First-principles study on linear and nonlinear optical properties of $ZnGeP_2$*

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The study of the linear and nonlinear optical properties of $ZnGeP_2$ based on density functional theory has been carried out. In order to get a more physical picture in the infrared region, terms which are considered as the phonon effect were added to the calculated refractive dispersion curves. The phonon-corrected calculation curves show excellent agreement with experimental refractive indexes, which gives a better comprehension of the linear optical proprieties in the transparent region. The static nonlinear optical susceptibility was investigated using approaches based on the "sum over states" and the $2n+1$ theorem methods. Both of the results of these two methods reasonably coincided with the experimental results.

Keywords: $ZnGeP_2$, phonon effect, $2n+1$ theorem, "sum over state" method

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1. Introduction

Ternary chalcopyrite $A^{II}B^{IV}C_2^V$ (A = Zn, Cd; B = Ge, Si; C = P, As) crystals are promising for optical conversion applications in solid state laser systems. Among these, zinc germanium phosphide ($ZnGeP_2$) is an excellent infrared (IR) nonlinear optical (NLO) crystal, which not only has the common merits of chalcopyrite structure crystals but also exhibits very good thermal and mechanical properties. Owning to these advantages, $ZnGeP_2$ is widely used for frequency conversion in the mid-IR region.[1,2]

Normally, the transmission window of $ZnGeP_2$ is bounded by the band edge at 620 nm and by an intense two-phonon absorption peak at 13 μm,[3,4] the phonon effect related to dispersion should be considered in this region. Density functional theory (DFT) is a widely used method in NLO crystal theoretical studies. Most of previous DFT studies[5–10] on linear optical property calculation for NLO crystals were simply based on the electronic response to the light. This method gave a relative reliable birefringence result. However, the phonon effect was ignored in the calculation, which caused obvious discrepancies between the experimental and the calculated refractive dispersion curves; that is to say, the calculated curves were nearly flat in the mid/far-IR regions while the experiment curves were downward.

In fact, there are hardly any reports on the influence of the phonon effect, except for the $CdSiP_2$ and $CdSiAs_2$[11] crystals first-principles optical calculation. In this paper, the calculated refractive dispersion curves of $ZnGeP_2$ crystal were corrected with the phonon effect considered. The agreement between phonon-corrected calculation curves and the experiment data is very good, which gives a reasonable description of the linear optical property for $ZnGeP_2$.

Moreover, static nonlinear optical susceptibility is also important to nonlinear crystals, and extensive attention is attracted to obtain the coefficients from the calculation aspect. With the progress of theory, DFT calculation can now be used to calculate and predict nonlinear optical properties directly. There are two common methods which are used in the framework of DFT to calculate static nonlinear optical susceptibility: traditional "sum over states" [12,13] and the recently implemented $2n+1$ [14,15] theorem. In this work, both of these approaches are used intentionally to calculate the static nonlinear optical susceptibility of $ZnGeP_2$ to give more reliable calculated results.

This paper is organized as follows. In Section 2, we describe briefly the details of our computational approach. The calculated results are listed in Section 3. A summary of this work is given in Section 4.

2. Computational method

In a crystal, the polarization $\boldsymbol{P}$ can be expressed as a Taylor expansion of the macroscopic electric field, $\boldsymbol{E}$, according to

$$\boldsymbol{P} = \varepsilon_0(\chi_{ij}^{(1)} \cdot \boldsymbol{E} + \chi_{ijk}^{(2)} : \boldsymbol{E}\boldsymbol{E} + \cdots), \tag{1}$$

where $\chi_{ij}^{(1)}$ and $\chi_{ijk}^{(2)}$ are linear and nonlinear optical susceptibilities, respectively.

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Usually, in the framework of random-phase approximation (RPA), the expression of the linear optical susceptibility $\chi^{(1)}$ is

$$\chi_{ij}^{(1)} = \frac{e^2}{\hbar\Omega}\sum_{n,mk} f(\boldsymbol{k})\frac{r_{nm}^{i}(\boldsymbol{k})r_{nm}^{j}(\boldsymbol{k})}{\omega_{nm}(\boldsymbol{k})-\omega'} = \frac{\varepsilon_{ij}-\delta_{ij}}{4\pi}, \tag{2}$$

where ε_{ij} is the ij component of the dielectric tensor and r_{nm} is the position matrix element.

The "sum over state" method considers that the nonlinear optical susceptibility $\chi_{ijl}^{(2)}$ can be divided into three major contributions: the inter-band transitions $\chi_{ijk}^{(2)}$ (inter), the intra-band transitions $\chi_{ijk}^{(2)}$ (intra), and the modulation of inter-band terms by intra-band terms $\chi_{ijk}^{(2)}$ (mod)

$$\chi_{ijk}^{(2)} = \chi_{ijk}^{(2)}(\text{inter}) + \chi_{ijk}^{(2)}(\text{intra}) + \chi_{ijk}^{(2)}(\text{mod}). \tag{3}$$

