BiS_2-Layer Gives Giant Birefringence: First-Principles Calculations

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Birefringence attracts increasing attention due to its extensive applications in the imaging spectrometer, laser devices and optical components. Stimulated by the discovery of the giant birefringence (GBF) in $LaOBiS_2$ and $AFBiS_2$, we explore its origin by checking three compounds with and without the BiS_2 layer: Bi_2OS_2 (i.e., $BiOBiS_2$), Bi_2O_2S and $LaOAlS_2$. It is demonstrated that GBF appears only in the compounds with the BiS_2 layer and is furthermore confirmed in $MOBiS_2$ (M=Al, Ga, In and Sc) compounds. The result is useful for discovering/developing new-type birefringent crystal or even multifunctional materials.

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Birefringence (BF) is the optical anisotropy in refractive index due to the different light propagation velocity within the material.[1] The natural birefringent materials have calcite $CaCO_3$ ($\delta_n = 0.172$), quartz SiO_2 ($\delta_n = 0.009$) and MgF_2 ($\delta_n = 0.006$), all measured at the wavelength of 590 nm.[1] In fact, birefringent crystals have been extensively used in the imaging spectrometer, laser devices,[2] optical components, photonic crystal fibers[3] and quantum metrology.[4] To date, the extensively used birefringent crystal in laser devices and optical components is artificial crystal YVO4 due to its easy growth, large refractive index and good mechanical properties.[5] However, YVO_4 has a birefringence of 0.22, which is inferior to rutile TiO_2 (0.28). Naturally, it is of importance to seek new birefringent materials for both fundamental research and industrial application.[6–8]

Zhang *et al.* have synthesized a new birefringent material $Na_3Ba_2(B_3O_6)_2F$ (NBBF),[9] which not only maintains a birefringence (Δn =0.255–0.075 from 175 nm to 3.35 μm) and extends its UV cutoff edge to 175 nm (14 nm shorter than α-BBO), but also eliminates the phase transition and has the lowest growth temperature (820℃) among birefringent materials. These results demonstrate that NBBF is an attractive candidate for the next-generation deep UV birefringent materials. In 2014, we predicted that $LaOBiS_2$ has a giant birefringence (GBF) of 1.0, which is about 111 times larger than that of quartz[10] and 4 times larger than NBBF. This is also interesting due to the fact that the single-crystal compound is first-time shown to have a superior BF than nanostructured materials.[10] Then, layered compounds of $AFBiS_2$ were theoretically predicted to be superior birefringent crystals with BF as large as 1.66.[11] First-principles calculations demonstrate that A-ions play an important role in turning the structural, electric properties and refractive index of $AFBiS_2$. The different influences of A-ions on the refractive index along [100] and [001] directions make $AFBiS_2$ have superior birefringence.

The origin of GBF plays a key role in developing new birefringent crystals. Compared with LaOZnP, the GBF of $LaOBiS_2$ is conjectured from the lone pair of Bi^{3+} ions of the BiS_2 layer.[10] It is well known that lone pairs of Bi^{3+} ions are extensively present in Bi-containing compounds. Recently, Bi–O–S compounds Bi_2OS_2 ($[Bi_2O_2]BiS_2$, i.e., $BiOBiS_2$) and Bi_2O_2S ($[Bi_2O_2]S$) have been synthesized.[12] Now, one question whether they have GBF due to the fact that they are Bi-containing compounds arises. On the other hand, although $[A_2F_2]$ has substantial influence on the birefringence (here 1.1–1.66) of $AFBiS_2$, the BiS_2 layer gives superior BF compared with $LaOBiS_2$.[11] Another question whether the BiS_2 layer providing GBF is preserved in other Bi-containing compounds arises. To check this, here we use $MOBiS_2$ (M=Al, Ga, In and Sc) as prototype systems.

