The linear and nonlinear optical response of CsGeX$_3$ (X = Cl, Br, and I): The finite field and first-principles investigation

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ABSTRACT

In this paper, the linear and second order nonlinear optical properties of CsGeX$_3$ (X = Cl, Br, and I) compounds have been investigated using the finite field method combined with the density functional investigation. The obtained results are in good agreement with the experimental values. The electron density distribution nearby the fermi level is the lobe-like lone pair electrons which make the germanium-halogen polyhedra distorted. The atomic contribution to the birefringence and SHG response is analyzed using the Born effective charges, the variation of the atomic charges, and the SHG density method. The results show that the germanium and halogen atoms give main contribution to the optical anisotropic birefringence and the SHG response.

1. Introduction

Since 1960s, lots of attentions have been paid to the nonlinear optical (NLO) compounds which can be used to produce coherent light via second-harmonic generation (SHG) in solid state lasers [1]. Many NLO compounds with perfect nonlinear optical properties have been successfully synthesized, such as the very famous ultraviolet (UV) nonlinear optical crystals BBO [2], LBO family [3–6], KBBF family and KBBF-like compounds [7–24], some other acentric borates [25–40], carbonates [41–48], phosphates [49–53], and so on. Except the deep ultraviolet/ultraviolet (DUV/UV) nonlinear optical compounds, the infrared (IR) nonlinear optical compounds have also attracted plentiful attentions. Besides the commercially widely used IR NLO crystals AgGaS$_2$, AgGaSe$_2$, and ZnGeP$_2$ [54–56], lots of IR NLO compounds have also been obtained, examples including Li$_3$VO$_4$ [57,58], Pb$_{17}$O$_8$Cl$_8$ [59], BaGa$_2$X$_7$ (X = S, Se) [60,61], ATeMoO$_6$ [62–65], ABX$_3$ (A = Cs, Rb; B = Ge, Cd; X = Cl, Br, and I) [66–71], and so on [72–76]. While comparison with the DUV/UV NLO compounds, the IR NLO compounds are still relatively rare, which push people to design and synthesize more IR NLO compounds to meet the needs.

To promote designing novel IR NLO compounds, lots of efforts have been made to investigate the electronic structures, the linear and nonlinear optical response. Tang et al. have investigated the linear and second-order optical response of CsGeX$_3$ (X = Cl, Br, and I) using the first principles method [77], the results show that the lattice distortion give main contribution in determining the linear and nonlinear optical responses of CsGeX$_3$ (X = Cl, Br, and I) compounds. Kang et al. have investigated the bandgap and the SHG response of the halide crystals using the first principles method [78], the results show that the [MX$_6$] (M = center cation, X = halide anion, $k = 6, 4, 3$, or $2$) anionic units play an important role in determining the optical response. Grant Walters et al. have investigated the electro-optic response in germanium halide perovskites using the first principles method [70].

Recently the finite field combined with first principles method have been utilized to investigate the linear and nonlinear optical
response under external electric field. Using the finite field one can get the macroscopic polarization and the linear and nonlinear optical response under different external photoelectric field, and one can also get the atomic charges and the variation of the atomic charges under external photoelectric field, which can be used to distinguish atomic contribution to the total SHG response [79–81]. This strategy has been used to investigate the microscopic origination of the SHG response in BPO₄ [82,83], KBBF family [80], ATeMoO₆ (A = Mg, Zn, and Cd) compounds [79], ABCO₃F compounds [81], and so on.

In this paper, the finite field method combined with first principles investigation will be used to investigate the linear and nonlinear optical response of CsGeX₃ (X = Cl, Br, and I) compounds. The obtained refractive indices, birefringence and SHG tensors are in good agreement with the experimental values and first-principles results. The lone-pair electrons of germanium atoms are verified by the orbitals nearby the fermi level. And the atomic contribution to the optical anisotropic birefringence and the SHG response are analyzed using the Born effective charges, the variation of the atomic charges, and the SHG density method. The results show that the germanium and halogen atoms give main contribution to the birefringence and the SHG response.

