Tellurium–oxygen group enhanced birefringence in tellurium phosphates: a first-principles investigation†

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Phosphates possess a relatively large UV/DUV cutoff edge, but these compounds usually have very small birefringence. Recently the Te$_2$P$_2$O$_9$ crystal was synthesized and its birefringence was reported to be as large as 0.106 at 1013.98 nm. Herein, we investigated the electronic structure and optical properties of Te$_2$P$_2$O$_9$ using the first-principles method. The obtained results are in good agreement with the experimental values. The Born effective charges and SHG density of Te$_2$P$_2$O$_9$ show that the contribution to the birefringence and SHG response mainly originates from the TeO$_5$ group. The electronic structures and optical response of Ba$_2$TeO(PO$_4$)$_2$ and Te$_2$O$_2$(PO$_4$)$_2$ were also investigated for comparison. The results show that these two tellurium phosphates also possess a large birefringence similar to Te$_2$P$_2$O$_9$. Also, the birefringence originates from the TeO$_5$ polyhedrons, which was confirmed by the real-space atom-cutting results and distortion indices.

1. Introduction

Nowadays, nonlinear optical (NLO) materials have attracted widespread attention because they can be used to obtain wideband and tunable laser sources via the second order NLO effect.1–5 During the past decades, numerous inorganic NLO materials have been obtained, including infrared, visible and ultraviolet (UV) materials.6–10 Also, borates, phosphates and carbonates are thought to be good candidates for UV/Deep-UV NLO compounds, such as BBO,11–12 Li$_2$O$_5$ (LBO),13–15 CsLiB$_5$O$_{10}$ (CLBO),16–18 Cs$_2$B$_2$O$_5$ (CBO),19,20 and KBe$_2$BO$_3$F$_2$ (KBBF).21–24 It has been proven that the introduction of fluorine into borates is beneficial to obtain short UV cutoff edges and suitable birefringence and large NLO responses,25–26 and new deep-UV fluorooxoborates with good performances were obtained such as Li$_2$B$_6$O$_5$F$_2$25 AB$_2$O$_5$F (A = NH$_4$, K, Rb, and Cs),27,28 and SrB$_2$O$_5$F$_2$.29

Recently, phosphates have been reported to be good candidates as UV and deep-UV NLO crystal materials because of their short UV cut-off edge,30,31 including Rb$_2$Ba$_3$(P$_2$O$_7$)$_3$ (<200 nm),32 Ba$_3$P$_2$O$_{20}$ (about 167 nm),33 and KLa[PO$_4$]$_4$ (162 nm).34 However, phosphates also have drawbacks. Most of the reported phosphates have a relatively small birefringence, which has relationship with the regular tetrahedron of the PO$_4$ units. First principles investigations show that the anisotropic polarization of the regular PO$_4$ unit is relatively small. Thus, to overcome this inherent drawback, different types of d$^0$ transition metal cations (Ti$^{4+}$, Mo$^{6+}$, etc.)35 and lone pair electrons (Bi$^{3+}$, Te$^{4+}$, Pb$^{2+}$, etc.) are introduced to phosphates. Wang et al. at Shandong University36 obtained large-size Te$_2$P$_2$O$_9$ crystals via the Czochralski method. The crystals had the acentric polar space group _Cc, and their basic building units were the PO$_4$ tetrahedron and TeO$_5$ square pyramid. Their linear and nonlinear optical properties were also investigated.36 The SHG response and birefringence of Te$_2$P$_2$O$_9$ are relatively large, which is 1.3 × KDP, and 0.13786–0.10615 at 404.66–1013.98 nm, respectively. Curiously, how can it possess such a large birefringence in comparison with other phosphates? Also, what is the origination of this large birefringence in phosphates?

