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***Ab initio* Assessment of $\text{Bi}_{1-x}\text{RE}_x\text{CuOS}$ (RE=La, Gd, Y, Lu) Solid Solution as Semiconductor for Photochemical Water Splitting**

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Abstract

The investigation of BiCuOCh (Ch = S, Se and Te) semiconductors family for thermoelectric or photovoltaic materials is an increasing topic of research. These materials can also be considered for photochemical water splitting if one representative having a bandgap, E_g , around 2 eV can be developed. With this aim, we simulated the solid solution $\text{Bi}_{1-x}\text{RE}_x\text{CuOS}$ (RE = Y, La, Gd and Lu) from pure BiCuOS ($E_g \sim 1.1$ eV) to pure RECuOS compositions ($E_g \sim 2.9$ eV) by DFT calculations based on the HSE06 range-separated hybrid functional with inclusion of spin-orbit coupling. Starting from the thermodynamic stability of the solid solution, a large variety of properties were computed for each system including bandgap, dielectric constants, effective masses and exciton binding energies. We discussed the variation of these properties based on the relative organization of Bi and RE atoms in their common sublattice to offer a physical understanding of the influence of the RE doping of BiCuOS. Some compositions were found to give appropriate properties for water splitting application. Furthermore, we found that at low RE fractions the transport properties of BiCuOS are improved that can find applications beyond water splitting.

I. Introduction

The search for novel, green and efficient energy sources rapidly increased over the past years. In this field, water-splitting technology, that is the photoelectrochemical conversion of water into O₂ and high energetic H₂, is of great interest, as it would permit the direct conversion of solar energy to hydrogen chemical fuel.¹ This technology would offer a way to a sustainable production of H₂. Two approaches are developed to achieve that goal; the first one consists in connecting an electrolyser to the photovoltaic cell and the second one consists in developing a photoelectrochemical cell. In principle, the second technology must achieve higher efficiencies of H₂ production, but up to now the best efficiencies are still obtained by connecting an electrochemical system to a photovoltaic cell.² For that reason, the development of new photoelectrochemical catalysts still remains an important field of research to be deeply explored.

Heterogeneous photocatalysts developed for that purpose have a specific architecture composed of a semiconductor particle functionalised by an electrocatalyst deposited on the surface. The role of the semiconductor is to absorb the sunlight creating charge carriers (electrons and holes) and to make them diffuse to its surface. These charge carriers are then transferred to the electrocatalyst to perform the two half-reactions characterizing the water splitting, namely the proton reduction (reaction (1)) and the water oxidation (reaction (2)). The development of efficient semiconductors for sunlight absorption and charge carrier diffusion on one side and efficient electrocatalysts having low overpotential for the two half-reactions on the other side are the two main fields of research for developing heterogeneous photocatalysts for water splitting.^{3–7} In this manuscript, we mainly focus on the development of new semiconductors.

The first semiconductor investigated for water splitting was TiO₂ in 1972.⁸ Since that year, several families of semiconductors were developed for water splitting beyond simple oxides including sulfides^{9–11}, nitrides^{12,13}, oxynitrides,^{14,15} and several reviews have been published on that topic.^{1,5,6,16} In line with the experimental design of new semiconductors, theoretical efforts have contributed to the advances in this field, and computational tools, mainly based on density functional theory (DFT), are available to compute several key properties of semiconductors.^{17–21} As some of these properties are sometimes difficult to obtain experimentally, such as effective masses or exciton binding energies, the use of DFT as a tool complementary to experiment is crucial to characterize new semiconductors. The good accuracy of DFT to compute semiconductor's properties has been assessed in several published works, paving the way to a theoretical design of semiconductors for specific applications including photocatalytic water splitting.^{20,22–27}

For water splitting, requirements on several properties have been addressed. These requirements are clearly defined and discussed in the next section "Methodology" but the one on bandgap is clearly more important and is going to be discussed now. The difference of the redox potentials corresponding

to the two half reactions of water splitting is 1.23 V. This means that the potential difference of photogenerated holes and electrons must have at least this value leading to a semiconductor having a bandgap, E_g , greater than 1.23 eV. Because of the need of excess energy for transferring the photogenerated charges toward the electrocatalyst and the kinetic consideration of the redox reaction on top of the electrocatalyst surface, the optimum bandgap for the semiconductor is considered to be in the 1.8-2.2 eV range.¹ Therefore, any new semiconductor developed for water splitting should ideally possess its bandgap in this energy window.