Anther method to calculate the nonlinear optical susceptibility $\chi_{ijl}^{(2)}$, as described above, is the $2n+1$ theorem. In this scheme the computation of energy derivatives up to third order only requires the ground-state and first-order wavefunctions, the nonlinear optical susceptibility is calculated by a third-order derivative of the energy with respect to low-frequency electric field, that is

$$\chi_{ijl}^{(2)} = -\frac{3}{\Omega}E^{\varepsilon_i\varepsilon_j\varepsilon_l}. \tag{4}$$

Earlier studies indicated that the electronic band of $ZnGeP_2$ crystal could be derived from the indirect gap in GaP, and the experiment indicated a direct band gap.[16,17] The calculated band gaps were indirect when local density approximation (LDA) exchange-correction energy was used,[16,18] while the result was direct when generalized gradient approximation (GGA) was employed.[17] Therefore, GGA (PBE[19]) is applied to calculate the linear and nonlinear optical susceptibilities in "sum over states" method.

Our calculation is based on density functional theory (DFT) and pseudo-potential plane wave method implemented in ABINIT[20,21] package. LDA[22] is used to calculate the static nonlinear optical susceptibility in $2n+1$ theorem calculation. Troullier–Martins[23] norm-conserving pseudo-potentials are used in both two methods. All of our calculations involve an eight-atom tetragonal primitive cell. The original lattice constants and internal coordinate used in our calculation are taken from the experimental values.[24] For Zn $3d^{10}4s^2$ electron, for Ge $4s^24p^2$, and for P $3s^23p^3$ electrons are treated as valence electrons. A high plane-wave energy cutoff of 40 Hartree and $4\times4\times4$ Monkhorst–Pack k-points mesh are found to be sufficient to reach convergence for the lattice relaxation and the band structure calculation. In the "sum over state" optical property calculation, the k-points mesh increases to $10\times10\times10$, and the valence bands increase to 70.

The calculated band gap by GGA is 1.06 eV, while the experimental data are 2.0 or 2.1 eV;[25] GGA is well known to underestimate the band-gap by up to 100%. Therefore, a scissors operator is usually introduced to shift all of the conduction bands to agree with the measured value of the band gap.

3. Results

3.1. Refractive indexes and birefringence

For chalcopyrite structure with space group of $\bar{4}2m$, the dielectric tensor is

$$[\varepsilon_{ij}] = \begin{bmatrix} \varepsilon_{11} & 0 & 0 \\ 0 & \varepsilon_{11} & 0 \\ 0 & 0 & \varepsilon_{33} \end{bmatrix}, \tag{5}$$

i.e., there are two independent tensor elements. Below the gap, the imagined parts of the tensor compounds trend to zero, and can be ignored. Normally, the relationship between dielectric tensor and the refractive index are

$$\varepsilon_{11} = n_{\text{o}}^2, \quad \varepsilon_{33} = n_{\text{e}}^2, \tag{6}$$

where n_{o} and n_{e} are two principal refractive indexes which are parallel and perpendicular to the optical axis respectively.

The calculated refractive dispersion curves in the transparent region are shown in Fig. 1(a). First, the refractive indexes are overestimated compared with the experimental data. This may be mainly caused by the lack of local field effect in the calculations.[26] Second, and more importantly, the origin of dispersion properties for semiconductors in the transparent regions is mainly attributed to two basic physical processes: the electronic transition and phonon effect, and these processes to dispersion properties can be exactly described by the Sellmeier[27–29] equation. Normally, the Sellmeier equation containing two poles terms, which is

$$n^2 = A + \frac{B}{1-C/\lambda^2} + \frac{D}{1-E/\lambda^2}, \tag{7}$$

is sufficient for most IR NLO crystals, where the second term can be interpreted as electronic band gap absorption and the last term is related to phonon effect.[11,30,31] However, previously and in our calculation, only the electronic response to the light is considered. Therefore, the calculated curves are fitted using formula (7) initially without the last term, the coefficients A, B, and C are extracted. Since the phonon effect is not included in our first-principles calculation, a term acting as the phonon effect is added to the calculated refractive dispersion curve equation. For both the ordinary and extraordinary refractive dispersion curves, the phonon effect can be considered equal in the two curves, approximately, so the two phonon effect terms are the same here. The E represents the square of the average absorption wavelength in units of μm for phonon absorption frequency[30,32] (or transverse optical (TO) phonon frequency), while the D here is like a "scale factor" of the phonon effect. Here, the selections of parameters D and

