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Giant Birefringence in Layered Compound $LaOBiS_2$

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Birefringent crystals (BFCs) have been extensively used in imaging spectrometers, laser devices, and optical components. Seeking new BFCs is important for both fundamental research and industrial applications. Employing first-principles density functional theory, we find that $LaOBiS_2$ (space group: $P4/nmm$) appearing in the parent phase of the recently discovered BiS_2-superconductor exhibits superior birefringence with a maximum value of 2.94, which is 13.4 times larger than the extensively used YVO_4 (0.22). Furthermore, $LaOBiS_2$ is an indirect semiconductor with a band gap of 0.9 eV, which is suitable for optical applications. The origin of giant inherent birefringence is also discussed.

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Layered compounds have received increasing attention due to their excellent superconductivity,[1] thermoelectricity,[2] giant magnetoresistance,[3] and so on. They exhibit various electronic, optical and magnetic properties as well as good tunability. For example, the artificial layered structures are designed for high-efficiency light-emitting diodes (LEDs)[4] and optical communication.[5] Hosono *et al.* have explored novel layered oxides LaT_MPnO, where a pnicogen anion (Pn^{3-}) replaces a chalcogen anion (Ch^{2-}) in LaCuOCh, and a transition metal cation (T_M^{2+}) can substitute for Cu^+. There are many combinations (T_M and Pn) to form two-dimensional (2D) layered structures. Interestingly, the doped-F LaOFeAs is found to be a superconductor with T_c as large as 26 K. The discovery has received worldwide attention on iron-based superconductivity. A large number of other layered compounds have been examined to reveal their superconductivity. Recently, a novel BiS_2-based layered superconductor $LaO_{1-x}F_xBiS_2$ (T_c ~10.6 K) has been reported.[6] Its parent compound $LaOBiS_2$ has a LaFeAsO-type structure and is a semiconductor rather than a metal as LaOFeAs.[7] More and more researches are focused on the superconductivity. As mentioned above, layered compounds also have various excellent properties. To demonstrate this, using $LaOBiS_2$ as an example, we reveal a giant birefringence based on first-principles density function calculations. We also discuss the origin and propose the promising potential applications.

The calculations were performed by using density functional theory with generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof.[8] The ion-electron interaction was modeled by PAW[9] pseudopotentials in VASP.[10] A plane-wave cutoff energy of 500 eV was employed throughout the calculation. For the sampling of the Brillouin zone, the electronic structures and optical properties used $12 \times 12 \times 6$ and $18 \times 18 \times 9$ Monkhorst-Pack[11] k-point grids, respectively. Whenever possible, we cross-check the results using the quantum Espresso package (QE).[12] The consistency of our results for two sets of calculations is satisfactory.

The optical properties are determined by the frequency-dependent dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ that is mainly connected with the electronic structures. The imaginary part $\varepsilon_2(\omega)$ of the dielectric function is calculated from the momentum matrix elements between the occupied and unoccupied within selection rules and given by

$$\varepsilon_2 = \frac{2e^2\pi}{\Omega\varepsilon_0} \sum_{k,v,c} |\langle\psi_k^{\rm c}|\hat{u}\cdot r|\psi_k^{\rm v}\rangle|\delta(E_k^{\rm c} - E_k^{\rm v} - E), \quad (1)$$

where ω is the light frequency, e is the electronic charge, $\psi_k^{\rm c}$ and $\psi_k^{\rm v}$ are the conduction and valence band wavefunctions at k, respectively. The real part $\varepsilon_1(\omega)$ of the dielectric function $\varepsilon(\omega)$ can be derived from the imaginary part $\varepsilon_2(\omega)$ by using the Kramers–Kronig dispersion equation. The refractive index can be derived from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$,[13]

$$n(\varepsilon) = (1/\sqrt{2})[\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} + \varepsilon_1(\omega)]^{1/2}. \quad (2)$$

Employing density functional theory (DFT) calculations, we have reported the optical of $ZnSnO_3$, where the maximum of birefringence is only 0.2 at 6.90 eV.[14] In 2010, we found the giant optical anisotropy in the parent compounds of iron-based superconductors: LaFeAsO, $BaFe_2As_2$ and LiFeAs.[15]

As iron-based superconductor LaFeAsO, $LaOBiS_2$ has a layered structure with space group $P4/nmm$ (No 129). Its structure is composed of one La_2O_2 and two BiS_2 layers (Fig. 1). Table 1 lists our calculated results on the structural parameters of $LaOBiS_2$ as well as the corresponding experimental and theoretical values. Awana *et al.*[7] reported the detailed structural parameters. It is clear that our results are in good agreement with the previous reports. Note that only S1 ions have a large difference as compared to the experimental report; similar theoretical results have been presented in the case of LaFeAsO.

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Table 1. Lattice parameters and Wyckoff positions of $LaOBiS_2$. Here O sites at origin $(0, 0, 0)$.