All calculations in this work were performed by using density functional theory (DFT). More details can be found in Ref. [10]. For the Bi_2O_2S compound, having been experimentally synthesized, XRD patterns indexed that it has an orthorhombic space group $Pnnm$, here $a \neq b \neq c$.[13] Bi_2O_2S is constituted by one S layer alternating with one $[Bi_2O_2]$ layer. Similar to $LaOBiS_2$, $BiOBiS_2$ has a layered structure with space group $P4/nmm$ (No. 129) and is composed of two $[BiS_2]$ layers alternating with one blocking layer $[Bi_2O_2]$ (see Fig. 1). Through the substitution of Bi ions with Al in $LaOBiS_2$, one can obtain a hypothetical compound $LaOAlS_2$.

For the three compounds ($BiOBiS_2$, Bi_2O_2S and $LaOAlS_2$), the fully structural optimizations were first carried out and the results (lattice parameters a and c) are listed in Table 1. Here the corresponding experimental values are also given for comparison. Our theoretical equilibrium lattice constants of $LaOBiS_2$ agree well with the previous theoretical[14] and experimental report.[15] For Bi_2O_2S, its theoretical lattice constants ($a = 3.890$, $b = 3.842$ and $c = 11.955$ Å) are only up to 0.4% larger than the corresponding experi-

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mental values (3.874, 3.840, 11.916).[16] For $BiOBiS_2$, the lattice constant a (3.945) is 0.5% less than the experimental one (3.966), while the lattice constant c (14.042) is 1.8% larger than the experimental value (13.798). The trend is consistent with that of $LaOBiS_2$ and is in contrast to the case of $SrFBiS_2$, where the lattice constant a is 1.1% larger than the experimental value, while the lattice constant c is 2.2% smaller. Still, these theoretical results are correct in the DFT calculation error (<5% is right).

Table 1. Lattice parameters (a, c in Å), band-gap (G in eV), the absolute value of the static birefringence (|sBF|) at 0 eV, A-ionic radii (IR in Å), the electronegativity of A-ion (EE) and the electronegativity difference between A-ion and F/O ions ($\delta EE = EE_{\mathrm{A-ion}} - EE_{\mathrm{F/O-ion}}$) in the compounds with/without the BiS_2 layer. Bi_2O_2S has an orthogonal structure with space group of $PNNM$ (No. 58). For a, c 500 eV, 4 × 4×1 k-point meshes. For G, 500 eV, 12 × 12 × 4 k-point meshes. |sBF| at 0 eV. GGA-PBE.

	a	c	G	|sBF|	IR[a]	EE	δEE
$BiOBiS_2$	3.945	14.042	1.06	1.10	1.35	2.02	1.42
	3.966[b]	13.798[b]					
Bi_2O_2S	3.890/b=3.842	11.955	0.85	0.04	1.35		
	3.874/b=3.840[c]	11.916[c]	1.12[d]				
$LaOAlS_2$	3.993	12.464	1.80	0.01	1.00	1.11	2.33
$LaOBiS_2$	4.063	14. 224	0.98	1.10	1.03	1.11	2.33
	4.066[e]	13.862[e]					
$AlOBiS_2$	3.676	14.222	0.38	1.00	0.72	1.61	1.83
$GaOBiS_2$	3.762	14.082	metallic	1.39	1.00	1.81	1.63
$InOBiS_2$	3.901	14.022	0.25	1.61	1.00	1.78	1.66
$ScOBiS_2$	3.786	14.116	0.90	1.40	1.00	1.36	2.08

[a]Shannon ionic radii, Ref. [17]. [b]Experimental, Ref. [12]. [c]Experimental, Ref. [16]. [d]Experimental, Ref. [13]. [e]Experimental, Ref. [15].

