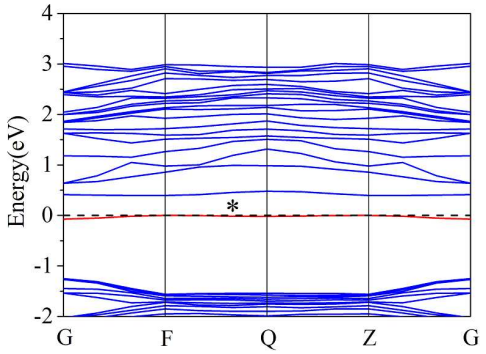
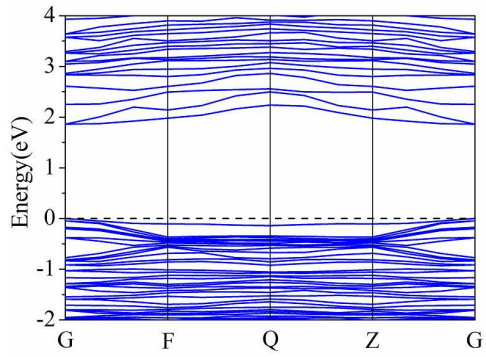
**Supporting information**

## (1) The effect of symmetry structure in $Bi_{26}O_{39}$




**(a) un-optimized $Bi_{26}O_{39}$**




**(b) optimized $Bi_{26}O_{39}$**

Figure S1. (Color online) The band structures of un-optimized $Bi_{26}O_{39}$ (a) and optimized $Bi_{26}O_{39}$ (b), where an energy level (labeled by star) lies in the band gap of un-optimized $Bi_{26}O_{39}$, but it is absent in the band structure of optimized $Bi_{26}O_{39}$.

