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Temperature dependent phonon modes and ionicity of $LiGaO_2$ single crystal*

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This paper reports that polarized far-infrared reflectivity measurements have been done on $LiGaO_2$ single crystal along two crystalline axes at different temperatures. The temperature dependent frequencies of the longitudinal and transverse optical phonon have been obtained from the real part of optical conductivity and the loss function respectively. A small Drude component is observed at frequency below 300 cm^{-1} which could arise from Li ions or oxygen deficiencies. The ionicity of $LiGaO_2$ has been studied from the analysis of the Born effective charge of different ions.

Keywords: infrared, optical conductivity, $LiGaO_2$ single crystal, phonon
PACC: 3320E, 6320，7830G，7820D

1. Introduction

$LiGaO_2$ crystal has traditionally been a refractory piezoelectric transducer material which is widely used in lasers. It has also been considered as an excellent substrate for the epitaxial growth of GaN film due to the small mismatch ($\leq$ 0.2 %) of their lattice parameters. During the past years, various optical and structural properties of $LiGaO_2$ have been studied. The crystalline structure of $LiGaO_2$ was carefully determined by Marezio using x-ray diffraction.[1] Knoll and Kuzmany measured the Raman spectra as well as the infrared reflectivity spectra of $LiGaO_2$ and analysed its nonlinear optical properties.[2] Subsequently, the lattice vibration properties of $LiGaO_2$ has been studied with polarized infrared reflectivity by Neumann *et al*[3] and Sobotta *et al*[4] consistent vibrational phonon modes with those by Knoll *et al* have been obtained. Kabelka *et al* measured its Raman spectra over a wide temperature region from 6 K to 700 K and they concluded that there was a second order phase transition at 65 K.[5] The nonlinear optical properties of $LiGaO_2$ have recently been studied by first principle calculation.[6] It is shown that $LiGaO_2$ has the potential to be used as a frequency doubler crystal into the ultraviolet region. Far infrared spectroscopy is very useful in analysing the lattice vibration properties. All those infrared results mentioned above were limited at room temperature, no report on the infrared reflectivity spectra at low temperatures has been given. In the mean time, it is of great interest to study the ionicity of $LiGaO_2$ which could relate to its nonlinear optical properties. It is important to explore its properties at low temperature in order to extend its application to temperatures lower than room temperature.

The structure of $LiGaO_2$ crystal is orthorhombic and has the $Pna2_1$ (C^9_{2v}) space-group symmetry.[1] Its structure is derived from wurtzite with a particular ordering of the Li and Ga cations accompanied by structural relaxation. Each of the basal planes contains both Ga and Li atoms in a 2×2 supercell of the wurtzite unit cell. There are four molecules in one unit cell with all the atoms in general positions. The atoms are arranged in a way that oxygen tetrahedra containing Li and Ga atoms in the centre are alternately edge-linked. The tetrahedra containing Ga are slightly smaller than those containing Li because the mean distance of Li–O bond is larger in comparison with that of Ga–O bond. Its lattice parameters are a=0.5402 nm, b=0.6372 nm, and c=0.5007 nm.[1] The nominal valence of Ga, Li and O is +3, +1 and –2, respectively.

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2. Experiment details

A single crystal of $LiGaO_2$ with the size of 10 mm×10 mm×0.5 mm was cut and one-side polished with the surface parallel to the (001) plane. The crystal was transparent to visible light. To study its low-temperature lattice vibration properties, we measured the polarized infrared reflectivity spectra along a and b axes at different temperatures. The sample was first mounted in an optical crystal in which the temperature can be controlled between 10 K and 300 K with a precision better than 0.2 K. Near-normal incidence (with the incident angle of about 8°) reflectivity spectra R (ω) were taken by using a Fourier transform infrared (FTIR) spectrometer (Bomen DA8) with a resolution of 4 cm^{-1}. A polarizer was settled in the light path to obtain spectra along the a and b axes. In the far infrared region of 50–700 cm^{-1}, a bolometer and a 6 μm mylar beam-splitter were used. In the mid infrared region of 700–7000 cm^{-1}, a combination of a liquid nitrogen cooled HgCdTe MCT detector and a KBr beam-splitter coated with Ge film was utilized. In both regions, a SiC (Globar) was used as the light source. To obtain the absolute reflectivity, the reflectance of an evaporated gold film was taken at each temperature as the reference.