2. Numerical calculations details

The macroscopic polarization under different electric field can be expressed as [79]

\[ P_{i}^{(mac)} = \sum_{j} x_{ij}^{(1)} E_{j} + \sum_{jk} x_{ijk}^{(2)} E_{j} E_{k} \]  

(1)

More details can be found in Ref. [79]. In this paper, the macroscopic polarization \( P_{i}^{(mac)} \) was firstly calculated using the finite field methods implemented in ABINIT code [84–86], and then the refractive indices (and birefringence) and the nonlinear optical coefficients were obtained [79,80]. The ICSD data (CsGeCl₃: ICSD-62557; CsGeBr₃: ICSD-62558; CsGeI₃: ICSD-62559) were used to do the finite field calculations. During the calculations, the PBE-GGA functional were used, and the norm-conserving pseudopotentials(NCP) [87] were adopted. The energy cutoff was set as 40.0 hartree along with a dense k-point sample (12 × 12 × 12). For comparison, the SHG response were also calculated using the Density-Functional Perturbation Theory (DFPT) method [88] implemented in ABINIT code. During the calculation, the LDA functional was used, and same values about energy cutoff and k-point sample like finite field calculations were used.

The electronic structure, the Born effective charges, and the variation of the atomic charges, and the SHG density method. The results show that the germanium and halogen atoms give main contribution to the birefringence and the SHG response.

3. Results and discussions

3.1. The electronic structures and the lone pair electrons

Using the method described above, the band structures, the projected density of states (PDOS), and the electron structures of CsGeX₃ (X = Cl, Br, and I) were obtained. The obtained band structures of CsGeX₃ (X = Cl, Br, and I) are shown in Fig. 1. As shown in Fig. 1, all of these compounds are direct bandgap compounds whose maximum valence band and minimum conduction band are all located at the Z point. The obtained bandgaps of CsGeX₃ (X = Cl, Br, and I) compounds are 1.95, 1.27, and 0.80 eV, respectively. The obtained projected densities of states (PDOS) are also shown in Fig. 1. As shown in Fig. 1, all of these compounds own similar projected densities of states. Take CsGeCl₃ for example. For CsGeCl₃ compound, the localized Cs-p states are found nearby -8.2 eV, indicating its ionic character. The hybrid Ge sp – Cl p states are found at the top of the valence band (from −8.5 eV to the Fermi level), indicating the covalent interaction between germanium and halogen atoms. The hybrid states from the cesium, germanium and halogen atoms are also found at the bottom of the conduction bands. It is well known that the optical properties have relation with the electron transition among the states at the top of the valence band and the bottom of the conduction band [40,50,58,97–103], hence one can deduce that polyhedron containing germanium and halogen atoms would give main contribution to the linear and nonlinear optical properties of CsGeX₃ (X = Cl, Br, and I) compounds.

The obtained projected densities of states (PDOS) are also shown in Fig. 1. As shown in Fig. 1, these compounds own similar projected densities of states. Take CsGeCl₃ for example. For CsGeCl₃ compound, the localized Cs-p states are found nearby -8.2 eV, indicating its ionic character. The hybrid Ge sp – Cl p states are found at the top of the valence band (from −8.5 eV to the Fermi level), indicating the covalent interaction between germanium and halogen atoms. The hybrid states from the cesium, germanium and halogen atoms are also found at the bottom of the conduction bands. It is well known that the optical properties have relation with the electron transition among the states at the top of the valence band and the bottom of the conduction band [40,50,58,97–103], hence one can deduce that polyhedron containing germanium and halogen atoms would give main contribution to the linear and nonlinear optical properties of CsGeX₃ (X = Cl, Br, and I) compounds.

