Structural, Electronic, and Optical Properties of BiOX$_{1-x}$Y$_x$ (X, Y = F, Cl, Br, and I) Solid Solutions from DFT Calculations

Zong-Yan Zhao$^{1,2}$, Qing-Lu Liu$^3$ & Wen-Wu Dai$^1$

Six BiOX$_{1-x}$Y$_x$ (X = F, Cl, Br, and I) solid solutions have been systematically investigated by density functional theory calculations. BiOCl$_{1-x}$Br$_x$, BiOBr$_{1-x}$I$_x$, and BiOCl$_{1-x}$I$_x$ solid solutions have very small bowing parameters; as such, some of their properties increase almost linearly with increasing x. For BiOF$_{1-x}$Y$_x$ solid solutions, the bowing parameters are very large and it is extremely difficult to fit the related calculated data by a single equation. Consequently, BiOX$_{1-x}$Y$_x$ (X = Cl, Br, and I) solid solutions are highly miscible, while BiOF$_{1-x}$Y$_x$ (Y = Cl, Br, and I) solid solutions are partially miscible. In other words, BiOF$_{1-x}$Y$_x$ solid solutions have miscibility gaps or high miscibility temperature, resulting in phase separation and F/Y inhomogeneity. Comparison and analysis of the calculated results and the related physical–chemical properties with different halogen compositions indicates that the parameters of BiOX$_{1-x}$Y$_x$ solid solutions are determined by the differences of the physical–chemical properties of the two halogen compositions. In this way, the large deviation of some BiOX$_{1-x}$Y$_x$ solid solutions from Vegard’s law observed in experiments can be explained. Moreover, the composition ratio of BiOX$_{1-x}$Y$_x$ solid solutions can be measured or monitored using optical measurements.

Energy shortages and environmental pollution have resulted in the development and utilization of new energy sources. In particular, photocatalytic technology has attracted considerable interest. Under solar light irradiation, photocatalysts can decompose water to produce hydrogen, convert greenhouse gas (i.e., carbon dioxide) into hydrocarbon fuel, and decompose harmful gases and pollutants in water to harmless inorganic substances. That is, photocatalysis can use solar energy to alleviate energy shortage and environmental pollution. Although this is an attractive prospect, the current development of photocatalytic technology faces two major bottlenecks. First, most of current conventional photocatalysts are wide band-gap semiconductor materials. They only exhibit photocatalytic activity under UV-light irradiation, meaning they cannot fully utilize solar energy. Second, because of the existence of impurities and defects, the recombination rate of the photogenerated electron–hole pairs is high, leading to very low quantum efficiency of solar energy conversion. To realize the efficient use of solar energy, either conventional photocatalysts need to be modified, or novel photocatalysts need to be developed.

Bismuth oxyhalides (BiOX, X = F, Cl, Br, and I) are layered semiconductors. The structure of BiOX compounds is composed of strong intralayer interactions within [Bi$_2$O$_2$]$_{1-x}$ slabs and weak van der Waals interlayer interactions between adjacent X$^-$ slabs. The interleaved [Bi$_2$O$_2$]$_{1-x}$ and X$^-$ slabs along the c-axis direction produce an internal electric field, which remarkably accelerates the transfer and reduces the recombination rate of photogenerated electron–hole pairs. In addition, they do not contain toxic and heavy metals. Therefore, they have numerous applications, such as in pigments in the cosmetic industry, magnetic materials, pharmaceuticals, and catalysts in the oxidative coupling of methane reaction$^{1-3}$. Because of the above advantages, BiOX compounds have attracted much attention in the field of photocatalysis$^{4-8}$. In 2008, Zhang et al. found that all of the BiOX (X = Cl, Br, and I) compounds exhibit photocatalytic activity and BiOI exhibits excellent activity under both

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$^1$Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, People’s Republic of China. $^2$Yunnan Key Laboratory of Micro/Nano Materials & Technology, School of Materials Science and Engineering, Yunnan University, Kunming 650504, People’s Republic of China. $^3$Key Laboratory of Nanodevices and Applications, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, People’s Republic of China. Correspondence and requests for materials should be addressed to Z.-Y.Z. (email: zzy@kmust.edu.cn)
UV–vis and visible-light irradiation. The preparation, properties, and photocatalytic performance of BiOX compounds have subsequently been extensively investigated.

BiOX compounds have the same structure and similar characteristics. The band gaps of BiOX compounds decrease from ~3.9 to ~1.8 eV with increasing atomic number of the halogen. This unique feature provides the opportunity to tailor the basic photoelectric physical properties and photocatalytic performance of BiOX compounds by intentionally mixing halogens. In other words, BiOX_{1–x}Y_{x} (X = F, Cl, Br, and I) solid solutions (or semiconductor alloys) may meet the requirements for photocatalytic applications. Semiconductor solid solutions have some benefits over other band-gap tailoring techniques (e.g., impurity doping) because it is possible to alter the electronic properties without introducing impurity states that could act as recombination centres. Moreover, semiconductor solid solutions provide a natural way of tuning the magnitude of the band-gap energy and other photoelectric properties to optimize and increase the application of semiconductor devices. The most successful example in the field of photocatalysis is (Ga_{1–x}Zn_{x})(N_{1–x}O_{x}) solid solutions, which show excellent photocatalytic performance for hydrogen production from photocatalytic water splitting under visible-light irradiation, while the two components (GaN and ZnO) only absorb UV-light. Generally, choosing a solid-solution partner can be difficult because elements with partially filled valence shells that can accept electrons or holes risk reducing the overall photocurrent for redox reactions. However, the features of BiOX compounds can avoid these problems. Recently, it has been reported that BiOX compounds are able to form solid solutions through various synthesis processes. For example, Keller et al. found that there are no quaternary phases in BiOX_{1–x}Y_{x} (X = Cl, Br, and I) solid solutions, BiOCl_{1–x}Br_{x} and BiOBr_{1–x}I_{x} form systems of unlimited mutual solubility, and BiOCl_{1–x}I_{x} has limited solubility when it is iodine rich. Ren et al. demonstrated that optimized BiOX_{1–x}Y_{x} solid solutions possess higher photocatalytic activity than pure BiOX compounds because of the wider range of the visible light response and the reduced recombination rate of electron–hole pairs.