Herein, we calculated the electronic structure and optical properties of Te$_2$P$_2$O$_9$. The obtained refractive indices, birefringence and SHG tensor agree well with the experimental values. Utilizing its electronic structures, Born effective charges, and the SHG density method, the atomic contribution to the birefringence and SHG tensors of Te$_2$P$_2$O$_9$ are investigated. The results show that the TeO$_5$ polyhedrons give the main contribution to the optical anisotropic birefringence and SHG response. Furthermore the optical response of the other tellurium phosphates Ba$_2$TeO(PO$_4$)$_2$ (ref. 37) and Te$_2$O$_2$(PO$_4$)$_2$ (ref. 38) were also investigated for comparison. These two...
compounds possess similar basic building units as Te$_2$P$_2$O$_9$, which are an isolated PO$_4$ tetrahedron and TeO$_5$ polyhedrons (more details can be found in Table S1 in the ESI†). These two compounds also have very large birefringence like Te$_2$P$_2$O$_9$. The large birefringence in these tellurium phosphates originate from the TeO$_5$ polyhedrons, which was further confirmed by the real-space atom-cutting results and the distortion indices.

2. Computational details

To better understand the relationship between the structure and optical properties, the electronic structure and Born effective charges were investigated using the first-principles method implemented in the CASTEP package. During the calculation, the exchange-correlation functional with the Perdew–Burke–Ernzerhof (PBE) functional and the norm-conserving pseudopotentials (NCP) was adopted. The kinetic energy cutoffs were set as 830 eV for Te$_2$P$_2$O$_9$, 830 eV for Te$_3$O$_3$(PO$_4$)$_2$, and 830 eV for Ba$_2$TeO(PO$_4$)$_2$. The k-point mesh in the Monkhorst-Pack was set as $5 \times 5 \times 3$ (Te$_2$P$_2$O$_9$), $2 \times 3 \times 3$ (Te$_3$O$_3$(PO$_4$)$_2$), and $4 \times 4 \times 3$ (Ba$_2$TeO(PO$_4$)$_2$). After the electronic structures were obtained, the refractive indices and the birefringence were further calculated via the OPTADOS code. The nonlinear optical tensors of Te$_2$P$_2$O$_9$ were further investigated using the method described in ref. 45–47. For comparison, the electronic structures and optical properties of Te$_2$P$_2$O$_9$ were also investigated using the LDA(CA-PZ), GGA(PW91) and GGA(RPBE) functionals (shown in Table S2 in the ESI†). The results show that the GGA-PBE functional gives more reliable results in comparison with the experimental values. Hence, herein, we only discuss the GGA-PBE results.

3. Results and discussions

3.1 The electronic structures of Te$_2$P$_2$O$_9$

Using the method described above, the band structures and the projected density of states of Te$_2$P$_2$O$_9$ were obtained. It can be seen clearly from Fig. 1 that Te$_2$P$_2$O$_9$ is an indirect bandgap compound with the bandgap of 3.43 eV. The obtained bandgap is smaller than the experimental value (about 4.30 eV). This underestimation of the bandgap may be related with the derivative discontinuity of the exchange-correlation energy.48

The projected density of states (PDOS) of Te$_2$P$_2$O$_9$ is shown in Fig. 2. For the Te$_2$P$_2$O$_9$ compound, the states of the valence bands (VB) from $-10$ eV to the Fermi level are mainly the Te sp, P sp and O sp states. The states at the bottom of the conduction bands (CB) from 3 eV to 6.5 eV are dominated by the Te 5p and O 2p orbitals. From the states at the valence band and the conduction band, the hybrid states of the P–O and Te–O chemical bonds can be determined. According to the revised model,50–53 the lone pair states from the Te–O chemical bond can be deduced. The optical properties of the material are closely related to the electronic transition between the top of the valence band and the bottom of the conduction band. Hence, we believe that the Te–O and P–O chemical bonds play an important role in determining the optical properties of Te$_2$P$_2$O$_9$.

3.2 The refractive indices and Born effective charges of Te$_2$P$_2$O$_9$

The obtained refractive indices and birefringence of Te$_2$P$_2$O$_9$ are shown in Fig. 3. From the data shown in Fig. 3, it can be determined that the calculated refractive indices follow the order of $n_x > n_y > n_z$. The calculated birefringence is 0.12496–0.09236 in the wavelength range of 404.65–1013.61 nm. It is interesting to note that the reported experimental birefringence of Te$_2$P$_2$O$_9$ is 0.13786–0.10615 in the wavelength range of 404.66–1013.98 nm. Thus, it is obvious that the calculated value matches well with the experimental value.