E are taken from Ref. [11]: the E parameters take the same values of 660 μm^2, and the D parameters do not vary much between the various chalcopyrite structures and are taken as 1.5. As mentioned above, the refractive indexes are overestimated, so the A parameters are slightly adjusted to correct the overestimate to match the experimental data. Finally, the expressions of phonon-corrected calculation curves are

$$\begin{aligned} n_{\rm o} &= 6.32566 + \frac{3.40019}{1-0.20045/\lambda^2} + \frac{1.5}{1-660/\lambda^2}, \\ n_{\rm e} &= 7.48661 + \frac{2.50092}{1-0.26573/\lambda^2} + \frac{1.5}{1-660/\lambda^2}, \end{aligned} \tag{8}$$

where λ is given in micrometers. The corrected calculated curves are shown in Fig. 1(a), the maximal relative deviations of calculated results with experiment data were less than 2% in the whole transparent region and less than 0.1% after 1 μm. Generally, the transparent regions are $\sqrt{C} < \lambda < \sqrt{E}$, hence the phonon effect term is negative, and makes the refractive dispersion curve downwards. The phonon-corrected calculation birefringence ($n_{\rm e}$–$n_{\rm o}$) curve is shown in Fig. 1(b). It is found that the agreement of phonon-corrected birefringence with the experimental values is better than 10%. Besides, calculated birefringence curve without phonon effect correction is nearly flat after 3 μm; the phonon-corrected calculation birefringence curve increases with the increasing of the wavelength, so do the experimental birefringence. This method may be suitable for other IR crystals with the determination of phonon effect term parameters D and E.

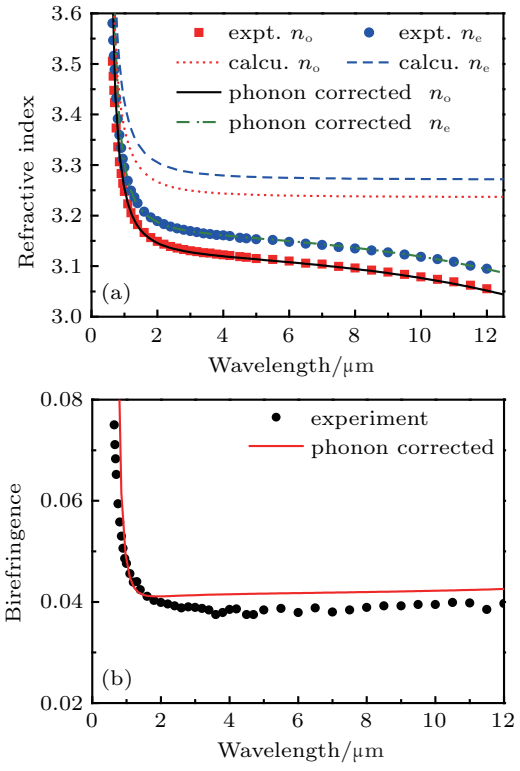


Fig. 1. (color online) (a) Calculated, phonon-corrected and experimental refractive dispersion curves of $ZnGeP_2$, (b) phonon-corrected calculation birefringence curve of $ZnGeP_2$. Experimental data are taken from Ref. [25].

3.2. Static nonlinear optical susceptibility

Now, we focus on the results for the nonlinear optical susceptibility in the zero-frequency limit. The second-order nonlinear optical susceptibility $\chi^{(2)}_{ijk}(\omega)$ is a third-rank tensor. In the literature about nonlinear optics, instead of using this $\chi^{(2)}_{ijk}(\omega)$ tensor, $d_{ijk} = 1/2\chi^{(2)}_{ijk}$ was used preferably, which can be contracted to a 3×6 matrix d_{il} using the following simplified indices:

$$\begin{array}{cccccccc} jk \rightarrow & 11 & 22 & 33 & 23,32 & 31,13 & 21,12 \\ l \rightarrow & 1 & 2 & 3 & 4 & 5 & 6. \end{array}, \tag{9}$$

For $ZnGeP_2$, the d_{il} tensor has only one independent element. The form of this tensor is given by

$$d_{il} = \begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{14} \end{bmatrix}. \tag{10}$$

The calculated results obtained by these two methods are listed in Table 1, both of which coincide with the experimental results reasonably. The "sum over state" result in our calculation is closer to the experimental data than that in Ref. [16]. In all probability, this mainly happens because a linear muffin-tin orbitals method, which is efficient but less precise, was adopted in Ref. [16], while the more precision pseudo-potential plane wave method is adopted in this paper.

Table 1. The measured and calculated static nonlinear optical susceptibilities (in units of pm/V) of $ZnGeP_2$.

Expt.	Semi-empirical method		DFT	
	bond charge model	plasma oscillations theory	sum over state	$2n+1$ theorem
70±7 75±8[25]	75.3[33]	56.9[34]	51[16] 72.7[a)]	86[a)]

Note: [a)] this work.

In general, polarization depends on electrons as well as phonons. The second-order nonlinear optical polarization belongs to higher-order polarization, the phonon effect should affect the SHG coefficients. In the present paper, we deal only with the electronic contribution of the two methods. Compared with the previous results,[16,35,36] the calculated SHG coefficients matched to the experiments reasonably, even though only the electronic effect was considered, which indicated less contribution from the phonon effect.

4. Conclusion

The phonon-corrected refractive dispersion curves give a reasonable description of the linear optical property of $ZnGeP_2$, which indicates the importance of phonon effect in the transparent region for IR NLO crystals. Phonon effect coefficients D and E are taken from experimental and empirical values, so the method to obtain two coefficients directly from the calculation approach must be improved in the future. The static nonlinear optical susceptibility calculated by

the two methods is in reasonable agreement with experimental results, the $2n+1$ theorem provides a new method to predict static nonlinear optical susceptibility for a NLO crystal.

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