Although the synthesis and photocatalytic performance of BiOX_{1–x}Y_{x} solid solutions have been investigated by independent research groups, the basic concepts and determination of the photocatalytic performance have been hampered by a lack of fundamental knowledge about BiOX_{1–x}Y_{x} solid solutions. Furthermore, studies have been limited to one or two types of BiOX_{1–x}Y_{x} solid solutions. To understand the structural and electronic properties of BiOX_{1–x}Y_{x} solid solutions, it is necessary to systematically investigate their properties using theoretical calculations or simulations. However, only a few theoretical articles have been reported. Zhang et al. calculated the electronic structures of BiOX_{1–x}Y_{x} solid solutions by density functional theory (DFT), and considered that the alloying effect in BiOX results in a substantially lower electron–hole recombination rate and much higher photocatalytic efficiency. Their work is of great practical value, and provides a reasonable explanation for some experimental observations. However, they did not provide a basic rule for BiOX_{1–x}Y_{x} solid solutions. In particular, they did not analyse the large deviation of some BiOX_{1–x}Y_{x} solid solutions from Vegard’s rule reported by Keller et al.

The main purpose of this study is to provide a comprehensive understanding of BiOX_{1–x}Y_{x} solid solutions for photocatalytic applications. The topics discussed in this article include the structural, electronic, and optical properties of BiOX_{1–x}Y_{x} solid solutions, and their relationship with photocatalytic performance. We also provide a possible explanation for previous experimental observations and some useful data for tailoring the properties of BiOX photocatalysts.

Results and Discussions

Formation energy. Isolated atoms can combine to form a crystal because the combined system has lower energy. That is, the free atoms combined in a crystal will release energy, or decomposition of a crystal requires energy. This energy is referred to the binding energy (E_b) defined as following for BiOX_{1–x}Y_{x} solid solutions:

\[ E_b(x) = \frac{E_{\text{tot}(\text{BiOX}_{1-x}Y_x)} - \sum_i n_i E_i(\text{atom})}{\sum n_i} \]

where \( E_{\text{tot}(\text{BiOX}_{1-x}Y_x)} \) is the total energy of the BiOX_{1–x}Y_{x} solid solution. If \( x = 0 \), it is the total energy of pure BiOX. \( n_i \) and \( E_i(\text{atom}) \) are the number and energy of an isolated \( i \) atom, respectively. The definition of \( E_b \) indicates that the crystal structure of a solid solution is more stable when the value of the binding energy is larger. The calculated binding energies of the BiOX_{1–x}Y_{x} solid solutions are shown in Fig. 1. In the cases of the pure BiOX compounds, BiOF has the largest binding energy. The binding energy decreases with increasing atomic number of the halogen. This may be related to fluorine having the highest electronegativity, resulting in the van der Waals interactions between the [Bi_{2}O_{2}]^{2+} slabs of BiOF being the largest. In the van der Waals interactions between [Bi_{2}O_{2}]^{2+} slabs of BiOF, the lattice constant of BiOF along the \( c \) axis is the smallest. The van der Waals interactions between [Bi_{2}O_{2}]^{2+} slabs of BiOF are the smallest, and its lattice constant along the \( c \) axis is the largest. For BiOX_{1–x}Y_{x} solid solutions, when \( Y \) is incorporated into BiOX, the value of \( E_b \) increases, indicating that the incorporation of heavy halogen atoms will decrease the stability of the crystal. With increasing \( Y \) content, the binding energies of all of the BiOX_{1–x}Y_{x} solid solutions linearly increases. In the complete range of the \( Y \) content, the variation of the binding energy of the BiOCl_{1–x}Br_{x} solid solutions is the smallest (~0.19 eV/atom), while that of the BiOF_{1–x}I_{x} solid solutions is the largest (~0.95 eV/atom). These calculated results indicate that only small energy is needed to incorporate \( Y \) into the BiOX (\( X = \text{Cl and Br} \) ) crystal matrix to form solid solution. The above phenomena are quantitatively reflected by the fitting curves in Fig. 1 and the fitting parameters in Table 1: the correlation coefficients for all of the linear fitting curves are greater than 0.99 and the slope of the curve is smallest for the BiOCl_{1–x}Br_{x} solid solutions and largest for the BiOF_{1–x}I_{x} solid solutions.