To better understand the atomic contribution to the optical anisotropic birefringence, the Born effective charges were also investigated in this work. Because the optical anisotropic birefringence is closely related with the difference in the macroscopic polarizability along different optical axes, we focused on the anisotropic polarization.54–59 The Born effective charges are defined as:

$$q_{ij}^{\text{Born}} = \left( \frac{q}{e} \right) \frac{\partial \delta_{pq}}{\partial q_{ij}}$$

where $\delta_{pq}$ is the change in polarization along the displacement direction $\delta_{qj}$. More details can be found elsewhere.60,61 The obtained Born effective charges are shown in Table 1 and Table S3 in the ESI†. It is interesting to note that unlike ABCO$_3$F described in ref. 61, which has nondiagonal tensors of atomic Born effective charges of almost zero, nonzero nondiagonal tensors are found in Te$_2$P$_2$O$_9$. As described in ref. 61, the base unit of ABCO$_3$F compounds are CO$_3$ groups, and the CO$_3$ groups are all in a coplanar plane, which makes the nondiagonal tensors of the Born effective charges in these carbonates vanish. In contrast, for the Te$_2$P$_2$O$_9$ compound described herein, it crystallizes in a 3D structure with PO$_4$ tetrahedrons and a TeO$_5$ square pyramid connected by Te–O and P–O chemical bonds. This complicated 3D structure makes it possess nonzero Born effective charges (shown in Table S3 in ESI†). Specifically, when the Te$_2$P$_2$O$_9$ compound is exposed to an external electric field along the special direction, the electrons move everywhere, not
only in the direction of the external electric field, but also the vertical direction. Hence, nonzero nondiagonal Born effective charges can be found in Te$_2$P$_2$O$_9$. Furthermore, we also performed a detailed investigation into the diagonal Born effective charges along the optic principal axis and calculated the difference in the Born effective charges. As described above, the refractive indices follow the sequence of $n_x > n_y > n_z$, thus the difference in the Born effective charges was obtained by the $q_{xx} - q_{zz}$. The obtained diagonal tensor of the atomic Born effective charges of Te$_2$P$_2$O$_9$ $q_{ij}^{(\text{Born})}$ is shown in Table 1. As shown in Table 1, a relatively large difference in the Born effective charge tensors was found in the Te and O atoms, while the P atoms possess a relative small difference in comparison, implying that the Te and O atoms make a relatively large atomic contribution to the anisotropic birefringence. We believe that the contribution to the birefringence is provided mainly by the TeO$_5$ group.