3. Results and analysis

The polarized reflectivity spectra along the a axis and b axis at several representative temperatures are shown in Fig.1. The spectra at 300 K resemble those obtained by Knoll and Kuzmany.[2] The reflectivity in both directions are dominated by the contribution from the phonons, no structures can be observed above 800 cm^{-1}. This agrees with the fact that $LiGaO_2$ is an insulator. Within the reststrahlen band, the reflectivity increases with decreasing temperature due to the reduced anharmonic thermal motion, so the oscillation strength of the vibration modes increases. In the frequency region below 300 cm^{-1}, the reflectivity between the neighbouring phonon peaks shows an abnormal increase with the decreasing temperature, the reflectivity in the frequency region below that of the lowest phonon mode shows the same behaviour. This suggests that the reflectivity has two components, one is that caused by the vibrational phonon modes, the other resembles the behaviour of free carriers, i.e., a Drude component with a very low plasma frequency, which would suggest the presence of small density of free carriers below 200 K. We will come back to this point later.

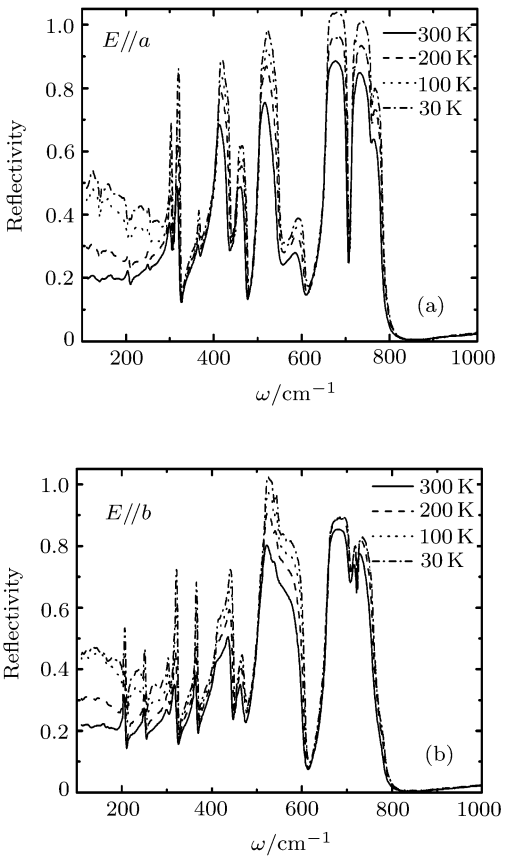


Fig.1. The polarized reflectivity spectra of $LiGaO_2$ along two crystalline directions at different temperatures. (a) $E//a$; (b) $E//b$.

To further analyse the lattice vibration properties, the real part of the optical conductivity σ_1 and energy loss function $\mathrm{Im}(-1/\varepsilon)$ are obtained by applying the Kramers–Kronig (K–K) transformation to the reflectivity spectra. The obtained σ_1 and $\mathrm{Im}(-1/\varepsilon)$ along a axis and b axis at several representative temperatures are shown in Fig.2.

The frequencies of each transverse (ω_{TO}) and longitudinal (ω_{LO}) optical modes are determined from the maxima in σ_1 and $\mathrm{Im}(-1/\varepsilon)$, respectively. The obtained ω_{TO} and ω_{LO} for both directions at 300 K and 30 K are listed in Table 1 and Table 2 respectively. For comparison, the phonon frequencies of $LiGaO_2$ single crystals along the a axis reported by Knoll and Kuzmany[2] and Neumann *et al*[3] are also listed in Table 1. It can be found that the phonon frequencies at 300 K obtained in the present study agree well with those reported by Knoll *et al* and Neumann *et al*. The frequencies of longitudinal (LO) phonon modes show a blue shift upon the decrease of tem-

perature, while those of the transverse optical (TO) phonon modes show a red shift. This indicates a enhancement in LO–TO phonon splitting and enhanced oscillation strength with the decreasing temperature.