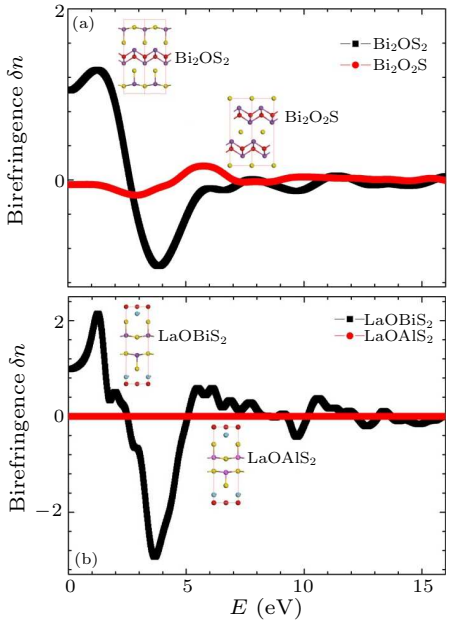

Fig. 1. Birefringence of $BiOBiS_2$ (Bi_2OS_2) and Bi_2O_2S (a), $LaOBiS_2$ and $LaOAlS_2$ (b). GBF appears (absent) in compounds with (without) the BiS_2 layer.

Now, we first examine the BF of the three compounds. Figure 1 shows the birefringence of $BiOBiS_2$, Bi_2O_2S, $LaOBiS_2$ and $LaOAlS_2$. It is clear that the birefringence is dependent on frequency as other optical properties. $BiOBiS_2$ with the BiS_2 layer has a birefringence as large as 1.1 at 0 eV, while the BF of Bi_2O_2S without the BiS_2 layer is very small (nearly zero). This answers the question whether Bi_2O_2S has GBF. It is not true that all Bi-containing compounds are the materials with GBF. When the BiS_2 layer is replaced by the AlS_2 layer, $LaOBiS_2$ will be changed to $LaOAlS_2$ and the GBF will disappear. Hence, one can conclude that GBF appears (disappears) in the compounds with (without) the BiS_2 layer. Furthermore, we can speculate that GBF originates from the BiS_2 layer.

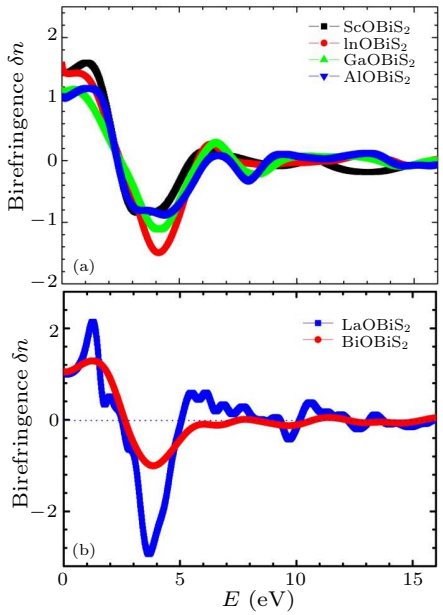

Fig. 2. Giant birefringence of $LaOBiS_2$ and $BiOBiS_2$ as well as in $MOBiS_2$ (M=Al, Ga, In and Sc).

To confirm this, we calculated the BF of $MOBiS_2$ (M=Al, Ga, In and Sc). Due to the fact that these compounds have not been experimentally synthesized, we considered that they have the same structure as $LaOBiS_2$. We also performed fully structural optimizations and the results (here lattice parameters a and c) are listed in Table 1. It is clear that the static BF of four $MOBiS_2$ (M=Al, Ga, In and Sc) increases

as the increase of lattice constant a. Then we conduct the same optical calculations, and their birefringence are depicted in Fig. 2. It is evident that the giant birefringence appears in all MOBiS$_2$ compounds, here we checked as well as in BiOBiS$_2$ and LaOBiS$_2$. This indicates that the BiS$_2$ layer does provide GBF and has good stability in different MO building blocks. Hence, BiS$_2$-containing compounds are attractive candidates for discovering/developing new birefringent artificial crystals.