To describe the miscibility of the BiOX_{1–x}Y_{x} solid solutions, the formation enthalpy was also calculated:
$\Delta = -\frac{H_x}{E_{iOXY}} - \frac{E_{BiOX}}{E_{BiOY}}$ (1), (2)

where $E_{BiOX}$ and $E_{BiOY}$ are the total energies of pure BiOX and BiOY with the same size of supercell, and $E_{BiOX_{1-x}Y_x}$ is the total energy of the BiOX$_{1-x}$Y$_x$ solid. The calculated results are shown in Fig. 2. The formation enthalpy $\Delta H_f(x)$ describes the energy cost of mixing X and Y halogens in a certain lattice. It is clear that all of the BiOX$_{1-x}$Y$_x$ solid solutions have an upward bowing in their $\Delta H_f$ dependence on $x$, which indicates they prefer decoherent phase separation into BiOX and BiOY at zero temperature. Comparing these calculated curves, the formation enthalpies of the BiOX$_{1-x}$Y$_x$ solid solutions are in the order $\text{BiOCl}_{1-x}\text{Br}_x < \text{BiOBr}_{1-x}\text{I}_x < \text{BiOCl}_{1-x}\text{I}_x < \text{BiOF}_{1-x}\text{Cl}_x < \text{BiOF}_{1-x}\text{Br}_x < \text{BiOF}_{1-x}\text{I}_x$ for the same $x$. This indicates that halogen mixing is easier with halogens with similar size. It is worth noticing that there is only one peak for BiOCl$_{1-x}$Br$_x$, BiOBr$_{1-x}$I$_x$, and BiOCl$_{1-x}$I$_x$, while there is more than one peak for the other three types of BiOF$_{1-x}$Y$_x$ solid solution. These peaks are located on the light-halogen-rich side of the $\Delta H_f$ against the $x$ curve ($x < 0.5$), indicating that limited solubility might occur

\[ \Delta H_f(x) = E_{BiOY_{1-x}X_x} - (1-x)E_{BiOX} - xE_{BiOY}, \] (2)

Table 1. Binding energies and formation enthalpies of BiOX$_{1-x}$Y$_x$ solid solutions as a function of composition. *$T$ is the estimated miscibility temperature (K).

| Formula          | BiOCl$_{1-x}$Br$_x$ | BiOB$_{1-x}$I$_x$ | BiOCl$_{1-x}$I$_x$ | BiOF$_{1-x}$Cl$_x$ | BiOF$_{1-x}$Br$_x$ | BiOF$_{1-x}$I$_x$ |
|------------------|---------------------|-------------------|--------------------|-------------------|-------------------|-------------------|
| Binding Energy:  | $E_b = -5.309$      | $E_b = -5.120$    | $E_b = -5.301$    | $E_b = -5.856$    | $E_b = -5.844$    | $E_b = -5.828$    |
| $a = 0.188$      | $a = 0.199$         | $a = 0.381$       | $a = 0.554$       | $a = 0.736$       | $a = 0.931$       |
| Formation Enthalpy: | $\Omega = 12.976$  | $\Omega = 13.065$ | $\Omega = 59.658$ | $\Omega = 128.339$ | $\Omega = 193.265$ | $\Omega = 297.797$ |
| $T = 150^\circ$ | $T = 150^\circ$     | $T = 700^\circ$   | $T = 1490^\circ$  | $T = 2240^\circ$  | $T = 3460^\circ$  |
on the heavy-halogen-rich side ($x > 0.5$). According to conventional solid-solution theory, the solid-solution formation enthalpy is almost a quadratic function of $x$: 
\[
\Delta H_f(x) = \Omega x (1 - x),
\]
where $\Omega$ is the interaction parameter, which is an indicator of the solid-solution solubility. A larger $\Omega$ indicates a smaller solubility. The fitting curves are shown in Fig. 2 as dashed lines, and the corresponding fitting parameters are listed in Table 1. The fitting curves for BiOCl$_{1-x}$Br$_x$ and BiOBr$_{1-x}$I$_x$ solid solutions have very large correlation coefficients, while the other four BiOX$_{1-x}$Y$_x$ solid solutions have small correlation coefficients. The $\Omega$ values of BiOCl$_{1-x}$Br$_x$ and BiOBr$_{1-x}$I$_x$ are very small and almost the same, suggesting that component-uniform BiOCl$_{1-x}$Br$_x$ and BiOBr$_{1-x}$I$_x$ solid solutions can be easily prepared at the standard growth temperature. The $\Omega$ values of the other four solid solutions are relatively large. Furthermore, according to the standard solid-solution model, the miscibility gap temperature is given by $\Omega$ (per mixed atom)/2$k_B$ 

Using this equation, the transition temperature is about 150 K for BiOCl$_{1-x}$Br$_x$ and BiOBr$_{1-x}$I$_x$ solid solutions, and 700 K for BiOCl$_{1-x}$I$_x$ solid solutions. These miscibility gap temperatures are less than or close to the typical growth temperatures in the common preparation process, suggesting that these three types of solid solution can be easily prepared. However, for the other three types of solid solution containing fluorine, the transition temperatures are above 1400 K, suggesting that BiOF$_{1-x}$Y$_x$ solid solutions are difficult to prepare in practice and have relatively large miscibility gaps. This may be the reason why there is still no relevant experimental work in the literature. In other words, good miscibility is expected for BiOCl$_{1-x}$Br$_x$ and BiOBr$_{1-x}$I$_x$ solid solutions, and thus it is expected that homogeneous unlimited solid solutions can be formed. For BiOCl$_{1-x}$I$_x$ solid solutions, component-uniform samples with variable compositions can be synthesized, but homogeneous limited solid solutions can only be formed for certain compositions. The above calculated results are in good agreement with experimental observations. Owing to the relatively large $\Omega$ values (i.e., miscibility gap temperatures) and multiple peaks in the $\Delta H_f(x)$ curve, phase separation and component inhomogeneity are a common problem in the production of BiOF$_{1-x}$Y$_x$ solid solutions.