In this work, we decided to investigate the properties of layered oxychalcogenides $MCuOCh$ (M = trivalent Bi, Y, Sc or lanthanide ion; Ch = S, Se, Te) for water splitting. They have been studied for various applications, mostly consisting in transparent p-type semiconductors^{28,29}, thermoelectric materials³⁰⁻³² and also for photovoltaic application³³. Their crystal structure belongs to the tetragonal system with the $P4/nmm$ space group, made of a stacking of MO oxide and $CuCh$ chalcogenide layers, as shown in Figure 1. The classical way of preparing these materials is by solid-state reactions involving high temperatures³⁴. But in the case of sulfides, like $BiCuOS$, a hydrothermal route of synthesis has been proposed in the literature leading to nanometer-sized particles generally more adapted for (photo)catalysis³⁵. For this reason, this work will be mainly focused on oxysulfides. $BiCuOS$ has a bandgap around 1.1 eV^{28,36} and $RECuOS$ ($RE=La, Ce, Pr, Nd$) compounds have bandgaps around 3 eV³⁶. These materials have respectively too low and too high bandgaps for water splitting application. The question of this article is the following: is it possible to design *in silico* a solid solution having the formula $Bi_{1-x}RE_xCuOS$ ($RE=rare\ earth\ element$) and satisfying all the requirements for water splitting including a bandgap between 1.8 eV and 2.2 eV? Since the solid solution will be a mixture of Bi and RE in the sublattice of Bi, the oxidation state of RE will be +3, like Bi. In other words, it corresponds to an isovalent substitution solid solution. Contrary to works dedicated to the aliovalent doping of $MCuOCh$ compounds for tuning the extrinsic charge carrier concentration,^{30,37,38} the objective of the isovalent doping is to modify the intrinsic properties of the semiconductor. Not all the RE elements were investigated. The selected ones have no f-electrons contributing to the frontier states, since localized electrons (like f-electrons) can create new states acting as recombination centers. At the +3 oxidation state, La and Lu have empty and fully occupied f-orbitals, respectively, thus these orbitals do not contribute to frontier states. Y was also selected, although it is not a lanthanide, but it belongs to the family of RE elements and has no f-orbitals. Finally, Gd was also chosen since the first f-f transition of the $Gd(+3)$ ion is higher than 3.8 eV,³⁹ so notably higher than the targeted bandgap. We assume that this f-f transition will not interfere with the valence to conduction bands excitations. By convention, the rare earth elements will be considered as dopants of the $BiCuOS$ structure, even when their concentration is higher than the Bi one.

The manuscript is organized as follows. In the next section the methodology of this work is presented, including the relevant properties of a semiconductor, how they are computed and what are the required values for water splitting application. Then the computational section presents the technical

parameters used for the calculations. The next section is dedicated to the presentation of the computed properties in the order: thermodynamic stability of the solid solution, bandgaps and density of states, effective masses, dielectric constants and exciton binding energies. The conclusions section will summarize the main results of the work.

Figure 1: Crystal structure of MCuOCh oxychalcogenides. $(2 \times 2 \times 1)$ supercell is shown for convenience. M, Cu, O and Ch atoms are represented in green, purple, red and yellow respectively.