**Table 1** Obtained diagonal tensor of the atomic Born effective charges of Te$_2$P$_2$O$_9$

| Compound  | Atom | $q_{xx}$ | $q_{yy}$ | $q_{zz}$ | $\Delta q_{ij}^{(\text{Born})}$ |
|-----------|------|----------|----------|----------|-------------------------------|
| Te$_2$P$_2$O$_9$ | Te1   | 4.34265  | 4.65936  | 6.63644  | -2.29379                     |
|           | Te2   | 6.4218   | 5.38842  | 3.37218  | 3.04962                      |
|           | Te3   | 4.34265  | 4.65936  | 6.63644  | -2.29379                     |
|           | Te4   | 6.4218   | 5.38842  | 3.37218  | 3.04962                      |
|           | P1    | 4.40285  | 3.49299  | 4.36297  | 0.03988                      |
|           | P2    | 4.70919  | 4.86415  | 3.77507  | 0.93412                      |
|           | P3    | 4.40285  | 3.49299  | 4.36297  | 0.03988                      |
|           | P4    | 4.70919  | 4.86415  | 3.77507  | 0.93412                      |
|           | O1    | -1.78151 | -1.84853 | 2.74356  | 0.96205                      |
|           | O2    | -3.2844  | -2.12701 | -1.33367 | -1.95073                     |
|           | O3    | -2.85789 | -1.94646 | -1.32288 | -1.53501                     |
|           | O4    | -1.40561 | -0.89945 | 3.71391  | 2.3083                       |
|           | O5    | -1.30274 | -2.25599 | -1.88828 | 0.58554                      |
|           | O6    | -1.56074 | -3.25254 | -1.86712 | 0.36038                      |
|           | O7    | -1.54143 | -1.92023 | -2.76231 | 1.22088                      |
|           | O8    | -3.00828 | -2.10674 | -1.13507 | -1.87321                     |
|           | O9    | -3.13389 | -2.04796 | -1.37986 | -1.75403                     |
|           | O10   | -1.78151 | -1.84853 | -2.74356 | 0.96205                      |
|           | O11   | -3.2844  | -2.12701 | -1.33367 | -1.95073                     |
|           | O12   | -2.85789 | -1.94646 | -1.32288 | -1.53501                     |
|           | O13   | -1.40561 | -0.89945 | 3.71391  | 2.3083                       |
|           | O14   | -1.30274 | -2.25599 | -1.88828 | 0.58554                      |
|           | O15   | -1.56074 | -3.25254 | -1.86712 | 0.36038                      |
|           | O16   | -1.54143 | -1.92023 | -2.76231 | 1.22088                      |
|           | O17   | -3.00828 | -2.10674 | -1.13507 | -1.87321                     |
|           | O18   | -3.13389 | -2.04796 | -1.37986 | -1.75403                     |
Table 2. The obtained refractive indices and birefringence (at 1064 nm) of Te₂P₂O₉, Ba₂TeO(PO₄)₂, and Te₃O₃(PO₄)₂ after real-space atom-cutting was performed.

| Crystal          | Contribution | nₓ | nᵧ | nᵧ | Δn |
|------------------|--------------|----|----|----|----|
| Te₂P₂O₉          | Cut-PO       | 1.484 | 1.458 | 1.405 | 0.079 |
|                  | Cut-TeO      | 1.232 | 1.226 | 1.203 | 0.029 |
|                  | Origin       | 2.031 | 1.974 | 1.939 | 0.092 |
| Ba₂TeO(PO₄)₂     | Cut-BaO      | 1.408 | 1.332 | 1.323 | 0.085 |
|                  | Cut-PO       | 1.555 | 1.486 | 1.475 | 0.080 |
|                  | Cut-TeO      | 1.600 | 1.588 | 1.563 | 0.037 |
|                  | Origin       | 1.877 | 1.860 | 1.767 | 0.110 |
| Te₃O₃(PO₄)₂      | Cut-PO       | 1.622 | 1.585 | 1.570 | 0.052 |
|                  | Cut-TeO      | 1.243 | 1.229 | 1.211 | 0.032 |
|                  | Origin       | 2.027 | 1.998 | 1.906 | 0.121 |

Table 3. The obtained distortion indices of the different polyhedrons in Te₂P₂O₉, Ba₂TeO(PO₄)₂, and Te₃O₃(PO₄)₂.

| Polyhedron | Te₂P₂O₉ | Ba₂TeO(PO₄)₂ | Te₃O₃(PO₄)₂ |
|------------|---------|-------------|-------------|
| PO₄        | 0.005   | 0.020       | 0.013       |
| TeO₅       | 0.034   | 0.039       | 0.051       |
| BaO        | 0.034   |             |             |