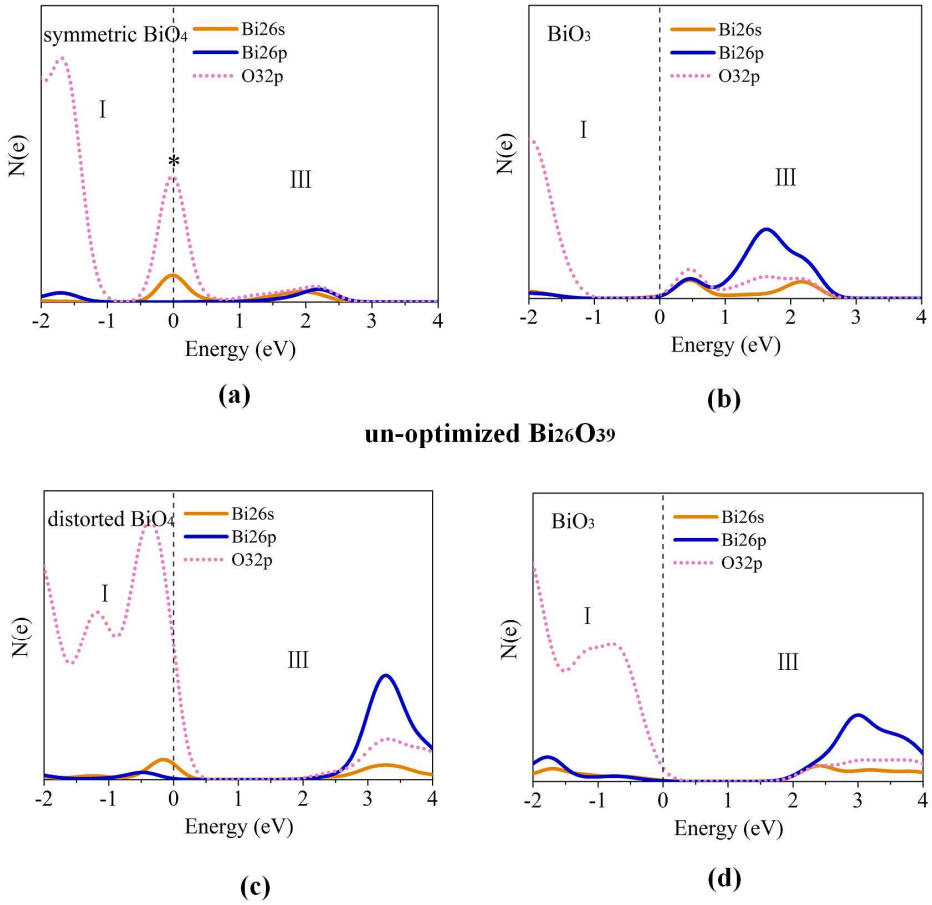



Figure S2. (Color online) PDOSs projected on (a) symmetric $BiO_4$, (b) $BiO_3$ units of un-optimized $Bi_{26}O_{39}$ and on (c) distorted $BiO_4$, (d) $BiO_3$ units of optimized $Bi_{26}O_{39}$, where the antibonding Bi 6s-O 2p states at the Fermi level of un-optimized $Bi_{26}O_{39}$ in (a) is labeled by star.

It can be seen from Figure S1 that an energy level present in the band gap of the un-optimized $Bi_{26}O_{39}$ (Figure S1(a)), whereas nothing appear in the band gap of the optimized $Bi_{26}O_{39}$ (Figure S1(b)). The comparison between the PDOSs projected on symmetric $BiO_4$ (Figure S2(a)) of un-optimized $Bi_{26}O_{39}$ and that projected on distorted $BiO_4$ (Figure S2(c)) of optimized $Bi_{26}O_{39}$ indicates that, under symmetric $BiO_4$ condition, the antibonding Bi 6s-O 2p

states at the Fermi level results in an energy level in the band gap of the un-optimized $Bi_{26}O_{39}$. Under the distorted $BiO_4$ condition, the antibonding Bi 6s-O 2p states interact with Bi 6p states and shift down along the valence band, they can not form any energy level in the band gap of the optimized $Bi_{26}O_{39}$. Compared with optimized $Bi_{26}O_{39}$, the un-optimized $Bi_{26}O_{39}$ does not have any additional oxygen atom and it has only a symmetric tetrahedral $BiO_4$ unit different from the distorted one of optimized $Bi_{26}O_{39}$. So it can be concluded that the energy level in the band gap of un-optimized $Bi_{26}O_{39}$ is just introduced by a symmetric structure. This symmetric structure is similar with the $BiO_4$ unit of $Bi_{26}O_{40}$.

**(2) The formation energies calculation of $S^{4+}$, $Se^{4+}$ or $Te^{4+}$ substitution**

The formation energies $E_f$ of $S^{4+}$, $Se^{4+}$ or $Te^{4+}$ doped systems were calculated according to the following formulas:

$$E_{\mathrm{f}} = E_{\mathrm{tot}}(\mathrm{doped}) - [E_{\mathrm{tot}}(\mathrm{host}) + n\mu_{\mathrm{dopant}} - n\mu_{\mathrm{Bi}}]$$

$$E_{\mathrm{f}} = E_{\mathrm{tot}}(\mathrm{doped}) - [E_{\mathrm{tot}}(\mathrm{host}) + n\mu_{\mathrm{dopant}} - n\mu_{\mathrm{O}}]$$

Table S1. The calculated formation energies $E_f$ for one $S^{4+}$ ion substituted at five different sites and for two identical $S^{4+}$, $Se^{4+}$ or $Te^{4+}$ ions substituted at two Bi2 (2a) sites.

| doping ions | $S^{4+}$ | | | | | $S^{4+}$ | $Se^{4+}$ | $Te^{4+}$ |
|---|---|---|---|---|---|---|---|---|
| number of doping ions (n) | 1 | | | | | 2 | | |
| substitutional sites | O1 | O2 | O3 | Bi1 | Bi2 | Bi2 | | |
| FormationEnergies (eV) | 94.77 | 45.01 | 46.94 | 0.54 | -1.27 | 4.519 | 3.286 | 2.809 |

The calculated formation energies $E_f$ for $S^{4+}$, $Se^{4+}$ or $Te^{4+}$ substituted at different sites are shown in Table S1. It can be seen that the formation energies for $S^{4+}$ substitutions on three different oxygen sites are extremely high, while the formation energies for $S^{4+}$ substitutions on bismuth sites are much lower. The formation energy for $S^{4+}$ substitutions on Bi2 (2a) site is the lowest (-1.27 eV), which indicates that the $S^{4+}$ ion is energetically preferred to substitute the Bi2 (2a) site.