### Structural properties

A solid solution with two components can be called a binary alloy or a quasibinary alloy. The resulting solid solution generally has significantly different properties from those of its components. DFT calculations allow an expression for the variation of the crystal lattice constants of BiOX$_{1-x}$Y$_x$ solid solutions in the complete range of $x$ to be constructed. For the pure BiOX compounds, the calculated lattice parameters are in good agreement with experimental measurements. We compare the calculated results and the available experimental results in Figures S1 to S6 (in the Supporting Information). The calculated results are consistent with the experimental results, especially the variation trend with $x$, indicating that the supercell models chosen in the present work are basically reasonable. For the DFT calculations, the size of supercell and the occupancy sites of Y in the supercell also impact the final total energy of models and the lattice parameters. So, it should carefully choose the configuration of solid solution structure. In the present work, we have found that if the model has higher symmetry, the total energy per cell is smaller. In this configuration, the Y atoms gather together at the same plane as much as possible. Thus, it is assumed the interaction between same halogen atoms (X-X or Y-Y) or different halogen atoms (X-Y) lead the variation of total energy per cell, as well as the variation of lattice constants. However, the interaction between halogen atoms are very small as mention in ref. 20, so the differences between the possible supercells for the same composition are relatively small ($< 0.5$ eV/cell, one cell contains 6 atoms). Of course, there are some differences between experimental measurements and DFT calculation, which can be ascribed to the following two aspects: (1) the uncertainty of the method of experimental measurement. The XRD characterization is the most conventional method in experimental measurement, which is a statistical method of analysis, and the accuracy of the results depends on the degree of proficiency of researcher. Fox example, in the Figure S6, the lattice parameter of BiOCl$_{1-x}$I$_x$ solid solution has two different values at the $x = 0.4$. (2) The choice of supercell model (including size and occupation pattern) and ordered solid solution have limitation, impacting the accuracy of DFT calculations. For example, the choice of models is not equal interval based on the value of $x$, so the continuity of variation trend cannot be determined in the present work. However, from the general situation, the variation trends of experimental measurements and DFT calculations are still basically consistent with each other. Thus, the calculated results in the present work can partly explain some experimental phenomena observed previously.

Figure 3 shows how the lattice constants vary with $x$. In the present work, the relationship between the lattice constants and the composition do not follow a linear relationship (i.e., a first-order function). Therefore, the second-order function of Vegard’s law was used to fit these data:

\[
\begin{align*}
\alpha_{\text{BiOX}_{1-x}Y_x}(x) &= (1 - x)\alpha_{\text{BiOX}} + x\alpha_{\text{BiOY}} + \theta x (1 - x) \\
\epsilon_{\text{BiOX}_{1-x}Y_x}(x) &= (1 - x)\epsilon_{\text{BiOX}} + x\epsilon_{\text{BiOY}} + \theta x (1 - x)
\end{align*}
\]

where $\theta$ is the bowing parameter. The fitting curves are plotted in Fig. 3, and the detailed fitting parameters are listed in Table 2. For BiOCl$_{1-x}$Br$_x$ and BiOBr$_{1-x}$I$_x$ solid solutions, the bowing parameters are very small. That is, the lattice constants almost linearly increase with increasing $x$ and almost obey the first-order function of Vegard’s law. For the BiOCl$_{1-x}$I$_x$ solid solutions, the bowing parameter is larger than those of the former two cases. The variations of the lattice constants for BiOF$_{1-x}$Y$_x$ solid solutions are complicated. In the range $0 \leq x \leq 1/2$, all of the lattice constants linearly increase with increasing $x$. Moreover, the slopes also increase with increasing atomic number of Y, except for lattice constant $c$ of the BiOF$_{1-x}$I$_x$ solid solution. In the range $1/8 \leq x \leq 1/4$, the variations of lattice constant $a$ of all three BiOF$_{1-x}$Y$_x$ solid solutions and lattice constant $c$ of the BiOF$_{1-x}$Cl$_x$ solid solutions obey the second-order function of Vegard’s law. Lattice constant $c$ of the BiOF$_{1-x}$Br$_x$ solid solutions increases with increasing $x$ in the range $1/8 \leq x \leq 1/4$, while lattice constant $c$ of the BiOF$_{1-x}$I$_x$ solid solutions slowly decreases...
Lattice constants of BiOX$_1$-$x$Y$_x$ solid solutions as function of composition.

Table 2. Lattice constants of BiOX$_{1-x}$Y$_x$ solid solutions as a function of composition.

with increasing x in the range 1/8 ≤ x ≤ 1/2. In the rest of the range of x, lattice constant c of the BiOF$_{1-x}$Br$_x$ and BiOF$_{1-x}$I$_x$ solid solutions obey the second-order function of Vegard’s law with a relatively large bowing parameter. It should be noted that for the BiOX$_{1-x}$Y$_x$ (X, Y = Cl, Br, and I) solid solutions, the bowing parameters of lattice constant a are smaller than those of lattice constant c. The situation for the BiOF$_{1-x}$Y$_x$ (Y = Cl, Br, and I) solid solutions is completely different. In the first linear variation region, the slopes of lattice constant a are larger than those of lattice constant c, especially in the case of the BiOF$_{1-x}$I$_x$ solid solutions. In contrast, the bowing parameters of lattice constant a are smaller than those of lattice constant c in the parabolic variation region.