Similarly, Li *et al.* proposed that the BiS$_2$ layer is the key structural block for discovering new superconductors.[18] The prior work on the superconductivity in a novel BiS$_2$-based superconductor is contributed to $Bi_4O_4S_3$ with a transition temperature T_c of 8.6 K.[19] After that, the other BiS$_2$-based superconductors, $LnO_{1-x}F_xBiS_2$ (Ln=La, Ce, Pr)[15,19–21] with the highest T_c of 10 K have been intensively studied. Analogous to cuprates and iron-based superconductors, the BiS$_2$-based compounds also possess a layered crystal structure consisting of superconducting BiS$_2$ layers intercalated with various block layers, e.g., $Bi_4O_4(SO_4)_{1-x}$ or $[Ln_2O_2]^{2-}$. Here superconductivity can be induced by chemical doping into the intercalated block layers. Indeed, through the replacement of the LaO layer by SrF block, a new BiS$_2$-based superconductor $Sr_{1-x}La_xFBiS_2$, which is iso-structural to LaOBiS$_2$, has been successfully synthesized and studied.[22,23]

Now, the BiS$_2$ layer is the key structural block in both superconductors[18] and giant-birefringent crystals (this work). It is interesting why the BiS$_2$ layer in different block layers can also provide giant birefringence. We turn to examine the micro-structure (atomic coordination and bond-length) of seven compounds with/without the BiS$_2$ layer. The results are listed in Table 2. It is found that M–O bond-length has the largest fluctuation of 0.412 Å, then O–O has 0.27 Å. S1–S2 bonds have two lengths with the fluctuation of 0.118 Å and 0.387 Å, respectively. Bi–S2 bond-length has 0.179 Å fluctuation. It is interesting that Bi–S1 bond-length (in fact, it is the lone-pair layer shown in Fig. 3) is very stable and locates in the range of 2.511–2.556 with a fluctuation of 0.045 Å. This indicates that the BiS$_2$ layer has good structural stability in these BiS$_2$-base compounds.

Table 2. Wyckoff positions and bond-length of LaOBiS$_2$, BiOBiS$_2$, LaOAlS$_2$ and MOBiS$_2$. O sites at origin (0, 0, 0).

	LaOBiS$_2$	BiOBiS$_2$	LaOAlS$_2$	AlOBiS$_2$	GaOBiS$_2$	ScOBiS$_2$	InOBiS$_2$
M $(0.5, 0, z)$	0.0902	0.1323	0.1069	0.0539	0.0626	0.0692	0.0765
Bi $(0.5, 0, z)$	0.6275	0.5895	0.5988	0.6512	0.6439	0.6446	0.6356
S1 $(0.5, 0, z)$	0.3973	0.3120	0.4181	0.4041	0.4018	0.3985	0.3945
S2 $(0.5, 0, z)$	0.8040	0.8960	0.7728	0.8310	0.8248	0.8244	0.8162
M–O	2.403	2.339	2.400	1.991	2.077	2.130	2.226
O–O	2.87	2.79	2.824	2.60	2.66	2.68	2.76
Bi–S1	2.511	2.524	2.253	2.556	2.549	2.539	2.533
Bi–S2	2.895	2.818	2.831	2.716	2.736	2.745	2.790
S1–S2	4.056	4.039	3.697	4.235	4.154	4.117	4.132
S1–S2	4.063	3.945	3.993	3.676	3.762	3.788	3.786

Electron localization function (ELF) characterizes the extent of spatial localization of the electrons and provides a method for the mapping of the electron pair. The ELF of MOBiS$_2$, including LaOBiS$_2$, BiOBiS$_2$, AlOBiS$_2$ and ScOBiS$_2$ were calculated and the results are given in Fig. 3. The anion O and M-cations (Al and Sc) have no visible electrons in the range where the isosurface value is ±0.017. As is expected, the lone pair on Bi^{3+} ions is evident for all MOBiS$_2$ compounds. The S1 ions in Bi–S plane also have pseudo lone-pair electrons, while for S1 ions along the z axis another pseudo lone-pair appears in LaOBiS$_2$ and BiOBiS$_2$. The two symmetric pseudo S1 lone-pairs are observable and should result in the reduction of anisotropy of electronic structure. This may be the reason why LaOBiS$_2$ and BiOBiS$_2$ have a smaller BF than that of other MOBiS$_2$ (M=Ga, In and Sc). Still, the electronic property of the BiS$_2$ layer (as shown in the middle third of Fig. 3) is high stability as its structural stability.