II. Methodology

All solid solutions were made by substituting Bi atoms into the BiCuOS structure with the corresponding RE atoms. In order to reach various Bi/RE ratios, a $2 \times 2 \times 1$ supercell containing 8 Bi positions was constructed, giving the opportunity to compute $\text{Bi}_{1-x}\text{RE}_x\text{CuOS}$ with $x=0.125, 0.25, 0.375, 0.5, 0.625, 0.75$ and 0.875 . In the case of $x=0.125$, there is only one possible conformation of substitution possible since all the 8 Bi positions are equivalent. But for $x=0.25, 0.375$ and 0.5 , several configurations are possible to locate the RE, giving place to several non-equivalent choices for relative positions of RE ions (see Figure 2 and Figure S1), leading to respectively 2, 3 and 6 possibilities. Therefore all non-equivalent structures were investigated. Finally, for the last three compositions above $x=0.5$, the structures were obtained by inverting Bi and RE positions from the corresponding “ $1-x$ ” structures.

Figure 2: Example of non-equivalent structures for $x=0.375$. Bi, RE, Cu, O and S atoms are represented in green, pink, purple, red and yellow respectively.

From each composition the most stable conformation of the RE ordering was determined after geometry relaxation. From a stability point of view, it is known that BiCuOS and RECuOS pure compounds can be synthesized, and thus they are likely to be thermodynamically stable. In order to ensure whether the solid solution $\text{Bi}_{1-x}\text{RE}_x\text{CuOS}$ is experimentally stable, the doping reaction (3) was considered, and its energy, presented in equation (4), was computed from the SCF electronic energies. A negative value means that the solid solution is thermodynamically more stable than the pure compounds while a positive value indicates that the system would prefer to give separated pure compounds rather than a solid solution. The Gibbs free energy associated to this reaction was computed (equation 5) by taking into account the mixing entropy between two solutions (equation 6) where the factor 8 stands for the 8 sites of the Bi sublattice in the supercell. For the calculation of ΔG , a temperature of 473 K was taken into account based on the standard temperature of the hydrothermal synthesis of BiCuOS.

$$\Delta E = E(\text{Bi}_{(1-x)}\text{RE}_x\text{CuOS}) - (1-x)E(\text{BiCuOS}) - xE(\text{RECuOS}) \quad (4)$$

$$\Delta G = \Delta E - T\Delta S_{\text{mix}} \quad (5)$$

$$\Delta S_{\text{mix}} = -8k_B[x\ln(x) + (1-x)\ln(1-x)] \quad (6)$$

Some selected properties were computed on the most stable solid solution for each composition. The list of the relevant properties of a semiconductor for photocatalysis has been established by some of us²³. It includes the bandgap (noted E_g), the effective masses (noted m^*), the dielectric constants including both the electronic (noted ϵ_∞) and the vibrational (noted ϵ_{vib}) contributions and finally the exciton binding energies (noted E_b).

In this work, E_g is approximated by the energy difference between the top of the valence band and the bottom of the conduction band. Using the range separated hybrid functional HSE06, it has been

proven that E_g can be reliably computed with this monoelectronic approximation.^{23,40} As presented in the Introduction, E_g must be in the 1.8-2.2 eV range for water splitting application. Assuming that the standard deviation of HSE06 functional for E_g is 10%, any computed bandgap in the range 1.6-2.4 eV should be considered as suitable for water splitting.

The dielectric constant, ϵ_r , is involved in the binding energy of the exciton generated by light absorption. Exciton dissociation is necessary to obtain free charge carriers in the semiconductor. Two components contribute to ϵ_r : the electronic contribution ϵ_∞ that is directly related to the electron density polarizability of the material and the vibrational contribution ϵ_{vib} , that depends on the polarization induced by the softest vibrational modes. Empirically, we can expect that all semiconductors having ϵ_r higher than 10 leads to low exciton binding energies.

The exciton binding energy can be calculated within the Mott-Wannier model.⁴¹ This model treats the exciton as a hydrogen-like atom in a dielectric medium. It has been assessed for systems in which the exciton has a Bohr radius higher than several unit cells. This criterion is fulfilled for MCuOS compounds and this model will be used to compute the exciton binding energy of these materials.³³ From a quantitative point of view, excitons having a binding energy lower than the room thermal energy (~25 meV) are considered to be efficiently dissociated.