3.3 The contribution from TeO₅ polyhedrons in tellurium phosphate

To better understand the contribution from the TeO₅ polyhedrons to the birefringence, the electronic structures and the optical response of the other tellurium phosphates Ba₂TeO(PO₄)₂ and Te₃O₃(PO₄)₂ were also investigated. The obtained band structures and projected density of states (PDOS) of Ba₂TeO(PO₄)₂ and Te₃O₃(PO₄)₂ are shown in Fig. S1–S4 in the ESI. As shown in Fig. S1 and S3, the obtained bandgap of Ba₂TeO(PO₄)₂ and Te₃O₃(PO₄)₂ are 4.11 and 3.63 eV, respectively. To overcome the underestimation of the bandgap, HSE06 calculations were performed using the PWmat code. The obtained HSE06 bandgap of Ba₂TeO(PO₄)₂ and Te₃O₃(PO₄)₂ is 4.47 and 4.18 eV, respectively. As shown in Fig. S2 and S4, the states at the top of the valence band and at the bottom of the conduction band are mainly the Te-sp states, O-sp states, and P-sp states. Also, the chemical bonds of Te–O and P–O can also be found at the top of the valence band. Hence, it can be deduced that the TeO₅ polyhedron and PO₄ tetrahedron play an important role in determining the optical response of these tellurium phosphates.

The refractive indices and birefringence of Ba₂TeO(PO₄)₂ and Te₃O₃(PO₄)₂ were also obtained using the method described above, and the results are shown in Fig. S5 and S6, respectively, and Table 2. As shown in Fig. S5 and S6, the Ba₂TeO(PO₄)₂ and Te₃O₃(PO₄)₂ possess a relatively large birefringence of 0.110 and 0.121 (at 1064 nm), respectively. The birefringence of these compounds follow the sequence of Δn(Ba₂TeO(PO₄)₂) > Δn(Ba₂TeO(PO₄)₂) > Δn(Te₃O₃(PO₄)₂).

The contribution from different polyhedrons was further investigated using the real-space atom-cutting method. During the calculation, the atom-cutting radius of O, P, Te, and Ba was set as 1.10, 0.95, 0.96, and 1.74 Å, respectively. After the real-space atom-cutting method was performed, the refractive indices and birefringence of Te₂P₂O₉, Ba₂TeO(PO₄)₂, and Te₃O₃(PO₄)₂ were obtained, which are shown in Table 2, and Fig. S7–S9 in the ESI, respectively. As shown in Table 2, in comparison with the PO₄ tetrahedron and BaO polyhedrons, the TeO₅ polyhedrons give the main contribution to the total birefringence. Taking Te₂P₂O₉ as example, the its birefringence is about 0.092 at 1064 nm. However, after the TeO₅ polyhedron was removed, the obtained birefringence of the other part (marked as cut-TeO) is only about 0.029, implying that the TeO₅ polyhedrons may give a contribution of about (0.092 − 0.029 = 0.063) to the total birefringence of Te₂P₂O₉. Thus, in comparison with the PO₄ tetrahedron, the TeO₅ polyhedron gives main contribution to the total birefringence. A similar conclusion was also found for the other tellurium phosphates, Ba₂TeO(PO₄)₂, and Te₃O₃(PO₄)₂ (as shown in Table 2). It is interesting to note that the conclusion obtained from the real-space atom-cutting is consistent with the results obtained from the Born-effective charges analysis (as described above).

The optical anisotropic birefringence is related with the anisotropic optical response from the different polyhedrons. The relatively small anisotropic polarization of the regular PO₄ unit may be related with the relatively small distortion with the regular PO₄ unit. Herein, the distortion indices of the different polyhedrons in these tellurium phosphates were also investigated. The distortion indices, defined by Baur as $D = \frac{1}{n} \sum_{i=1}^{n} \frac{|l_{ix} - l_{iy}|}{l_{iy}}$, was calculated using the VESTA software. The obtained distortion indices of the different polyhedrons in these tellurium phosphates are shown in Table 3. As described above, the TeO₅ polyhedrons give the main contribution to the total birefringence, and hence was focused on the distortion indices of the TeO₅ polyhedron. As shown in Table 3, the distortion indices of the TeO₅ polyhedrons follow the sequence of $D(\text{TeO}_5(\text{PO}_4)_2) > D(\text{Ba}_2\text{TeO}(\text{PO}_4)_2) > D(\text{Te}_3\text{O}_3(\text{PO}_4)_2)$, which is consistent with the sequence of the birefringence of $\Delta n(\text{TeO}_5(\text{PO}_4)_2) > \Delta n(\text{Ba}_2\text{TeO}(\text{PO}_4)_2) > \Delta n(\text{Te}_3\text{O}_3(\text{PO}_4)_2)$.