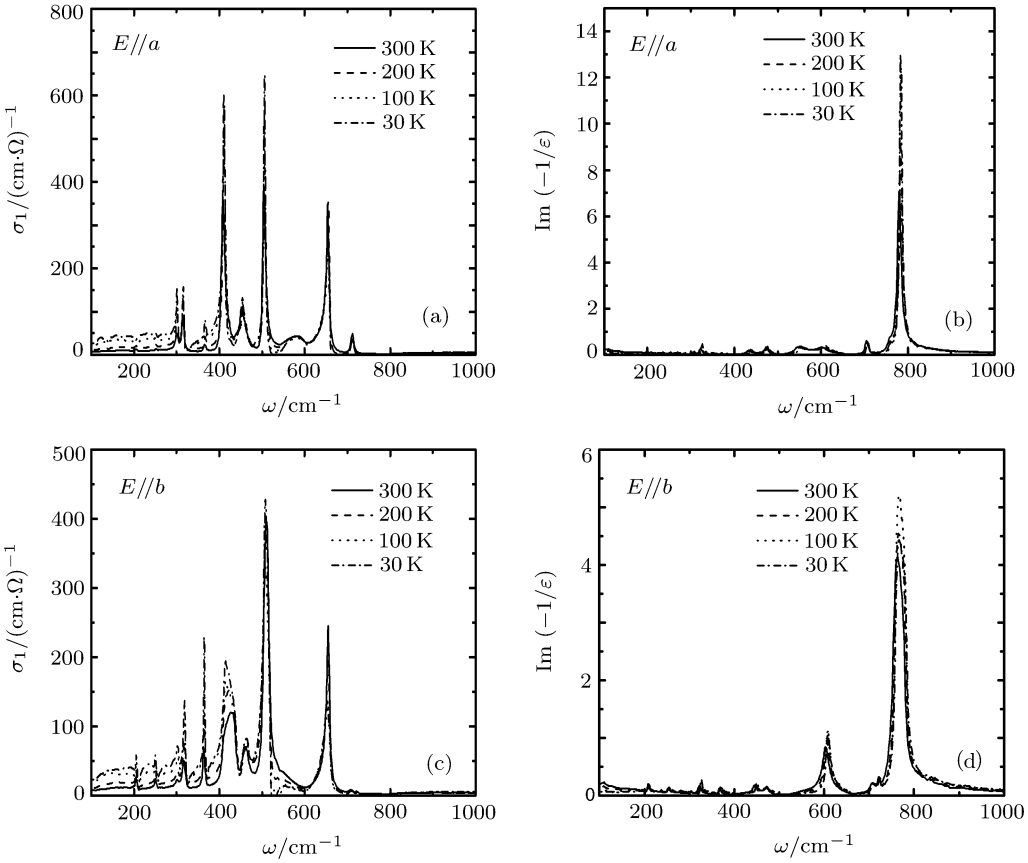


Fig.2. The real part of optical conductivity σ_1 and the energy loss function $\mathrm{Im}(-1/\varepsilon)$ spectra at different temperatures. The spectra of $E//a$ are shown in (a) and (b), the spectra of $E//b$ in (c) and (d).

Table 1. ω_{TO} and ω_{LO} of B_1 mode at two representative temperatures.

300 K						30 K	
$\omega_{\mathrm{LO}}/\mathrm{cm}^{-1}$			$\omega_{\mathrm{TO}}/\mathrm{cm}^{-1}$			$\omega_{\mathrm{LO}}/\mathrm{cm}^{-1}$	$\omega_{\mathrm{TO}}/\mathrm{cm}^{-1}$
this work	Knoll	Neumann	this work	Knoll	Neumann	this work	this work
303.4	302.5	305.0	300.0	301.0	303.0	306.8	300.8
322.3	322.0	324.0	314.6	314.5	316.0	325.7	315.4
366.8	—	368.0	366.0	—	364.0	370.3	366.0
432.8	435.0	438.0	408.0	406.5	409.0	439.7	411.1
474.0	472.0	474.0	453.4	451.5	455.0	478.3	455.1
546.8	537.0	543.0	504.0	503.0	505.0	552.0	505.7
601.7	—	606.0	579.4	—	591.0	608.5	581.1
703.9	704.0	704.0	653.8	656.5	661.0	705.8	653.8
756.0	—	716.0	711.6	714.0	710.0	761.8	711.6
779.1	776.0	782.0	757.9	—	721.0	782.9	761.7

Table 2. ω_{TO} and ω_{LO} of B_2 mode at two representative temperatures.