It is interesting to note that, for the CsGeCl₃ compound, the hybrid Ge s-Cl p states are found at the energy region (-8.5 , -7) eV which is the bonding stats of Ge-Cl chemical bond, and the hybrid Ge sp – Cl p states are found at the energy region (-5 , 0) eV which is coming from the interaction between the antibonding states of Ge-s Cl p and the Ge p states. Similar hybrid states from the germanium and halogen atoms can also be found in other CsGeX₃ (X = Br, I) compounds (shown in Fig. 1). According to the revised model about the formation of the lone-pair electrons in post transition-metal atoms [104–106], the authors believe that the germanium sp – halogen p states nearby the Fermi level would own the electron density distribution like lone-pair electrons. The states nearby the Fermi level are shown in Fig. 2. It clearly shows the lobe-like lone pair electrons. The lone pair electrons around the germanium make the germanium-halogen polyhedron distorted, which would play an important role in determining the linear and nonlinear optical response under the external photoelectric field. The distorted germanium-halogen polyhedrons are further shown in Fig. S1 in supporting information (SI).
3.2. The refractive indices, birefringence and the Born effective charges

Using the method described above, the macroscopic polarization under different external electric field was obtained. The refractive indices along different optical principle axis can be obtained using the equation about the first order linear optical term of the macroscopic polarization \( P^{(1)}_{ij} = \sum \chi_{ij} E_i \) and \( n_i = \sqrt{1 + 4\pi \chi_{ii}} \) [79,80]. The obtained refractive indices and the birefringence are shown in Table 1. For comparison, the refractive indices and birefringence of CsGeX₃ (X = Cl, Br, and I) are also obtained using density functional theory implemented in the CASTEP code. As shown in Table 1 and Fig. 3, the refractive indices and birefringence obtained from the finite-field methods implemented in ABINIT code [84–86] are similar with the one obtained using the CASTEP code [89]. One can also find out that although the birefringence of these CsGeX₃ (X = Cl, Br, and I) compounds are relative small, but they own relative small refractive indices dispersion which would make these compounds meet the phase-matching conditions. Actually these compounds are all phase matchable [66,67].

To better understand the atomic contribution to the refractive indices and the birefringence, the Born effective charges have also been calculated. More details about the Born effective charges can be found in Ref. [1], and Ref. [107]. The obtained Born effective charges are listed in Table 2 and Table S1 in SI. For CsGeX₃ (X = Cl, Br, and I) compounds crystallized into the 3m point group, the polarization of the ordinary light is in the xy plane, and the polarization of the extraordinary light is in the z axis. As shown in Table 2, for the alkali metal atoms, the Born effective charges in xy plane are similar with the Born effective charges along Z axis. The difference of the Born effective charges along the direction of \( n_x \) and \( n_z \) (\( \Delta q^{(\text{Born})} \)) is very small (from 0.008 to 0.03 for CsGeX₃ compounds), implying the alkali metal atoms give relative small contribution to the birefringence. For the germanium and halogen atoms, as shown in Table 2 and Table S1 in SI, the Born effective charges in xy plane are larger than the Born effective charges along the z axis, indicating these atoms give positive contribution to the birefringence. The positive contribution from the germanium and
halogen atoms may have relation with the covalent interaction between the germanium and halogen atoms, and the distorted polyhedron induced by the lone pair electrons around the germanium atoms.

3.3. The SHG response and the atomic contributions

For the CsGeX₃ (X = Cl, Br, and I) compounds crystallized in 3m point group, there are three different independent nonzero SHG tensors: d₁₅, d₂₂, and d₃₃. Hence the second term of the macroscopic polarization can be expressed as:

\[ P_{1}^{(2)} = 2\chi_{15} E_1 E_2 - 2\chi_{22} E_1 E_2 \]  

(2)

Fig. 2. The lobe-like electron density found in the orbitals nearby the fermi level of CsGeX₃ (X = Cl, Br, and I) compounds.
Table 1
The obtained refractive indices, birefringence and nonlinear optical coefficients using different methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>CsGeCl₃</th>
<th>CsGeBr₃</th>
<th>CsGeI₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>finite field</td>
<td>n₀</td>
<td>1.927</td>
<td>2.219</td>
</tr>
<tr>
<td></td>
<td>n₁</td>
<td>1.884</td>
<td>2.193</td>
</tr>
<tr>
<td>DFT</td>
<td>Δn</td>
<td>0.043</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>n₂</td>
<td>1.912</td>
<td>2.174</td>
</tr>
<tr>
<td>finite field</td>
<td>Δn</td>
<td>0.045</td>
<td>0.040</td>
</tr>
<tr>
<td>DFT</td>
<td>d₁₅</td>
<td>3.569</td>
<td>15.506</td>
</tr>
<tr>
<td></td>
<td>d₂₂</td>
<td>-0.412</td>
<td>-7.917</td>
</tr>
<tr>
<td>DFPT</td>
<td>d₁₅</td>
<td>8.502</td>
<td>20.968</td>
</tr>
<tr>
<td></td>
<td>d₂₂</td>
<td>5.391</td>
<td>21.313</td>
</tr>
<tr>
<td></td>
<td>d₃₃</td>
<td>1.468</td>
<td>13.080</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.633</td>
<td>25.295</td>
</tr>
</tbody>
</table>