More quantitatively, we listed the Mulliken charges of MOBiS$_2$ (M=La, Bi, Al, Ga, In and Sc) in Table 3. Although M (O) ions have large changes of 0.17 (0.32) in the range of [0.99, 1.16] ([−1.03, −0.71]), Bi and S ions have only 0.06–0.12 flu. This is consistent with that of ELF (Fig. 3) and the structural change such as the bond-length (Table 2). In a word, the structural and electronic properties of the BiS$_2$ layer is high stability in all MOBiS$_2$ compounds here studied.

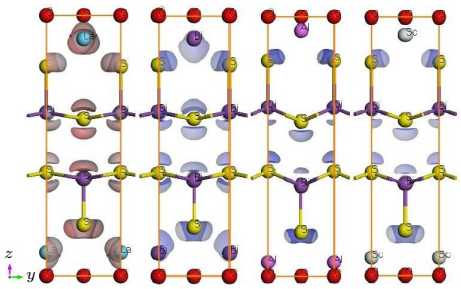

Fig. 3. ELF of LaOBiS$_2$, BiOBiS$_2$, AlOBiS$_2$ and ScOBiS$_2$. The isosurface value is ±0.017.

Our previous study on AFBiS$_2$[11] shows that the trend of their BF can be explained through ionic radii and the electronegativity difference. Here Table 1 also lists the absolute value of the static birefringence

(|sBF|) at 0 eV, A-ionic radii (IR, Å), the electronegativity of A-ion ($\mathcal{E}$) and the electronegativity difference between A-ion and F/O ions ($\delta\mathcal{E} = \mathcal{E}_{\mathrm{A-ion}} - \mathcal{E}_{\mathrm{F/O-ion}}$) in the compounds with/without the BiS_2 layer. In contrast to that in AFBiS_2 (A=Mg, Ca, Sr and Ba),[11] both IR and $\delta\mathcal{E}$ cannot explain the trend in MOBiS_2 (M=Al, Ga, In and Sc). This indicates that the BiS_2 layer has unexpected stability in different building blocks of M–O and A–F. In addition, we also give the band-gap in Table 1. MOBiS_2 (M=La, Bi, Al, Ga, In and Sc) exhibit metallic or semiconductor with band-gap of 0.25–1.06 eV, indicating that they have potential extensive applications without the band-gap constrain.

Table 3. Mulliken charges of MOBiS_2 (M=La, Bi, Al, Ga, In and Sc).

	LaOBiS_2	BiOBiS_2	AlOBiS_2	GaOBiS_2	ScOBiS_2	InOBiS_2
M	1.14	1.35	1.38	1.06	0.99	1.16
O	−0.79	−0.90	−1.03	−0.80	−0.71	−0.87
Bi	0.90	0.86	0.89	0.87	0.91	0.92
S1	−0.62	−0.65	−0.61	−0.53	−0.57	−0.58
S2	−0.62	−0.67	−0.64	−0.61	−0.63	−0.64

In summary, first principles calculations on Bi_2OS_2 (i.e., $BiOBiS_2$), Bi_2O_2S and $LaOAlS_2$ show that giant birefringence appears in compounds with the BiS_2 layer but is absent in those without. This is furthermore demonstrated in the four MOBiS_2 (M=Al, Ga, In and Sc) compounds. The bond-length and Mulliken charges as well as ELF reveal that the BiS_2 layer exhibits unexpected stability in both structural and electronic properties. This makes the BiS_2 layer the giant-birefringent layer with good stability. The result can guide experimental searching and developing of artificial birefringent crystal or even multifunctional materials.

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