	Expt.[a]	Theor.[b]	Theor.[c]	This work[d]	This work[e]
a	4.066	4.039	4.0677	4.043	4.051
c	13.862	14.123	14.3085	14.220	14.247
La (0.5, 0, z)	0.090	0.0889	0.0890	0.0855	0.0879
Bi (0.5, 0, z)	0.632	0.6304	0.6309	0.6328	0.6321
S1 (0.5, 0, z)	0.371	0.3932	0.3945	0.3950	0.3937
S2 (0.5, 0, z)	0.819	0.8090	0.8073	0.8111	0.8089

[a]Experimental, Ref. [9]. Theoretical QE: [b]Ref. [16] and [c]Ref. [17], 60 Ry/600 Ry. [d]QE. [e]VASP.

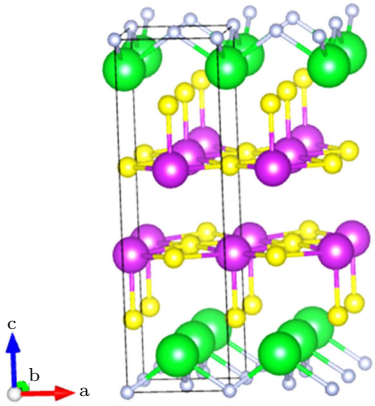

Fig. 1. Crystal structure of $LaOBiS_2$. Here, violet stands for Bi, green for La, yellow for S and red for O.

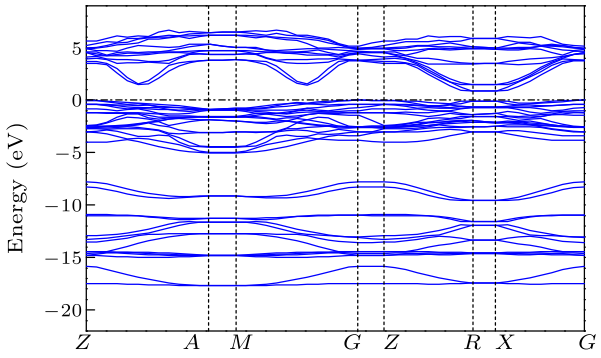

Fig. 2. Band structure of $LaOBiS_2$. Fermi level locates at zero and the band gap is 0.90 eV.

The band structures along high symmetry are depicted in Fig. 2. It is clear that $LaOBiS_2$ is a semiconductor. The top of the valence band locates at Γ (or Z), while the bottom of the conductor band is at R (or X). Hence, an indirect gap of 0.90 is formed between Γ and R (or Z and X), which is consistent with the VASP value of 0.7 eV (see Fig. 5(b)).[7] The GGA band gap is usually underestimated. Unfortunately, there is no experimental value reported so far. The following optical properties are calculated by PBE without scissors correction.

The optical properties of $LaOBiS_2$ (shown in Fig. 3) have large anisotropy in both absorptions and refractive index. This is expected due to its layered structure. For example, the infinite-layer iron oxide $SrFeO_2$ has a giant optical anisotropy.[18] Note that birefringence is the optical property of a material having a refractive index that depends on the polarization and propagation direction of light.[19] It is quantified by the maximum difference in refractive index within the material, i.e., birefringence $\delta n = n_e - n_o$.[19] This effect was first described in calcite by the Danish scientist Rasmus in 1669. There are three well-known natural materials that are birefringent in bulk form: calcite $CaCO_3$ ($\delta n = 0.172$), quartz SiO_2 ($\delta n = 0.009$), and magnesium fluoride MgF_2 ($\delta n = 0.006$), all measured at a 590 nm wavelength.[19] Among artificial crystals, YVO_4 has an excellent birefringence of about 0.22, which is inferior to rutile TiO_2 (0.28). Owing to its easy growth, large index of refractivity and good mechanical properties, YVO_4 crystals have been extensively used in laser devices and optical components.[20] At all events, seeking new birefringent crystals is of importance for both fundamental research and industrial application, especially the device miniaturization.

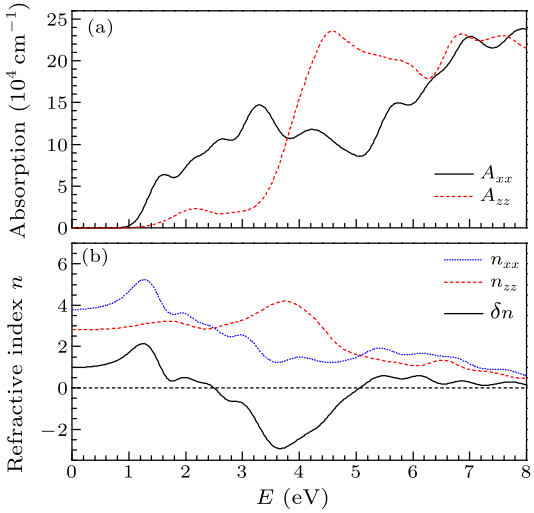

Fig. 3. Absorption (a), refractive index and birefringence $\delta n = n_{xx} - n_{zz}$ (b) of $LaOBiS_2$.

