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Temperature-dependent far-infrared properties of $Bi_{12}GeO_{20}$ single crystal*

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Far-infrared reflectivity spectra of bismuth germanium oxide ($Bi_{12}GeO_{20}$) single crystals are measured from room temperature down to 10 K. All the reflectivity spectra are fitted to a complex dielectric function $\varepsilon(\omega)$ in the factorised form. Phonon modes at low frequency are found to develop upon decreasing temperature and gain considerable spectrum weight below 150 K. The temperature-dependent static dielectric constants are obtained from the Lyddane–Sachs–Teller relation based on the obtained oscillator parameters. The dielectric constants are found to increase upon decreasing temperature, which is attributed to the charge transfer among the ions in the unit cell with the temperature varying.

Keywords: infrared reflectivity, dielectric properties, phonon
PACC: 7000, 6300, 7700

1. Introduction

High dielectric constant materials play an important role in the dynamic random access memory devices whose miniaturization will ultimately be determined by the static dielectric constant ε_0. In general, materials with ε_0 larger than 7 are classified as high dielectric constant material. Because of the potential technical applications of high dielectric constant materials, great efforts have been made to study their various physical properties and the factors that influence the behaviours of their dielectric functions. Bismuth germanium oxide $Bi_{12}GeO_{20}$ (BGO) is a member of the well-known sillenite compounds $Bi_{12}MO_{20}$ (M=Si, Ti, Ge, Mn, etc.), which has a static dielectric constant of about 50.[1] Besides, BGO also exhibits remarkable piezoelectric and photorefractive effects which are strongly related to its dielectric properties. BGO has a body centred cubic structure with I23 space group, and there are two formula units in the crystallographic unit cell with the lattice parameter a = 1.01471(8) nm.[2] Ge ions occupy the corners and centre of the cubic cell and are surrounded by oxygen isolated from tetrahedrons (GeO_4). The valances of Bi, Ge, and O are +3, +4, and –2, respectively. The overall research of BGO began in 1967 when its single crystal was first successfully grown by Ballman,[3] afterwards various aspects of its physical properties were studied.[4−8] Although a lot of studies have been carried out on the infrared spectra and Raman scattering spectra of BGO, there are few reports on the temperature-dependent dielectric properties of BGO.[9−12] The operation of the memory and optical devices related to the dielectric properties to a large extent will be influenced by the stability upon varying the environment parameters such as temperature. Therefore, it is of great interest to study the temperature-dependent optical properties of the large dielectric constant materials. In this paper, we report on the temperature-dependent optical properties of BGO by studying the far-infrared reflectivity spectra from room temperature down to 10 K. The temperature-dependent static dielectric constants are obtained.

2. Experiment

Single crystals of $Bi_{12}GeO_{20}$ were grown by the Czochralski method. It was cut with the dimen-

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sions of 10×10×0.5 mm^3 and was one-side polished into a surface parallel to the (001) crystalline plane. The sample was mounted in an optical cryostat in which the temperature could be well controlled between 4.2 K and 300 K with an accuracy of better than 0.2 K. Near-normal incident (at an incident angle of about 8°) reflectivity spectra $R(\omega)$ were obtained by using a Fourier transform infrared (FTIR) spectrometer (Bomen DA8) in the frequency range 50–7000 cm^{-1} with a resolution of 4 cm^{-1}. In the far-infrared region (FIR), a DTGS detector and a 6-μm mylar beam-splitter coated with Ge were used. In the mid-infrared region (MIR), a combination of a liquid nitrogen cooled MCT detector and a KBr beam-splitter was utilized. In both regions, SiC (globar) was used as the light source. To obtain the absolute reflectivity, the reflectance of an evaporated gold film was used as a reference at each temperature.