In the above relationship between formation energy and x, the lattice mismatch between the two components of the BiOX$_{1-x}$Y$_x$ solid solution is not the deciding factor for the variations of the lattice constants. For example, the c lattice mismatch between BiOCl and BiOI is 21.46% and the variations of the lattice constants of the BiOCI$_{1-x}$I$_x$ solid solution obey the second-order function of Vegard’s law in the complete range of x. However, although the c lattice mismatch between BiOF and BiOCl is 16.42%, the variations of the lattice constants of the
BiOF$_{1−x}$Cl solid solutions follow different rules. Keller et al. observed a large deviation from Vegard’s rule for the cell parameter of BiOCl$_{1−x}$ solid solutions and assumed that the strong bowing of $c(x)$ is mainly because of the weak anion–anion interactions across the interface between two vicinal sandwiches. Their assumption is mainly based on the one-sidedness of the halogen coordination polyhedra induced by weak van der Waals attractions between halogen atoms, which is hindered by strong X–X and X–O repulsions and by the rigidity of the [Bi$_2$O$_2$]$^{2+}$ layers. The crystal structures of two typical examples are shown in Fig. 4. The bowing parameter is the smallest for the BiOCl$_{1−x}$Br$_x$ solid solutions, while the deviation from Vegard’s rule is the largest for the BiOF$_{1−x}$I$_x$ solid solutions. For the BiOCl$_{1}$.Br$_x$ solid solutions, the Cl–Bi$_1$ (~3.041–3.047 Å) and Br–Bi$_1$ (~3.117–3.152 Å) bond lengths are almost constant with increasing $x$, while the Cl–Bi$_2$ (~3.514–4.317 Å) and Br–Bi$_2$ (~3.402–4.100 Å) bond lengths linearly increase with increase $x$. Furthermore, in the complete range of $x$, the distance between Cl and Br along the $c$ axis is very small (~0.218 Å) and the [Bi$_2$O$_2$]$^{2+}$ layers are hardly affected (no obvious distortion). In contrast to the above situation, for the BiOF$_{1−x}$I$_x$ solid solutions, the F–Bi$_1$ (~2.699–3.057 Å), I–Bi$_1$ (~3.249–3.337 Å), F–Bi$_2$ (~2.767–6.288 Å), and I–Bi$_2$ (~2.981–4.939 Å) bond lengths are in a relative large range, and these variations do not follow a definite trend with increasing $x$. Furthermore, the distance between F and I along the $c$ axis varies from 0.393 to 1.285 Å, and the [Bi$_2$O$_2$]$^{2+}$ layers are greatly affected (obvious distortion) for the F-rich compositions ($x = 1/18$ and 1/4). The microstructure variation of the other BiOX$_{1−x}$Y$_x$ solid solutions are determined by changes of the internal microstructure, and confirm the assumptions of Keller et al.

In the previous experimental report ref. 20, the authors found the BiOCl$_{1−x}$I$_x$ solid solutions also show abrupt changes for the cell parameters, and they assumed that the strong bowing or deviation of $c(x)$ is mainly due to the weakness of anion–anion interaction across the interface between two vicinal sandwiches. In our present work, we have strengthened this view, and found that the interactions between the halogen atoms, as well as the interaction between the halogen atom and [Bi$_2$O$_2$]$^{2+}$ layers, are closely related to the nature of the halogen atom itself. So we list these parameters and their differences in Table 3. Furthermore, at the different solubility or content of Y/(X + Y), these differences have different influence on the behavior of solid solutions as shown in Fig. 4. Comparison of these parameters, one can be found that the greater the difference, the more obvious bowing or abruption. Because this explanation is valid for the experimental findings of BiOCl$_{1−x}$I$_x$ solid solutions, so it could speculate that it also valid for BiOF$_{1−x}$X$_x$ solid solutions.

Another worth notice phenomenon is the symmetry breaking in some cases. In Fig. 4, two extreme examples are provided: the BiOCl$_{1}$.Br$_x$ represents almost no symmetry breaking (i.e. fully obey the Vegard’s law) solid solutions; the BiOF$_{1}$.I$_x$ represents dramatic symmetry breaking (i.e. obviously disobey the Vegard’s law) solid solutions. The similar phenomenon could be observed in BiOF$_{1}$.Cl$_x$ and BiOF$_{1}$.Br$_x$ solid solutions. When the content ($x$) of Y (Y = Cl, Br, and I) is increasing, the symmetry breaking always exists. We think the main possible reason low content ($x$) of Y means impurity doping, which destroys the integrity of the interaction in the F anion plane and then make the [Bi$_2$O$_2$]$^{2+}$ layer distortion, because there is no self-interaction between Y anions. When the content ($x$) of Y is larger than 1/12, the two ordered anion (F$^−$ and Y$^−$) planes are still maintain, owing the larger interaction of F with [Bi$_2$O$_2$]$^{2+}$ layer, so the symmetry of the atomic positions is keeping. This phenomenon is more obvious if the differences between F and Y atomic properties are larger.

Figure 4. Crystal structures of BiOCl$_{1−x}$Br$_x$ and BiOF$_{1−x}$I$_x$ with $x = 1/18$, 1/4, and 17/18.
Table 3. Band gaps, static dielectric functions, and refractive indices of BiOX$_{1-x}$Y$_x$ solid solutions as a function of composition.