Fig. 3. The obtained refractive indices and birefringence using the DFT methods.
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Table 2
The obtained diagonal tensor of atomic Born effective charges of CsGeX₃ (X = Cl, Br, and I) compounds. More details about the Born effective charges of CsGeX₃ (X = Cl, Br, and I) can be found in Table S1 in SI.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Atoms</th>
<th>qₓₓ</th>
<th>qᵧᵧ</th>
<th>qzz</th>
<th>ΔQ(Born)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsGeCl₃</td>
<td>Cs</td>
<td>1.12383</td>
<td>1.12383</td>
<td>1.11552</td>
<td>0.00831</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>3.05867</td>
<td>3.05867</td>
<td>2.69519</td>
<td>0.36348</td>
</tr>
<tr>
<td></td>
<td>Cl1</td>
<td>−0.94109</td>
<td>−1.84724</td>
<td>−1.27024</td>
<td>0.32915</td>
</tr>
<tr>
<td></td>
<td>Cl2</td>
<td>−1.62070</td>
<td>−1.16763</td>
<td>−1.27024</td>
<td>0.10261</td>
</tr>
<tr>
<td></td>
<td>Cl3</td>
<td>−1.62070</td>
<td>−1.16763</td>
<td>−1.27024</td>
<td>0.10261</td>
</tr>
<tr>
<td>CsGeBr₃</td>
<td>Cs</td>
<td>1.13943</td>
<td>1.13943</td>
<td>1.11047</td>
<td>0.02896</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>3.36581</td>
<td>3.36581</td>
<td>2.90198</td>
<td>0.46383</td>
</tr>
<tr>
<td></td>
<td>Br1</td>
<td>−0.90513</td>
<td>−2.09837</td>
<td>−1.33748</td>
<td>0.43235</td>
</tr>
<tr>
<td></td>
<td>Br2</td>
<td>−1.80006</td>
<td>−1.20344</td>
<td>−1.33748</td>
<td>0.13404</td>
</tr>
<tr>
<td></td>
<td>Br3</td>
<td>−1.80006</td>
<td>−1.20344</td>
<td>−1.33748</td>
<td>0.13404</td>
</tr>
<tr>
<td>CsGeI₃</td>
<td>Cs</td>
<td>1.12719</td>
<td>1.12719</td>
<td>1.09251</td>
<td>0.03468</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>3.80943</td>
<td>3.80943</td>
<td>3.12286</td>
<td>0.68567</td>
</tr>
<tr>
<td></td>
<td>I1</td>
<td>−0.94299</td>
<td>−2.34809</td>
<td>−1.40513</td>
<td>0.46214</td>
</tr>
<tr>
<td></td>
<td>I2</td>
<td>−1.99682</td>
<td>−1.29427</td>
<td>−1.40513</td>
<td>0.11086</td>
</tr>
<tr>
<td></td>
<td>I3</td>
<td>−1.99682</td>
<td>−1.29427</td>
<td>−1.40513</td>
<td>0.11086</td>
</tr>
</tbody>
</table>

\[
P^{(2)}_1 = -\chi_{12} E^2_1 + \chi_{12} E^2_2 + 2\chi_{13} E_2 E_3 \tag{3}
\]

\[
P^{(2)}_2 = \chi_{12} E^2_1 + \chi_{12} E^2_2 + \chi_{13} E^2_3 \tag{4}
\]

In which the \(P^{(2)}_1\), \(P^{(2)}_2\), and \(P^{(2)}_3\) are the macroscopic polarization along x, y, and z axes, and the \(E_1, E_2,\) and \(E_3\) are the external electric field along x, y, and z axes, the \(\chi_{12} = 2d_{15}, \chi_{23} = 2d_{22},\) and \(\chi_{33} = 2d_{33}\) are the SHG coefficients tensors. The obtained SHG tensors are also shown in Table 1. For comparison, the SHG tensors are also obtained using the DFPT methods. As shown in Table 1, the obtained SHG are in excellent agreement with the first principles results.