3. Results and discussion

Shown in Fig.1 are the far-infrared reflectivity spectra of BGO single crystal at several representative temperatures. It can be clearly seen that the spectra are dominated by the infrared active optical phonons. The reflectivity spectra become featureless from a frequency of about 680 cm^{-1} (high phonon mode) up to the highest frequency measurable. The reflectivity increases with temperature decreasing, which is due to a reduction in anharmonic thermal motion and an increase in oscillation strength of vibration modes. It is noticed that at room temperature, there are 13 visible phone modes. As the temperature decreases, the phonon modes around 105 cm^{-1} and 204 cm^{-1} obtain their spectrum weight rapidly. Below 150 K, the phonon modes around 173, 190 and 362 cm^{-1}

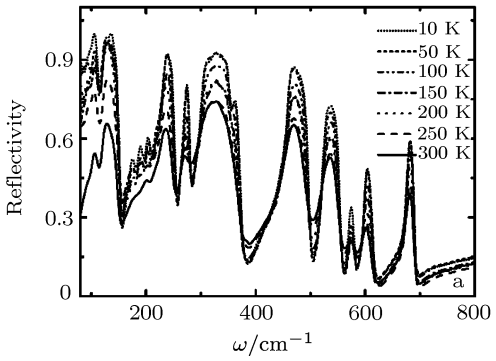


Fig.1. Far-infrared reflectivity spectra of $Bi_{12}GeO_{20}$ single crystal at different temperatures.

develop and becomes visible. This can also be seen in the Raman scattering spectra as shown in Fig.2. From the Raman spectra, we also notice that the phonon mode at 45 cm^{-1} is greatly enhanced upon decreasing temperature.

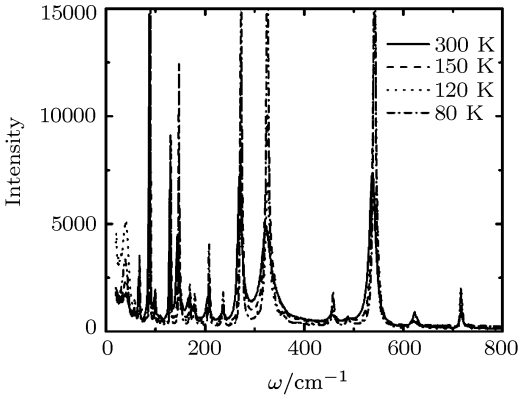


Fig.2. Raman scattering spectra of $Bi_{12}GeO_{20}$ single crystal at several representative temperatures.

The mode frequencies are obtained from a damped harmonic oscillator fitting to the reflectivity spectra with a complex dielectric function $\varepsilon(\omega)$ in the factorised form (generalised Lyddane–Sachs–Teller relation), i.e.[13,14]

$$\begin{aligned}\varepsilon(\omega) &= \varepsilon_1(\omega) + \mathrm{i}\,\varepsilon_2(\omega) \\ &= \varepsilon_\infty \prod_{j=0}^{n} \frac{\omega_{j,\mathrm{LO}}^2 - \omega^2 - \gamma_{j,\mathrm{LO}}\omega}{\omega_{j,\mathrm{TO}}^2 - \omega^2 - \gamma_{j,\mathrm{TO}}\omega},\end{aligned} \tag{1}$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and the imaginary parts of the complex dielectric function $\varepsilon(\omega)$, respectively, and ε_∞ is the high-frequency dielectric constant (at frequencies that are large compared with the lattice vibration frequencies but small compared with the electronic transition frequencies), n the number of phonon modes, $\omega_{j,\mathrm{TO}}$ and $\omega_{j,\mathrm{LO}}$ represent the transverse and the longitudinal eigen-frequencies of the j-th vibration respectively, and $\gamma_{j,\mathrm{TO}}$ and $\gamma_{j,\mathrm{LO}}$ the transverse and the longitudinal damping constants of the j-th vibration mode respectively. Using this dielectric function, all the reflectivity spectra in our measurements are fitted to the well-known Fresnel formula for reflectivity of a half space medium in vacuum, expressed as

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

Based on expressions (1) and (2), a fit of $R(\omega)$ to the observed reflectivity spectra can be obtained with an appropriate choice of the model parameters $\omega_{j,\mathrm{TO}}$,

$\omega_{j,\mathrm{LO}}$, $\gamma_{j,\mathrm{TO}}$, $\gamma_{j,\mathrm{LO}}$, and ε_∞. Adjustment of the parameters is made by trial-and-error fitting of expression (2) to the experimental spectra. This method yields the model parameters of the infrared active phonons which can be used to calculate $\varepsilon(\omega)$.

We have used 13 phonon modes in the fitting ($n = 13$ in expression (1)), the fitting results of the oscillator parameters for all the phonon modes of BGO are summarised in Table 1. The high frequency dielectric constant ranges from 7.6 to 8.0 at various temperatures. The frequencies of the transverse and the longitudinal optical (TO and LO) phonons accord well with those obtained in Refs.[9] and [15]. Figure 3 presents the experimental and fitting curves at two representative temperatures of 300 K and 50 K. It is evident that excellent fits have been obtained over all frequency regions.