3.4 The atomic contribution to the SHG response of Te₂P₂O₉

The SHG tensors of Te₂P₂O₉ were also obtained (shown in Table 4). For that crystallized in the Cc space group, there are six independent nonzero SHG tensors, $d_{11}, d_{12}, d_{13}, d_{14}, d_{24}$, and $d_{13}$. The calculated SHG tensors and experimental powder SHG (PSHG) intensity are shown in Table 4.

Table 4. The calculated SHG tensors and experimental powder SHG (PSHG) intensity.

| Crystal      | Space group | Calculated SHG tensors (pm V⁻¹) | PSHG intensity |
|--------------|-------------|---------------------------------|----------------|
| Te₂P₂O₉      | Cc          | $d_{11} = -0.17, d_{15} = -0.53, d_{14} = 0.59, d_{13} = -0.56, d_{24} = -0.95, d_{13} = 1.01$ | 1.3 × KDP |
As shown in Table 4, for Te$_2$P$_2$O$_9$, the maximum is $d_{33} = 1.01$ pm V$^{-1}$, which is about 2.6 times that of $d_{36}$ (KDP). The obtained SHG tensors are comparable with the experimental powder second-harmonic generation (PSHG) intensity (about 1.3 $\times$ KDP). The experimental values agree well with the calculated values, indicating that the method selected in this work is appropriate. To deeply investigate the atomic contribution to the SHG tensors, the spatial distribution of the atomic SHG density was also calculated. The SHG density method is a normalized weighting coefficient via the use of the effective SHG response of each occupied and unoccupied band.$^{59,60}$ Using this method, the states irrelevant to the SHG response will not be shown, and the distribution of the SHG density represents the origin of the SHG response. Herein, we only show the SHG density obtained from the virtual electron process (labeled as veocc) and the virtual hole process (labeled as vhunocc). The obtained SHG density of Te$_2$P$_2$O$_9$ is shown in Fig. 4, where the color part and white–black part represent the SHG density of the veocc and vhunocc process, respectively. As shown in Fig. 4, there is no SHG distribution around the P atoms, implying that the P atoms give a relatively small contribution to the total SHG response. It is shown that the SHG density is distributed mainly on the Te and O atoms, indicating that the TeO$_5$ polyhedrons give the main contribution to the total SHG response.

### 4. Conclusions

In this work, the refractive indices, birefringence, and the SHG coefficient of Te$_2$P$_2$O$_9$ were obtained using the first-principles method. The obtained results are in good agreement with the experimental values. The calculated birefringence of Te$_2$P$_2$O$_9$ is 0.12496–0.09236 in the wavelength range of 404.65–1013.61 nm. The maximum SHG tensor $d_{33}$ is 1.01 pm V$^{-1}$, which is about 2.6 times that of $d_{36}$ (KDP). The atomic contribution to the birefringence and SHG response was also investigated using the projected density of states, Born effective charges, and real-space SHG density method. The results show that the TeO$_5$ group play an important role in determining the birefringence and SHG response of Te$_2$P$_2$O$_9$. The electronic structures and optical response of Ba$_2$TeO(PO$_4$)$_2$ and Te$_3$O$_3$(PO$_4$)$_2$ were also investigated for comparison. The results show these two tellurium phosphates also possess a large birefringence like Te$_2$P$_2$O$_9$. Also, the birefringence originates from the TeO$_5$ polyhedrons, which was confirmed by the real-space atom-cutting results and distortion indices.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 11664037, 11864040), the Natural Science Foundation of Xinjiang Uygur Autonomous Region of China (Grant No. 2018D01C079, 2018D01C072), the Science and Technology Research Program for Colleges and Universities in the Department of Education in Xinjiang Uygur Autonomous Region of China (Grant No. XJEDU2017M006). The author Haibin Cao acknowledges support from Foundation for High-level Talents in Shihezi University (RCZX201511), and Applied Basic Research Foundation of Science and Technology in Shihezi University (2015ZRKXYQ07).

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