The mobility of charge carriers (noted $\mu_{e/h}$) are discussed based on the effective masses since they are linked by the equation (7). The effective masses are calculated by fitting the conduction band (for m_e^*) and the valence band (for m_h^*) computed in the <110> direction, corresponding to the intralayer direction of the BiCuOS structure, and the <001> direction corresponding to the interlayer direction. Effective masses lower than the rest mass of electron will be considered to yield good charge carrier mobilities.

$$\mu = \frac{e\tau}{m^*} \quad (7)$$

III. Computational Details

Total energy calculations were carried out within the context of periodic density functional theory (DFT) using the projected-augmented plane-wave (PAW) approach, as implemented in the Vienna Ab-initio Simulation Package (VASP, version 5.3.5)⁴²⁻⁴⁵. The core electrons were described in PAW pseudopotential. Electronic configurations of the adopted valence electrons for the various involved elements were 6s²6p³ for Bi, 3d¹⁰4s¹ for Cu, 3s²3p⁴ for S, 2s²2p⁴ for O, 5p⁶6s²5d¹ for La, 5p⁶6s²5d¹ for Gd, 5p⁶6s²5d¹ for Lu and 4s²4p⁶5s²4d¹ for Y. Geometry optimizations were performed using the generalized gradient approximation (GGA) within the Perdew–Burke–Ernzerhof (PBE) formalism⁴⁶. The corresponding first Brillouin zone was sampled by 8 x 8 x 8 Γ -centered k -points mesh. Cut-off energy of the plane wave was set to 600 eV and energy convergence criterion for the self-consistent-field (SCF) cycles was set to 10⁻⁷ eV per cell. The atomic positions and cell parameters were fully relaxed until the residual forces were below 0.01 eV Å⁻¹.

To improve the accuracy of the predicted electronic properties, we employed the range-separated hybrid HSE06 exchange-correlation functional^{47–49}, as implemented in VASP (version 5.3.5) with the aim to overcome the GGA functional underestimation of band gaps⁵⁰. The calculations have been performed as single points based on the optimized geometries obtained at the PBE level. For the HSE06 calculations, the electronic wave functions were expanded in the plane waves up to a cutoff energy of 400 eV on a 4 x 4 x 4 *k*-points mesh. Since we are dealing with heavy elements, calculations including spin–orbit coupling (SOC) were also conducted using the no-collinear approximation implemented in VASP⁵¹. Electronic occupancies were determined by Gaussian smearing method using a smearing of 0.01 eV. The electronic dielectric tensor (ϵ_{∞}) of each material was calculated at the HSE06 level of functional using the self-consistent-response to an external finite electric field (SCR- FEF)^{52,53}, which takes into account the local field effects. The vibrational dielectric constant tensor (ϵ_{vib}) was calculated at the PBE level of functional using the linear response method within the density functional perturbation theory (DFPT). Vibrational contributions to the dielectric constant were not computed using HSE06 due to its high computational cost and resources. The total macroscopic static dielectric tensor (ϵ_r) was then obtained in the three principle directions by summing the two electronic and vibrational contributions. This computational protocol, mainly based on HSE06 for electronic properties, has been tested on several Bi-based semiconductors highlighting its reliability.^{25,33} For larger systems, the HSE06 functional could be replaced by a GGA functional along with a Hubbard modification (called +U) to correct partially the self-interaction error leading to relatively accurate properties, both electronic and thermodynamic, at a lower computational cost but with the drawback of the U determination.^{54–57}

IV. Results

IV.1. Thermodynamic stability of the solid solution.

Figure 3: HSE06 computed energy (a) and Gibbs free energy (b) associated to the reaction (3) as a function of the doping concentration for the most stable configuration of dopant.