Table 1. Fitting parameters of all oscillators including transverse modes, longitudinal modes and their damping factors at 300 K and 50 K. All are in units of cm $^{-1}$.

300 K $\varepsilon_\infty = 7.6$				50 K $\varepsilon_\infty = 8.0$			
$\omega_{\mathrm{TO},j}$	$\gamma_{\mathrm{TO},j}$	$\omega_{\mathrm{LO},j}$	$\gamma_{\mathrm{LO},j}$	$\omega_{\mathrm{TO},j}$	$\gamma_{\mathrm{TO},j}$	$\omega_{\mathrm{LO},j}$	$\gamma_{\mathrm{LO},j}$
110	50	112	10	102	05	116	10
122	21	151	13	121	06	152	8.5
178	60	180	30	178	15	182	12
186	45	190	40	191	16	196	8
194	38	214	34	200	12	213	28
230	14	254	15	232	3.5	256	10
265	16	282	49	270	4	282	13
308	19	378	50	305	9	357.5	13
–	–	–	–	358	9.8	378	21
458	21	499	30	458	8	500	10
524	26	560	19	524	11.5	559	9
570	21	584	35	570	11	584	18
600	14	610	19	600	5	614	25
677	9	690	15	677	4	689	17

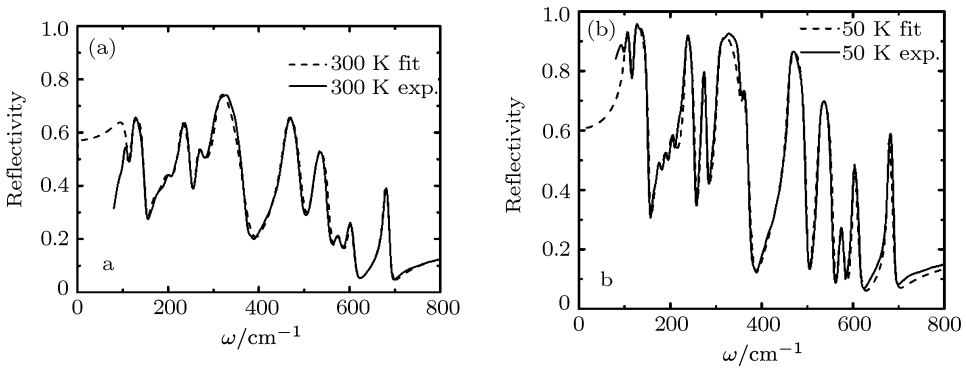


Fig.3. Experimental and fitted reflectivity spectra of $Bi_{12}GeO_{20}$ single crystal at (a) 300 K and (b) 50 K.

After the phonon modes have been obtained, the phone modes can be assigned. A comparison between those modes of BGO and $Bi_{10}SiO_{20}$[9,15] shows that the modes below 60 cm^{-1} are due to the motion of Bi atoms in the crystal lattice and the modes between 100 cm^{-1} and 450 cm^{-1} belong to the transition and rotation modes of GeO_4 unit, the four modes from 450 cm^{-1} to 620 cm^{-1} correspond to the asymmetric stretching modes of four Bi-O bonds with different lengths, and the highest phonon is taken to be due to the O–O vibration. The phonon mode at 356 cm^{-1} appears at 150 K may be due to a reduction in symmetry of GeO_4 unit.

With the above fitting results, the real part of the optical conductivity $\sigma_1(\omega)$ can be calculated from the complex dielectric function with the relation[16]

$$\sigma_1(\omega) = \mathrm{Im}(\varepsilon(\omega))\frac{\omega}{4\pi}. \quad (3)$$

Figure 4 shows the optical conductivity spectra at several representative temperatures. The optical conductivity is dominated by peak structures due to the contribution of optical phonon absorption, and no free carrier contribution can be observed. The conductivity tends to 0 when the frequency is extrapolated to zero frequency. This character accords with the fact that BGO is a good insulator with a band-gap of 3.25 eV. Upon reducing temperature, the intensity of the conductivity peak increases while the peak width narrows: this is a result of the enhancement of oscillation strength and the reduction of thermal broadening. Several phonon modes at low frequencies show considerable red-shifts with temperature decreasing.