Now we check the birefringence of $LaOBiS_2$. Surprisingly, we find that its birefringence is as large as 2.94 (the maximum), which is 13.4 times larger than that of the extensively used laser crystals YVO_4 (0.22). This is exciting. As is well known, the birefringence of $SrFeO_2$ is also only 0.2–0.5.[18] To the best of our knowledge, the value is the largest among the inherent birefringence so far. In the range of 0–0.9 eV below the band-gap value, the birefringence of $LaOBiS_2$ is larger than 1.0, which is also at least 4.5 times larger than that of YVO_4, the most important optical materials in optical communication. It is well

known that Nd:YVO_4 crystals have been used to generate a radially polarized laser, due to the fact that YVO_4 has more than three times larger birefringence than that of $LiNbO_3$ (0.08).[21] Compared to $LiNbO_3$, $LaOBiS_2$ has 12.5 times larger birefringence, which can make device design more compact. In this context, $LaOBiS_2$ may have promising potential applications in semiconductor laser devices, optical communications and so on. For optical display, it can be used to improve grey-scale stability and the contrast ratio, i.e., birefringent optical compensators are used to correct the polarization state of light entering and exiting the liquid crystal cell at oblique angles. In addition, owing to its semiconductor and large anisotropic conductivity (not shown here), $LaOBiS_2$ may have very promising potential applications in thermoelectricity and solar cells.

Up to now, it seems that nanostructure engineering is only one effective approach to obtain the larger birefringence that is expected for practical applications. For example, giant birefringence is reported in nanostructured silicon thin-film (0.3)[22] and GaP nanowires (0.7).[23] For the latter, the birefringence is enhanced to be about 75 times larger than that of natural quartz crystal (0.009). Here the birefringence of $LaOBiS_2$, we report in this work, is 111 times larger than that of quartz crystal. Hence, its birefringence is giant. Recently, the in-plane birefringence of ZnO nanowire arrays is almost one order of magnitude higher than that of quartz.[24] The glancing angle deposition (GLAD)[25] method has been demonstrated to be an effective method to obtain tunable birefringence in a large continuous range. For example, the in-plane birefringence (up to 0.4) of Si thin films is large compared with naturally anisotropic crystals and is comparable to two-dimensional photonic crystals.[26] In this context, the corresponding experimental investigation on the nanostructure engineering of $LaOBiS_2$ is highly expected. In any case, the giant birefringence of $LaOBiS_2$ means that it is now a wonderful idea to study the other properties of layered-structure compounds, rather than only its superconductivity. Here our results demonstrate that DFT is an effective method for this issue.

Why does $LaOBiS_2$ have a giant birefringence? To find the reason, we calculate the birefringence of LaOZnP, a layered compound with the same space group structure ($P4/nmm$) as $LaOBiS_2$. The results are depicted in Fig. 4. While the positive maximum 1.10 is located at 2.57 eV, the negative maximum is −1.26 at 3.64 eV. The corresponding maxima of $LaOBiS_2$ are 2.14 (−2.94) at 1.25 eV (3.66 eV), which are about two times larger than those of LaOZnP. For LaOZnP, its birefringence is only comparable to YVO_4 (0.22). Although the crystals with layered structures are expected to be birefringent, the comparison with LaOZnP demonstrates that the giant birefringence results from not only the layered structures but also other reasons that are so far unknown.

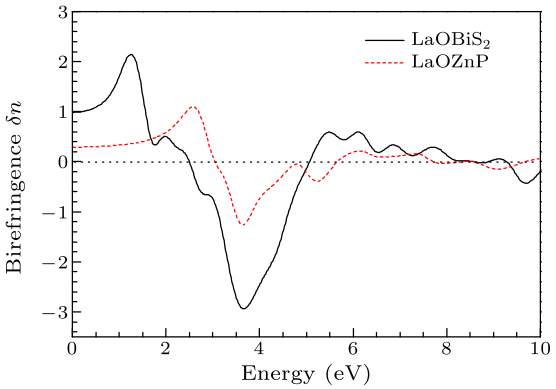

Fig. 4. Birefringence of $LaOBiS_2$ (solid line) and LaOZnP (dashed line).

While LaOZnP is 1111-type compound, $LaOBiS_2$ is 1112-type one. This means that S ions in $LaOBiS_2$ are two times the P ions in LaOZnP. In a comparison of the structures of both the compounds, we find that redundant S ions can form Bi-S bonds along the z-axis, which enhances the optical anisotropy and birefringence. It is not easy to answer why this 1112-type structure can exist. Further investigation is needed. We conjecture that the lone pair of Bi^{3+} ions may play an important role in this issue.

In summery, we have presented first-principles calculations on the structural, electronic and optical properties of $LaOBiS_2$. The structural parameters we obtained are in good agreement with previous theoretical values. Band structures reveal that it is an indirect semiconductor with a band gap of 0.9 eV. There is large optical anisotropy due to its layered structure. Interestingly, its inherent birefringence is found to be the largest among inorganic compounds to the best of our knowledge. The giant birefringence is attributed to its layered-structure and Bi^{3+} lone pair. Finally, $LaOBiS_2$ is suggested to have very promising potential applications in laser devices, optical communications, thermoelectricity and solar cells.

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