In term of crystal structure, the only compositions determined experimentally are the BiCuOS and LaCuOS ones.²⁸ The PBE computed cell parameters (given in Supporting Information) are in average 0.7% higher than experimental ones corresponding to the known PBE behaviour.²³ This result supports the choice of using PBE for geometry relaxations. All the structures of the most stable conformation for each dopant at each doping fraction are given in Supporting Information.

The thermodynamic stability of all the compounds as a function of the doping composition was analysed based on the calculated single point HSE06 electronic energy (Equation 4) and Gibbs free energy (Equations 5), as described in the methodology section, and corresponding to reaction (3). As explained in the methodology section, for each doping concentration several Bi-RE organizations were tested. Figure 3 presents the energy of mixing obtained for the most stable conformation of each dopant for a given doping concentration.

Clearly, La doping gives always the most stable solid solution. Although La doped BiCuOS was never investigated experimentally, the La doping of the parent compound BiCuOSe was the subject of two publications.^{58,59} The authors of these works incorporated La atoms in BiCuOSe up to 12.5% that

supports the stable doping of BiCuOS by La. Gd and Y doping are also thermodynamically stable, but the mixing entropy improves notably the stability of the solid solution. For Lu doping, the obtained behaviour is completely different from the previous ones. From a purely electronic energy point of view, the mixing is thermodynamically unstable for all concentrations. However, by taking into account the mixing entropy, the Gibbs free energy becomes slightly negative. This means that the solid solution $\text{Bi}_{1-x}\text{Lu}_x\text{CuOS}$ would be very difficult to obtain experimentally and possible only by working at high temperature to favour the entropic contribution.

As previously mentioned, several conformations were investigated for each doping concentration. It is interesting to note that the most stable conformation for La doping always corresponds to a perfect mixture of Bi and La ions in their sublattice. On the contrary, for Lu doping the most stable conformation reveals a clear separation of Lu and Bi ions on two separated layers of the sublattice. For Gd and Y doping, the behaviour is intermediate. A simple understanding of the affinity of Bi with La and the repulsion of Bi with Lu can be obtained by drawing the energy of mixing computed at 50% doping plotted as a function of the ionic radius of the dopant (Figure 4). The stability of the La-Bi mixing is rationalized by the similar ionic radius of the two ions, while the difficult Lu-Bi mixing is due to a large difference in the ionic radius. Again, the Gd and Y dopings are intermediate.

Figure 4: Energy of mixing for the 50% doping as a function of the ionic radius of rare earth element (+3 oxidation state) relative to the ionic radius of Bi (+3 oxidation state)⁶⁰

IV.2. Bandgaps and density of states.

The bandgap computed for the most stable conformation of each doping concentration and each dopant is presented in Figure 5. Experimentally, only the bandgaps of pure BiCuOS and LaCuOS are known, and they are equal to 1.07 eV and 3.14 eV, respectively^{28,36}. From Figure 5a, it can be seen that the computed bandgaps for these two compounds are 1.15 eV and 2.95 eV respectively, confirming the accuracy of the computational protocols.

For all RE dopants the bandgap increases monotonically from the one of pure BiCuOS (1.15 eV) to the one of pure RECuOS (around 2.7-2.9 eV). La doping offers smoother variation of the bandgap while the bandgap variation of Gd, Y and Lu dopants shows more a step function variation. This result

can be understood in line with the previous thermodynamic analysis. On one hand, La doping results in well mixed Bi and La ions in their sublattice whatever the La concentration. This leads to a smooth bandgap variation, see Figure 5a. On the other hand, for Gd, Y and Lu dopants the most stable structures correspond to Bi and RE elements located on separated layers in the $2 \times 2 \times 1$ supercell, and this could explain the bandgap variation showing step increments for Gd, Y and Lu, see Figure 5b-d. When $x < 0.5$, there are still enough Bi atoms to give a pure Bi layer. This is enough to give a pure BiCuOS bandgap around 1.15 eV. In contrast, for $x > 0.5$ the Bi atoms are more diluted in their layer by RE elements, leading to a bandgap quickly converged to the one of RECuOS, which is around 2.9 eV. For water splitting applications, only few compositions for each dopant lead to a bandgap standing in the window 1.6-2.4 eV, depicted by black horizontal lines in Figure 5.