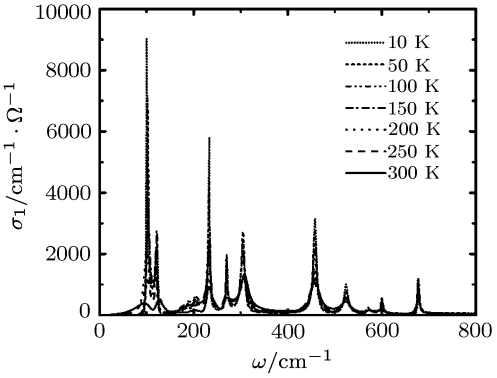


Fig.4. Curves for real part of the optical conductivity of $Bi_{12}GeO_{20}$ single crystal at different temperatures.

For spectrum analysis, the various sum rules provide useful tools to analyse the physical properties of the material in study. The partial conductivity sum rule for oscillators reads[17]

$$\frac{120}{\pi}\int_{\omega_l}^{\omega_h}\sigma_1(\omega)\mathrm{d}\omega = \omega_{p,j}^2, \quad (4)$$

where ω_l and ω_h are the high and the low bounds of the j-th optical oscillator. This sum rule implies that when there is no change in the bonding or coordination, the spectrum weight (the integrated area under the peak) of the corresponding phonon mode should keep constant. From Fig.4, we can see that the spectrum weights of the phonon modes at 102, 122, 204 cm^{-1} are enhanced considerably with temperature decreasing. The dramatic increase in the spectrum weight of low frequency phonon mode clearly violates the partial conductivity sum rule, which suggests that the charges are redistributed within the unit cell upon varying temperature. The low frequency modes display an anomalous increase in oscillation strength at low temperatures, indicating that the Born effective charge is increasing in the unit cell. Similar phenomena have also been observed in other large dielectric constant materials, such as $CaCu_3Ti_4O_{12}$ and $CdCu_3Ti_4O_{12}$.[16,17]

The Lyddane–Sachs–Teller (LST) relation, which can be obtained from expression (1) in the zero-phonon approximation, relates the static optical permittivity and high-frequency optical permittivity with transverse and longitudinal phonon frequencies as follows:

$$\frac{\varepsilon_0}{\varepsilon_\infty} = \prod_j \frac{\omega_{j,\mathrm{LO}}^2}{\omega_{j,\mathrm{TO}}^2}. \quad (5)$$

With expression (5) and the fitting parameters listed in Table 1, we obtain the values of static dielectric constant ε_0 at different temperatures. The results are plotted in Fig.5. The value of ε_0 increases with temperature decreasing. The obtained values, 50∼65, are in reasonable agreement with those reported in Ref.[1]. As we discussed above, when the temperature decreases, the Born effective charges in the ions increase, which induces an enhanced dipole moment. As a result, ε_0 is expected to increase with temperature decreasing, this is exactly what we obtained from the LST relation as shown in Fig.5. It is noticed that there is a kink at around 150 K in the plot of Fig.5. From the far-infrared spectra and Raman spectra, we know that an additional phonon mode appears at 150 K, which suggests a possible phase transition at this temperature. Such a phase transition would result in a redistribution of ions, thereby inducing a change in dielectric constant.

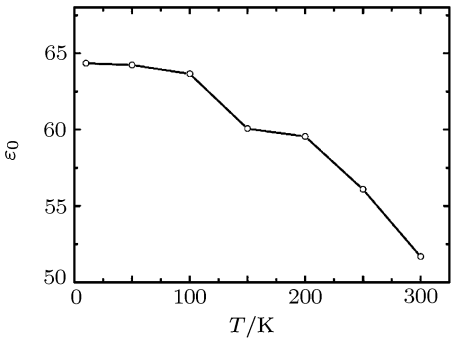


Fig.5. Temperature dependence of static dielectric constant ε_0 of $Bi_{12}GeO_{20}$ single crystal.

4. Conclusions

Temperature-dependent optical properties of BGO are studied by measuring the far-infrared reflectivity spectra. The reflectivity spectra are fitted to a complex dielectric function in the factorized form. New phonon modes at temperatures below 150 K are observed. Spectrum weight of phonons is found to violate the partial conductivity sum rule, which is related to the charge transfer among the ions in BGO. The increase of dielectric constant is attributed to the enhancement of dipole moment resulting from the enhancement of Born effective charges in ions.

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