T/K	phonon modes/cm^{-1}									
300ω_{TO}	204.8	250.27	301.69	317.10	363.40	426.83	461.97	509.97	654.82	707.7
ω_{LO}	209.1	252.80	302.55	323.10	367.69	444.83	469.69	603.39	707.74	721.2
30ω_{TO}	205.7	250.27	302.55	318.80	364.26	413.97	462.80	507.40	652.25	709.7
ω_{LO}	210.8	254.55	305.98	326.56	370.26	449.97	473.10	608.54	709.70	723.2

According to the group theory analysis, compounds of $Pna2_1$ (C_{2v}^9) symmetry with four chemical formulas in the primitive cell should have the Brillouin zone centre modes at the Γ point with

$$\Gamma = 11B_1(a) + 11B_2(b) + 11A_1(c) + 12A_2.$$

Among these modes, the B_1, B_2, and A_1 modes are infrared active, corresponding to the polarization directions $E//a$, $E//b$, and $E//c$, respectively.[3] There should be 11 each direction. We do observe 11 B_2 vibration modes in the in the spectra for $E//b$, however, only 10 B_1 vibration modes are present for $E//a$. According to the results of a comparative of $LiGaO_2$ and $LiAlO_2$ by Sobotta *et al*,[4] the Li–O bond related vibrations only appear below 515 cm^{-1} and optical modes above 515 cm^{-1} in $LiGaO_2$ should belong to the Ga–O bond vibrations. The phonon mode at 450 cm^{-1} can be attributed to the Li–O stretching mode according to the vibration mode analysis of Marezio *et al*[1] the temperature dependence of its width is shown in Fig.3.

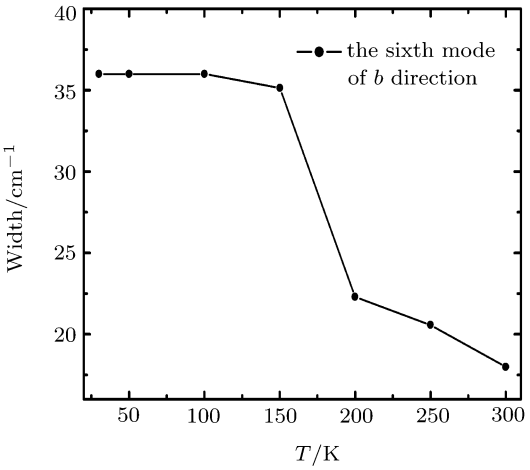


Fig.3. The temperature dependence of the width of the Li–O stretching mode at 430 cm^{-1} along b direction. The filled circles are data points and the solid line is guide for the eyes.

It is known that for a polar crystal, the incident light can couple to the induced dipole moments arising from the motion of cations and anions against the centre of mass, this could result in the splitting of the TO–LO phonon modes which can be experimentally determined as we have obtained above. Information about the Born effective charge per atom Z_k which characterizes the charge transfer between the cations and anions can be obtained from the strength of the splitting. Therefore, TO–LO splitting can be used to analyse the Born effective charge for each atom in a polar crystal. For ABO_2 compound, the relation between the normalized TO/LO splitting and the effective charge is given by[7,8]

$$4\pi^2 \sum_j (\omega_{LO_j}^2 - \omega_{TO_j}^2) = \frac{4\pi}{V_c} \sum_k \frac{(Z_k e)^2}{M_k}, \qquad (1)$$

where V_c is the volume of the unit cell; j and k indicate different lattice modes and atoms, respectively; e and M_k are elementary charge and mass of the kth atom respectively. Using the TO and LO phonon frequency listed in Tables 1 and 2, together with the assumption that $(Ze^*/e)_A = \frac{1}{3}(Ze^*/e)_B = -\frac{1}{2}(Ze^*/e)_O$ and $\sum_k Z_k = 0$,[9,10] we can calculate the effective charges from TO/LO splitting of the phonon modes at different temperatures. The calculated Born effective charges of Li, Ga and O from our experimental results at 300 K are 0.98, 2.94, and –1.96, respectively. The temperature dependent Born effective charges of Lithium ion in the a and b axes are shown in Fig.4. It is obvious that the values along these two directions are different. This suggests that $LiGaO_2$ has some degree of anisotropy along the a and b axes, the degree of polarity in the b direction is larger than that in the a direction at low temperature, which agrees with the fact that $LiGaO_2$ has a orthorhombic structure with different lattice parameters of a and b axes. The increased Born effective charge suggests that the polarity of $LiGaO_2$ enhances with the decreasing temperature.