The nature of the bandgap is indirect for BiCuOS while it is direct for RECuOS (at the Γ point). For the solid solution, $\text{Bi}_{1-x}\text{RE}_x\text{CuOS}$, in general, the bandgap remains indirect like in BiCuOS except for some compositions, marked by an asterisk in the Figure 5.

Figure 5: Computed bandgaps of the solid solution $\text{Bi}_{1-x}\text{RE}_x\text{CuOS}$ as a function of x at the HSE06+Spin Orbit level. The horizontal black lines indicate the target window of 1.6–2.4 eV for water splitting application. All bandgaps are indirect, except for the ones marked by an asterisk.

The density of states of all doping compositions of $\text{Bi}_{1-x}\text{La}_x\text{CuOS}$ and $\text{Bi}_{1-x}\text{Lu}_x\text{CuOS}$ were computed and plotted in Figure 6 to visualize the evolution of the electronic structure. The valence bands (VB) for all these compounds are constantly a combination of Cu 3d and S 3p orbitals. For pure BiCuOS the conduction band (CB) is made by almost pure Bi 6p orbitals. However, in the case of $\text{Bi}_{1-x}\text{RE}_x\text{CuOS}$ the conduction bands mainly consist of pure Bi 6p orbitals for $x < 0.5$, while a combination of RE 5d orbitals and Bi 6p orbitals becomes the predominant contribution for $x > 0.5$. By plotting the evolution of the Bi CB width (in eV) constituting the conduction bands of $\text{Bi}_{1-x}\text{La}_x\text{CuOS}$ and $\text{Bi}_{1-x}\text{Lu}_x\text{CuOS}$ as a function of doping content (Figure 7), it appears that the Bi bandwidth becomes narrower and narrower when the doping fraction x is increased. This observation is explained by the tight binding theory in solid state, where the bandwidth is directly proportional to the number of first neighbours (noted z_{Bi}) and the resonance integral (noted β_{Bi}), see Equation (8). The RE elements take the positions of other Bi atoms as first neighbour so reducing the width of the conduction band and increasing the bandgap.

$$W_{\text{Bi}} \propto z_{\text{Bi}} \cdot \beta_{\text{Bi}} \quad (8)$$

Since the La doping leads to a better mixing than Lu doping, Bi atoms are more diluted in the case of La solid solution as compared to the Lu one. This explains why, for a given doping fraction, the width of the Bi conduction band with La doping is thinner than that for the Lu doping.

Figure 6: Computed DOS for La and Lu doping. Black, red, yellow, purple, green and pink lines correspond to total DOS and projected DOS on O, S, Cu, Bi and RE respectively. The areas below the DOS projected on Bi and RE were filled in green and pink respectively to help the visualization.

Figure 7: Bandwidth, in eV, of the conduction band (mainly localized on Bi atoms) for the La (red) and Lu (green) doping.

IV.3. Effective masses

The calculation of effective masses is not a straightforward task and is a computational and time demanding procedure. For that reason, this property was computed only for compositions ranging from $x=0\%$ to $x=62.5\%$ of La and Lu dopants, because they are the most relevant concentration for water splitting application and because La and Lu have the most opposite behaviour with respect to the Bi substitution. For Gd and Y doping, only effective masses of compositions leading to bandgaps between 1.6 and 2.4 eV were computed (see Figure 5).

As described in the methodology section, the effective masses were computed for intralayer direction, $\langle 110 \rangle$, and interlayer direction, $\langle 001 \rangle$, of the structure. The results for the electron effective masses are presented in Figure 8 while the hole effective masses are given in Supporting Information (Table S11).

