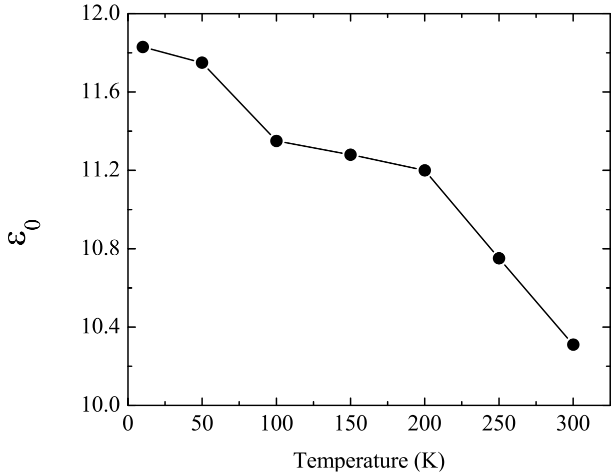


Fig. 5. The temperature dependence of the static optical permittivity ε_0.

Table 2. Effective charges of the ions in the YVO_4 single crystal. Z_Y^*, Z_V^* and Z_O^* are those of the yttrium, vanadium and oxygen atoms, respectively, in units of the fundamental electronic charge.

Temperature	Z_Y^*	Z_V^*	Z_O^*
300 K	2.476	3.774	–1.562
250 K	2.489	3.789	–1.569
200 K	2.501	3.783	–1.571
150 K	2.521	3.780	–1.575
100 K	2.521	3.786	–1.577
50 K	2.521	3.800	–1.580
10 K	2.538	3.793	–1.583

On the other hand, it is found that the V–O bond strength increases with increasing atomic number of the rare-earth element R in RVO_4 compounds from Raman experiments as well as from the force constants calculation [25,26]. Whether the same behavior will appear has not been confirmed by infrared measurement. Systematic work needs to be performed to resolve the effect of different rare-earth ions on the vibrational modes and structural distortion. Furthermore, the pressure response in the infrared spectrum is also worthy of investigation. In comparison with SiO_4^{4-} ion [17], the internal vibrations of VO_4^{3-} ion are found to have lower frequencies. This is probably due to the existence of the 3d states of vanadium relative to the O $2p$ valance band which results in more hybridization in the metal-oxygen band.

4 Conclusion

In summary, the infrared reflectivity spectra of YVO_4 single crystal at different temperatures have been measured. They are well described by the LST relation. Four phonon modes are assigned to the vibrational modes of the crystal, in agreement with theoretical predictions. The dielectric function and optical conductivity change little upon variation of the temperature. The intensity of the two external modes increases with decreasing temperature which can be explained based on the rigid character of the VO_4 tetrahedron. The effective charges suggest strong ionicity and they are independent of temperature. It appears that the structure of YVO_4 is almost stable and no obvious distortion is observed upon decreasing temperature.

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