| Formula | BiOCl$_{1-x}$Br$_x$ | BiOBr$_{1-x}$I$_x$ | BiOCl$_{1-x}$I$_x$ | BiOF$_{1-x}$Cl$_x$ | BiOF$_{1-x}$Br$_x$ | BiOF$_{1-x}$I$_x$ |
|---------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Band gap: $E_g^{BiOX} = (1-x)E_g^{BiOX} + xE_g^{BiOY} + bx (1-x)$ | $E_g^{BiOCl}_{0.0825} = 4.0105$ | $E_g^{BiOBr}_{0.0662} = 4.2502$ | $E_g^{BiOCl}_{0.0094} = 2.9945$ | $E_g^{BiOF}_{0.0825} = 4.5130$ | $E_g^{BiOF}_{0.0662} = 4.7236$ | $E_g^{BiOF}_{0.0094} = 3.5307$ |
| Static dielectric function: $\varepsilon_{ox}^{BiOX} = (1-x)\varepsilon_{ox}^{BiOX} + x\varepsilon_{ox}^{BiOY} + bx (1-x)$ | $\varepsilon_{ox}^{BiOCl}_{0.0481} = 4.1105$ | $\varepsilon_{ox}^{BiOBr}_{0.0094} = 4.1105$ | $\varepsilon_{ox}^{BiOCl}_{0.0094} = 4.1015$ | $\varepsilon_{ox}^{BiOF}_{0.0481} = 4.0105$ | $\varepsilon_{ox}^{BiOF}_{0.0094} = 4.1015$ | $\varepsilon_{ox}^{BiOF}_{0.0094} = 4.1015$ |
| Refractive index: $n_{ox}^{BiOX} = (1-x)n_{ox}^{BiOX} + xn_{ox}^{BiOY} + bx (1-x)$ | $n_{ox}^{BiOCl}_{0.02184} = 2.0256$ | $n_{ox}^{BiOBr}_{0.024849} = 2.2184$ | $n_{ox}^{BiOCl}_{0.0094} = 2.0256$ | $n_{ox}^{BiOF}_{0.02184} = 2.0256$ | $n_{ox}^{BiOF}_{0.024849} = 2.2184$ | $n_{ox}^{BiOF}_{0.0094} = 2.0256$ |

Figure 5. Band gap of BiOX$_{1-x}$Y$_x$ solid solutions as a function of content x.

Electronic and optical properties. The calculated band gaps of the pure BiOX compounds are 3.949 eV for BiOF, 3.499 eV for BiOCl, 2.837 eV for BiOBr, and 1.893 eV for BiOI, which are in good agreement with the experimental values (~3.46–3.51 eV, ~2.9 eV, and ~1.9 eV, respectively). Figure 5 shows the band gaps of the BiOX$_{1-x}$Y$_x$ solid solutions as a function of x. The variation trend of the band gaps calculated by the GGA + U method is similar to those calculated by the GGA method (Figures S7–S12 in the Supporting Information). Furthermore, the calculated results in the present work are consistent with available experimental values (Figures S13–S15). Based on the above comparison of the lattice constants and band gaps, we consider that the calculation method in the present work is reasonable and produces reliable results.

The electronic energy-band parameters of semiconductor solid solutions and their dependence on x are very important. However, investigation of BiOX$_{1-x}$Y$_x$–based photocatalysts has been hampered by a lack of definite knowledge about various material parameters. Therefore, it is necessary to investigate and explain the variation trends of the band gaps of BiOX$_{1-x}$Y$_x$ solid solutions. The expressions of Vegard’s law for the band gap or dielectric function constant are the same as Eq. (4) except that the symbol for the bowing parameter is b rather than t. For the BiOCl$_{1-x}$Br$_x$ and BiOBr$_{1-x}$I$_x$ solid solutions, fitting the second-order function of Vegard’s law to the complete range of data points in Fig. 5 produces a small bowing parameter. Although the bowing parameter of the BiOCl$_{1-x}$I$_x$ solid solutions is larger, it obeys the second-order function of Vegard’s law in the complete range of x. For the BiOF$_{1-x}$I$_x$ solid solutions, the band gap linearly decreases with increasing x for F-rich compositions, but it obeys the second-order function of Vegard’s law when x > 1/8 (BiOF$_{1-x}$Cl$_x$ and BiOF$_{1-x}$Br$_x$) or 3/4 (BiOF$_{1-x}$I$_x$). The variation trend of the BiOF$_{1-x}$I$_x$ solid solutions is separated into three parts: two linear variation
parts and one quadratic variation part. Another interesting result is that the bowing parameters are negative for the BiOCl$_{1-x}$Br$_x$, BiOBr$_{1-x}$I$_x$, and BiOCl$_{1-x}$I$_x$ solid solutions, while the bowing parameters are positive for the BiOF$_{1-x}$Y$_x$ solid solutions. In addition, the bowing parameters decrease with increasing atomic number of Y.

In addition to the variation of the band gap with $x$, the optical properties of the BiOX$_{1-x}$Y$_x$ solid solutions also show a similar variation trend. As shown in Fig. 6, the static dielectric constant ($\varepsilon_0$) and refractive index ($n_0$) of the BiOX$_{1-x}$Y$_x$ solid solutions increase with increasing $x$. Interestingly, expect for the BiOF$_{1-x}$I$_x$ solid solutions, the optical properties of the BiOX$_{1-x}$Y$_x$ solid solutions obey the second-order function of Vegard’s law in the complete range of $x$ with very small bowing parameters. In other words, the optical properties of the BiOX$_{1-x}$Y$_x$ solid solutions (expect for the BiOF$_{1-x}$I$_x$ solid solutions) almost linearly increase with increasing $x$. For the BiOF$_{1-x}$I$_x$ solid solutions, the optical properties linearly increase with increasing $x$ in the ranges $0 \leq x \leq 1/12$ and $1/8 \leq x \leq 1/2$, while the optical properties quadratically increase with increasing $x$ in the range $3/4 \leq x \leq 1$.

Because optical measurements are relatively easy to perform, we fitted the calculated optical parameters as a function of composition $x$. The fitting equations are provided in Table 3.