For pure BiCuOS there is a strong anisotropy of m_e^* , as already mentioned in a previous work³³. This is ascribed to the anisotropy of the structure that favours the intralayer charge transport compared to interlayer transport. Interestingly, while all RECuOS compounds have also this anisotropy of m_e^* , it is much less marked as compared to BiCuOS. Two reasons explain this behaviour that are the different nature of the orbitals involved in the conduction band of BiCuOS (Bi 6p orbitals) and RECuOS (La 5d orbitals) and the different nature of k-vector where the conduction band is minimum, Z point for BiCuOS and Γ point for RECuOS.

As expected, the effective masses are affected by doping. The variation is more difficult to interpret than for the bandgap. Several factors affect the effective masses evolution upon doping explaining this difficulty of interpretation. The three main parameters involved in this variation are the average number of Bi neighbours around one Bi atom, the Bi-Bi distance and the different nature of k-vector for the minimum of conduction band depending on the composition. But some general trends can be drawn. Surprisingly, for low RE doping ($x=12.5\%$), m_e^* reduces. This is ascribed to the reduction of

the shortest Bi-Bi distance from 3.770 Å in pure BiCuOS to 3.740 Å in $\text{Bi}_{0.875}\text{La}_{0.125}\text{CuOS}$ and 3.751 Å in $\text{Bi}_{0.875}\text{Lu}_{0.125}\text{CuOS}$ that increases the Bi-Bi interaction leading to lower effective masses. Experimentally, this surprising behaviour has been observed for La doped BiCuOS by Liu *et al.* who measured an increase of the conductivity for doping concentration going from 0% to 12.5%.^{58,59} For La doping, the general behaviour is an increase of the effective masses compared to BiCuOS for $x > 12.5\%$ for the intralayer direction while the interlayer direction is less affected. An important variation of the effective masses is found for the 50% and 62.5% concentrations because of the change of k-point nature for the bottom of conduction band as indicated in Figure 8. For the Lu doping, for $x < 50\%$, the effective masses are lower than for pure BiCuOS. The reason of this behaviour is the segregation of Lu dopants in one layer, keeping one full layer of Bi atoms as in pure BiCuOS but with a reduced Bi-Bi distance due to the cell parameters decrease. Above 50% of doping, there are no longer pure Bi layers and the effective masses starts to increase significantly.

Figure 8: Computed electron effective masses in the intralayer (<110>) and interlayer (<001>) directions for La (a) and Lu (b) doping. Letters above each concentration correspond to the k-vector notation of the minimum of the conduction band used to extract the effective masses.

IV.3. Dielectric constants.

Both the electronic contribution (ϵ_∞) and total dielectric constants (ϵ_r) were computed for the most stable conformation of each composition. The results are presented in Figure 9.

For the pure compounds, both ϵ_∞ and ϵ_r are notably higher for BiCuOS than for pure RECuOS. The reasons are the larger polarizability of Bi as compared to RE (influencing ϵ_∞) and vibrational modes that are softer for Bi-based compounds than for RE-based compounds because Bi is heavier than rare earth elements. For the solid solution, ϵ_∞ decreases almost linearly with the increase of the doping fraction, whatever the chemical nature of the dopant. On the contrary, the vibrational contribution that, is the major contribution to ϵ_r , is more sensitive to the doping concentration as well as to the nature of the dopant. For $x > 0.5$, ϵ_r becomes very close to those of pure RECuOS.

Finally, whatever the doping fraction, the final ϵ_r is always higher than 10 characterizing an efficient screening of the electron-hole pair by the semiconductor whatever the solid solution considered. But clearly, the higher the Bi molar fraction, the better will be the screening and the exciton dissociation leading to the conclusion that, for this property, the Bi molar fraction should be kept as high as possible.

Figure 9: Variation of the electronic (a) and total (b) dielectric constant as a function of the doping fraction.

IV.4. Exciton binding energies.