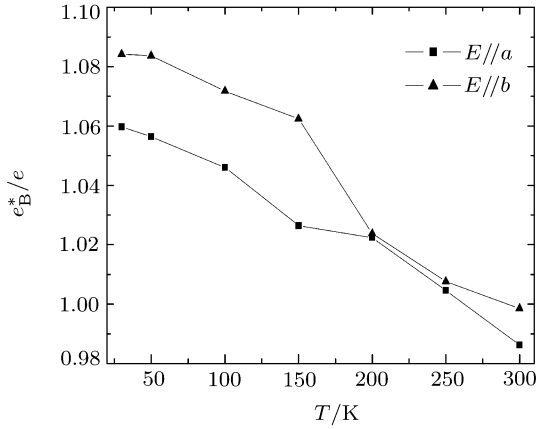


Fig.4. The temperature dependence of Born effective charge of Li along a and b directions. The solid circles are the values along the a axis and the solid triangles are the values along the b axis.

As shown in Fig.4, the Born effective charge e_B^*/e in these two directions separates at $T \approx 200$ K which is just the temperature at which the reflectivity at low

frequency increases. We can conclude that the Pauling electro-negativity for Li and Ga decreases at about 200 K and the polarity of $LiGaO_2$ enhances, which might result in the appearance of a few charge carriers. It would worth to carry out first principle calculation of the electronic structures of $LiGaO_2$ at low temperatures to clarify this point.

Using zero phonon approximation, we get the Lyddane–Sache–Teller (LST) relation which connects the static optical permittivity ε_0 and the high-frequency optical permittivity ε_∞ with the transverse and longitudinal phonon frequencies[11]

$$\frac{\varepsilon_0}{\varepsilon_\infty} = \prod_{j=0}^{n} \frac{\omega_{\mathrm{LO}_j}^2}{\omega_{\mathrm{TO}_j}^2}. \tag{2}$$

The static optical permittivities ε_0 of $LiGaO_2$ single crystal at different temperatures are obtained by using equation (2) and plotted in Fig.5. In the a direction, ε_{0a} is 6.99 at room temperature which well agrees with ε_{0a}=7.0 reported in Ref.[2] and ε_{0b} is 7.30 which is a little larger than that reported by Nanmatsu *et al.*[12]

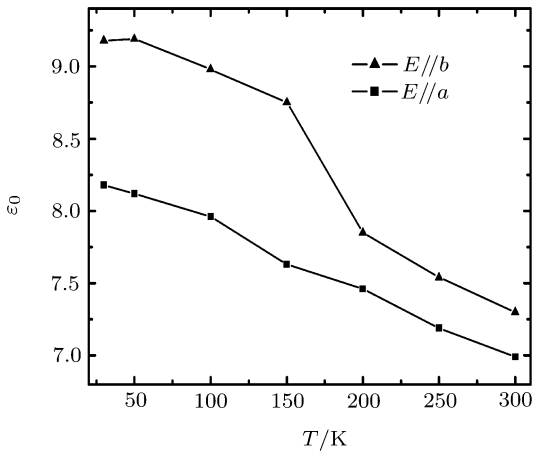


Fig.5. The temperature dependence of ε_0 in $E//a$ and $E//b$ directions. The dots mean the deduced values in $E//a$ temperatures and the triangles mean values in the other direction.

We notice that the reflectivity and optical conductivity show an increase at the low frequency region below 300 cm^{-1}. It cannot be simply attributed to the appearance of an additional phonon mode in the low frequency around 200 K. The optical conductivity exhibits a behaviour similar to that of a Drude component, which suggests some concentration of free charge carrier. We are not clear why the charge carrier appears at the low temperature, one possibility could be that the Li ions or oxygen deficiencies become mobile below 200 K, which could give rise to a certain degree of carrier concentration and thus the reflectivity shows a Drude component with low plasma frequency.

4. Summary

The temperature dependent infrared reflectivity spectra of $LiGaO_2$ in $E//a$ and $E//b$ directions have been studied. TO and LO frequencies were obtained with the K–K transformation and used to analyse the temperature dependence of the Born effective charge in these two directions. The ionicities for Li, Ga and O atoms were 0.98, 2.94 and –1.96 at room temperature, respectively, which show an increase upon the decreasing temperature. The abnormal increase at low temperature may be due to the presence of charge carriers because the optical conductivity at zero frequency was not zero. Using the LST relation, we calculate the static optical permittivity ε_{0a} and ε_{0b}, which increase with the decrease of temperature. They have the same temperature dependence as the Born effective charge e_{B}^*/e.

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