Then we calculated the formation energies for two identical $S^{4+}$, $Se^{4+}$ or $Te^{4+}$ ions substituted at two Bi2 (2a) sites and the results are 4.519 eV for $S^{4+}$, 3.286 eV for $Se^{4+}$, 2.809 eV for $Te^{4+}$, respectively. The formation energy of $Te^{4+}$ ions doped system is lower than that of $S^{4+}$ and $Se^{4+}$ ions doped systems, and the $Bi_{24}Te_2O_{40}$ structure is the most energetically preferred structure.

**(3) The relationship between ionic radius, ionization energies, Pauling electronegativities and formation energies**

Table S2. The ionic radius, ionization energies and Pauling electronegativities for $S^{4+}$, $Se^{4+}$or $Te^{4+}$ ion, and the formation energies for $Bi_{24}Te_2O_{40,}$ $Bi_{24}Te_2O_{40}$ and $Bi_{24}Te_2O_{40}$.

| eliments | $S^{4+}$ | $Se^{4+}$ | $Te^{4+}$ | $Bi^{3+}$ ($Bi^{5+}$) |
|---|---|---|---|---|
| ionic radius (nm) | 0.37 | 0.5 | 0.7 | 0.96 (0.74) |
| ionization energies (eV) | 4556 | 4144 | 3610 | 2466(5400) |
| Pauling electronegativities | 2.58 | 2.55 | 2.1 | 2.02 |
| formation energies (eV) | 4.519 | 3.286 | 2.809 | — |

The ionic radius, ionization energies and Pauling electronegativities for $S^{4+}$, $Se^{4+}$or $Te^{4+}$ ion, and the formation energies for $Bi_{24}Te_2O_{40,}$ $Bi_{24}Te_2O_{40}$ and $Bi_{24}Te_2O_{40}$ are shown in Table S2. We find that S, Se and Te in the same group exhibit a clear trend in properties, as the period increases, the ionic radii increase, whereas the ionization energy, Pauling electronegativity and formation energy decrease.

**(4) The calculated structural parameters of $Bi_{24}S_2O_{40}$**

The $Bi_{24}S_2O_{40}$ compound has been synthesized by our group, and its physical properties are under investigation. The calculated structural parameters of $Bi_{24}S_2O_{40}$ are given in Table S3.

Table S3. The calculated structural parameters of $Bi_{24}S_2O_{40,}$ where the atomic positions are given in fractional coordinates, and the symbols in the brackets are the multiplicity and Wyckoff letter. Z represents the number of molecules in one conventional cell.

| parameters | $Bi_{24}S_2O_{40}$ |
|---|---|
| numbers of space group | 197 |
| standard Hermann-Mauguin symbols | I23 |
| crystal system | body-centered cubic |
| crystallographic point groups | 23 |

| | | |
|---|---|---|
| Lattice parameters | a, b, c (Å) | 9.79683, 9.79683, 9.79683 |
| | α, β, γ (Deg) | 90, 90, 90 |
| | cell volume ($Å^3$) | 940.279 |
| | density ($g/cm^3$) | 10.1009 |
| Z | | 2 |
| cell formula | | $Bi_{12}SO_{20}$ |
| fractional coordinates | | Bi(24f) 0.01583,0.1723,0.3226 |
| | | S(2a)0.0000,0.0000,0.0000 |
| | | O(8c)0.1931,0.1931,0.1931 |
| | | O(24f)0.2440,0.4945,0.1305 |
| | | O(8c)0.3937,0.3937,0.3937 |