In the Mott-Wannier model of the exciton, the binding energy is obtained from equations (9) and (10) involving the computed dielectric constant and effective masses presented in the previous section. The variation of the binding energy was obtained only for the compositions on which the effective masses were evaluated. The values are presented in Figure 10.

$$E_b = 13.6 \frac{\mu}{\epsilon_r^2} \quad (9)$$

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*} \quad (10)$$

The exciton binding energy of pure BiCuOS is very low, mainly because of the high dielectric constant of this compound. Pure RECuOS have also relatively low exciton binding energy because of the low reduced mass of the exciton that compensates the decrease of the dielectric constant compared to BiCuOS. For $\text{Bi}_{1-x}\text{La}_x\text{CuOS}$ the exciton binding energy increases upon doping for two reasons. First, the dielectric constant is decreasing, second the exciton reduced mass is increasing because of the increase of electron and hole effective masses. E_b even assumes values higher than 26 meV for Y doping. Keeping in mind that room thermal energy is around 25 meV, it can be expected that exciton dissociation for systems having a dopant fraction around 50% could decrease the efficiency of the final device.

Figure 10: Variation of exciton binding energy in function of the doping fraction

V. Conclusion

We computed several electronic properties of the solid solution $\text{Bi}_{1-x}\text{RE}_x\text{CuOS}$ (RE=La, Gd, Y and Lu) by periodic DFT calculations using the well tested range-separated hybrid functional HSE06. The electronic properties selected are the most relevant ones for photocatalytic application and, more specifically, for light induced water splitting. The objective was to tune the bandgap of $\text{Bi}_{1-x}\text{RE}_x\text{CuOS}$ between the one of pure BiCuOS (~1.1 eV) to the one of pure RECuOS (~2.9 eV) and to analyse the evolution of the other properties induced by this tuning.

Our calculations show that, from a thermodynamic point of view, the most favoured doping is La while Lu doping seems very difficult and achievable only at high temperature. Because of the good La and Bi mixing in their sublattice, the bandgap of their solid solutions varies smoothly from the two extreme compounds. On the contrary, the bandgap for the other solid solutions varies abruptly between the two pure compounds mainly because the dopant tends to segregate, leaving a part of the Bi sublattice unaffected (for $x < 50\%$). The dielectric constants, both the electronic one (ϵ_∞) and static one (ϵ_r), vary smoothly upon doping, whatever the dopant nature. Because a high dielectric constant is always beneficial, the Bi content must be kept as high as possible for this property.

The conductivity of charge carriers is also affected by doping both for electrons and holes. Very surprisingly, for low dopant concentration we predict a reduction in m_e^* . The interpretation of this behaviour is the combination of a reduction of the Bi-Bi bond length and a Bi layer almost complete that favours electron delocalization, which results in a decrease of the m_e^* . This observation leads to an unexpected conclusion. BiCuOS and related compounds (BiCuOSe, BiCuOTe...) are investigated for thermoelectricity because of their low bandgap. It appears that by a small RE doping, the low bandgap of these compounds is preserved but the mobilities of charge carriers are improved, as observed experimentally for La doped BiCuOSe.^{58,59}

To achieve materials having a bandgap in the range 1.6-2.4 eV, therefore interesting for water splitting, the dopant concentration must be around 50%. At this concentration, the effective masses and exciton binding energies are notably increased meaning that, to obtain efficient water splitting photocatalysts with these materials a bulk heterojunction architecture must be used. This type of architecture has been developed for organic photovoltaics to overpass the low charge carrier mobilities and high exciton binding energies of the materials used. For water splitting, this type of architecture starts also to be used for materials having also this high exciton binding energy like carbonitrides.⁶¹ This result indicates that quantum chemical calculations not only give semiconductors intrinsic properties but can also support experiments in the design of photocatalyst architecture.

Supporting Information

The supporting information provides all the numerical values of the properties presented in the figures of the manuscript and all the optimized structures.

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Table of Content

The electronic properties of Bi_{1-x}RE_xCuOS (RE=La, Gd, Y and Lu) were computed by hybrid DFT to design new semiconductors for water splitting.