**Possible explanation.** In the present work, the properties of BiOX$_{1-x}$Y$_x$ solid solutions have an inherent connection with the differences between the physical–chemical properties of the two halogen components. The two extreme examples are BiOCl$_{1-x}$Br$_x$ and BiOF$_{1-x}$I$_x$. For the BiOCl$_{1-x}$Br$_x$ solid solutions, the miscibility temperature is very low and its properties (i.e., lattice constants, band gap, and optical properties) obey the second-order function of Vegard’s law in the complete range of $x$ with small bowing parameters. In contrast, for the BiOF$_{1-x}$I$_x$ solid solutions, the miscibility temperature is very high and its properties obey different rules in different ranges of $x$: at low I content, the downward/upward bowing is so weak that there is almost linear variation, while at high I composition the bowing is stronger. Therefore, the parameters of the BiOF$_{1-x}$I$_x$ solid solutions cannot be described using a single bowing parameter, which has also been reported for other semiconductor solid solutions$^{43,44}$. It is worth pointing out that BiOF$_{1-x}$I$_x$ solid solutions may show phase separation, which may change the photon-absorption mechanism.

In the above examples, Cl and Br are adjacent elements in the periodic table, while F and I are the end elements of the halogen group. In other words, the differences between Cl and Br are very slight, while the differences between F and I are very obvious. Keller et al. considered that Bi–X and Bi–Y bonds of different lengths coexist in a mixed crystal and the weak anion–anion interactions across the interface between two vicinal sandwiches induce the large deviation from Vegard’s law$^{49}$, which was confirmed in the present work. We suggest that
Finally, the composition ratio of BiOX$_1$ from ref. 45. bThe Mulliken electronegativity of a neutral atom is the arithmetic mean of the atomic electron equations are provided. The band gap of BiOX$_1$ is mainly determined by the interlayer interactions, so its variation is related to the differences in the radii of the different halogens, and it significantly varies with $x$. cFor low Y content, the downward/upward bowing is so weak that the variation is almost linear, while solid solutions have very small bowing parameters; thus, some of their properties almost linearly vary with $x$. (2) BiOF$_{1-x}$Y$_x$ solid solutions have very large bowing parameters. Furthermore, the properties of BiOF$_{1-x}$Y$_x$ solid solutions cannot be fitted to a single equation. In other words, its properties obey different rules in different ranges of $x$. For low Y content, the downward/upward bowing is so weak that the variation is almost linear, while high Y content the bowing is stronger. Consequently, BiOX$_{1-x}$Y$_x$ solid solutions that do not contain fluorine are highly miscible, while those that contain fluorine are partially miscible. Therefore, BiOF$_{1-x}$Y$_x$ solid solutions have a miscibility gap or high miscibility temperature, resulting in phase separation and F/Y inhomogeneity. To provide a possible explanation, we compared and analysed the calculated results and the physical–chemical properties for varying halogen compositions, and found that the parameters of BiOX$_{1-x}$Y$_x$ solid solutions are determined by the differences of the physical–chemical properties between two halogen compositions. In this way, the large deviation from Vegard’s law in some BiOX$_{1-x}$Y$_x$ solid solutions observed in experiments can be explained. Finally, the composition ratio of BiOX$_{1-x}$Y$_x$ solid solutions can be measured or monitored using optical measurements, because their optical properties approximately linearly vary as a function of $x$, and the corresponding equations are provided. The band gap of BiOX$_{1-x}$Y$_x$ solid solutions can be tuned from 1.7 to 4.0 eV by adjusting the halogen composition, which can meet some specific requirements of BiOX-based photocatalysts. The findings in this article provide useful information for designing efficient BiOX-based photocatalysts. Summary, this article achieves the following two purposes: (1) find the underlying mechanism that BiOX$_{1-x}$Y$_x$ solid solutions obey Végard’s law, which partially observed by different experimental researches; (2) provide some available data or formula for future experiments that want to determine or measurement the composition/band gap/optical properties of BiOX$_{1-x}$Y$_x$ solid solutions.

**Table 4.** Chemical and physical parameter of halogen elements and the corresponding differences. “Taken from ref. 45. aThe Mulliken electronegativity of a neutral atom is the arithmetic mean of the atomic electron affinity and the first ionization energy.”