In order to analyze the atomic contribution to the second order nonlinear optical coefficients, the atomic charges and the variation of the atomic charge (\(\Delta Q\)) were calculated using the finite-field method. The variation of the atomic charge \(\Delta Q\) are the difference of the atomic charges when the external electric field was changed as 0.00001 atomic unit (a.u.). The obtained \(\Delta Q\) values are shown in Table 3. As shown in Table 3, for these CsGeX₃ (X = Cl, Br, and I) compounds, the alkali metal atoms own the smallest \(\Delta Q\) values, which indicates these atoms give very little contribution to the total nonlinear optical response, while the germanium atoms and the halogen atoms own relative large \(\Delta Q\) values (especially for the halogen atoms) which indicates these atoms give main contribution to the nonlinear optical response under the external electric field.

To further investigate the atomic contribution to the nonlinear optical response, a SHG-density technique are adopted. The SHG-density method was used to visualize the states relevant to the SHG in real space [108]. It was performed by using the effective SHG of each band as weighting coefficient to sum the probability densities of all occupied or unoccupied states [108]. More details about the SHG-density method can be seen in Ref. [108]. The total SHG coefficients are divided into the contribution of virtual-electron, and virtual-hole processes. The SHG-density method can give the atomic contribution from the virtual-electron occupied (marked as veocc), the virtual-electron unoccupied (marked as veunocc), the virtual-hole occupied (marked as vhocc) and the virtual-hole unoccupied (marked as vhunocc) processes. Generally speaking the veocc and vhunocc process give main contribution to the total SHG response, hence herein the authors would just show the SHG density from the veocc and vhunocc process. The obtained SHG density of CsGeX₃ (X = Cl, Br, and I) compounds are shown in Fig. 4 (for CsGeCl₃) and Figure S2 (for CsGeBr₃) and Figure S3 (for CsGeI₃) in SI. In Figs. 4, S2 and S3, the color part represents the SHG density from the veocc process, and the white-black part represents the SHG density from the vhunocc process. As shown in Figs. 4, S2, and S3, the SHG density are mainly on the germanium and halogen atoms, indicating the germanium and halogen atoms give main contribution to the total SHG response.

4. Conclusions

In this paper, the linear and second order nonlinear optical properties of CsGeX₃ (X = Cl, Br, and I) compounds have been investigated using the finite field method combined with the density functional investigation. The obtained results are in good agreement with the experimental values. The electron density distribution nearby the fermi level is the lobe-like lone pair electrons which make the germanium-halogen polyhedron distorted. The Born effective charges analysis shows that the cesium give little

Table 3
The obtained variation of atomic charges (\(\Delta Q, \times 10^{-5}\)) of CsGeX₃ (X = Cl, Br, and I) under external electric field [111].

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Atoms</th>
<th>X1</th>
<th>X2</th>
<th>X3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsGeCl₃</td>
<td>0.002</td>
<td>0.782</td>
<td>0.705</td>
<td>3.074</td>
</tr>
<tr>
<td>CsGeBr₃</td>
<td>0.003</td>
<td>1.276</td>
<td>0.817</td>
<td>3.185</td>
</tr>
<tr>
<td>CsGeI₃</td>
<td>0.004</td>
<td>1.782</td>
<td>0.722</td>
<td>2.498</td>
</tr>
</tbody>
</table>
Fig. 4. The obtained SHG density of CsGeCl₃ compounds.
contribution to the optical anisotropic birefringence, and the germanium and halogen atoms give main contribution to the total birefringence. The analysis using the variation of atomic charges and the SHG density methods shows that the germanium and halogen atoms give main contribution to the SHG response.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.ijleo.2018.10.159.

References