| Halogen | van der Waals radius/Å | Covalent radius/Å | Ionic radius/Å | Electronegativity/eV | Electron affinity/eV | First ionization energy/eV | Mulliken electronegativity/eV |
|---------|------------------------|-------------------|---------------|----------------------|----------------------|---------------------------|-----------------------------|
| F       | 1.47                   | 0.60              | 1.33          | 3.98                 | 3.4011897            | 17.4228                   | 10.41199                    |
| Cl      | 1.75                   | 1.00              | 1.81          | 3.16                 | 3.612725             | 12.96763                  | 8.29018                     |
| Br      | 1.85                   | 1.17              | 1.96          | 2.96                 | 3.3635882            | 11.8138                   | 7.58869                     |
| I       | 1.98                   | 1.36              | 2.20          | 2.66                 | 3.0590368            | 10.45126                  | 6.75515                     |
| Cl–Br   | −0.10                 | −0.17             | −0.15         | 0.20                 | 0.2491368            | 1.15383                   | 0.70148                     |
| Br–I    | −0.13                 | −0.19             | −0.24         | 0.30                 | 0.3045514            | 1.36254                   | 0.83355                     |
| Cl–I    | −0.23                 | −0.36             | −0.39         | 0.50                 | 0.5536882            | 2.51637                   | 1.53503                     |
| F–Cl    | −0.28                 | −0.40             | −0.48         | 0.82                 | −0.2115553           | 4.45517                   | 2.21282                     |
| F–Br    | −0.38                 | −0.57             | −0.63         | 1.02                 | 0.0376015            | 5.609                     | 2.8233                      |
| F–I     | −0.51                 | −0.76             | −0.87         | 1.32                 | 0.3421529            | 6.97154                   | 3.65685                     |
Computational method and details. In the present work, all of the DFT calculations were periodic DFT calculations using the Cambridge Serial Total Energy Package (CASTEP)\(^46\). The interaction between core electrons (i.e., Bi: [Xe], O: [He], F: [He], Cl: [Ne], Br: [Ar], and I: [Kr]) and valence electrons was treated by the ultrasoft pseudopotential (USP) plane-wave method. The energy cutoff for the plane-wave basis wave function was 380 eV for the plane-wave basis set. The exchange–correlation interaction between valence electrons (i.e., Bi: 6s\(^6\)p\(^4\), O: 2s\(^2\)p\(^4\), F: 2s\(^2\)p\(^5\), Cl: 3s\(^2\)3p\(^5\), Br: 4s\(^2\)4p\(^5\), and I: 5s\(^2\)5p\(^5\)) was described by the revised Perdew–Burke–Ernzerhof functional for solids (PBEsol) with the generalized gradient approximation (GGA)\(^47\). To obtain accurate electronic structures, the GGA + U method was used to overcome the well-known shortcomings of the GGA\(^48\). Here, the GGA + U method was only used to obtain more accurate band-gap values. All of the calculations were first performed with the GGA method. The \(U_{\text{eff}}\) values were then determined by comparing the results of the GGA, and finally the GGA + U method was used to calculate the electronic and optical properties. In this way, the electronic structure characteristics obtained by the two methods are guaranteed to be as consistent as possible (except for the band-gap values). In the present work, the value of \(U\) were set as following: 4.8 eV for the p-states of Bi and O, 15 eV for the p-states of F, 7 eV for the p-states of Cl, 3.5 eV for the p-states of Br, 2.1 eV for the p-states of I. The Monkhorst–Pack scheme was used for \(k\)–point grid sampling in the range from \(1 \times 1 \times 2\) (for the \(3 \times 3 \times 1\) supercell) to \(4 \times 4 \times 2\) (for the pristine \(1 \times 1 \times 1\) unit cell) for the irreducible Brillouin zone. The fast Fourier transformation mesh was set in the range from \(120 \times 120 \times 90\) (for the \(3 \times 3 \times 1\) supercell) to \(40 \times 40 \times 90\) (for the pristine \(1 \times 1 \times 1\) unit cell). The minimization algorithm was the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm\(^49\). Its convergence criteria were as follows: the forces on the atoms were less than 0.03 eV/Å, the stresses on the atoms were less than 0.05 GPa, the atomic displacement was less than \(1 \times 10^{-3}\) Å, and the energy change per atom was less than \(1 \times 10^{-5}\) eV.

To construct the solid-solution model, a supercell was used. In other words, the present work used an ordered solid-solution model. Taking BiOF\(_2\)Cl\(_{1/2}\) as an example, one of the F atoms was replaced by a Cl atom in the \(3 \times 3 \times 1\) BiOF supercell. For each BiOX compound, \(3 \times 3 \times 1, 3 \times 2 \times 1, 2 \times 2 \times 1, 3 \times 1 \times 1, 2 \times 1 \times 1, \) and \(1 \times 1 \times 1\) supercells or cells were used to construct BiOX\(_{1-x}\)Y\(_x\) solid solutions with different solubility or content \(Y/(X + Y)\), in which one of X atom is replaced by Y atom. In this article, X in BiOX\(_{1-x}\)Y\(_x\) is the halogen with relatively low atomic number, while Y in BiOX\(_{1-x}\)Y\(_x\) is the halogen with relatively high atomic number. Although disordered models constructed by the special quasirandom structures (SQS) method can produce reasonable alloying solid-solution structures, ordered models allow analysis of the microstructure and the interaction between solute atoms and solvent atoms. From a statistical point of view, the distribution of solute atoms in a solid solution is disordered. However, if the microstructure is identified, a completely disordered solid solution can only exist at high temperatures when the solute concentrations are very low. In general, although there is not a completely ordered structure in the solid solution, the local arrangement of solute atoms can be regular, which is called short-range order. Therefore, the ordered solid-solution model still has considerable significance and value in practice, and this approach was used in this study.

Another important point should be mentioned: the size of supercell and the occupying sites of Y in the supercell also impact the final total energy of models. In primary test stage of this work, we used “coarse setting” (260 eV of energy cutoff, etc. in order to save computing time) to calculate all the possible models: the size of supercell is from \(1 \times 1 \times 1\) to 3\( \times 3 \times 1\), and the possible occupation patterns are determined by the enumeration method for every supercell. After geometry optimization, we compared the total energy per cell, and chose the supercell that has the smallest total energy per cell as the candidate for the next step. For the candidate model, we used “ultra-fine setting” (380 eV of energy cutoff, etc. as mentioned above) to get the accurate result. By this way, the supercell with high symmetry and as small as possible was finally constructed for every content of \(Y/(X + Y)\).

Supporting Information. Comparison of the calculated results with available experimental data, and comparison of the results calculated by the GGA + U method and the results calculated by the GGA method are available free of charge via the website of Scientific Reports.

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Author Contributions

Z.-Y. carried out the DFT calculations and prepared the manuscript. W.-W. contributed the assistance and discussion. Q.-L.L. contributed the assistance of data analysis and manuscript revision. All authors reviewed the manuscript.

Additional Information

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