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Effect of Doping on the Bandgap of the Organic–Inorganic Hybrid Ferroelectric Material $[C_6N_2H_{18}]Bi_{1-x}Sb_xI_5$ (0.0 < x < 1.0)

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Citation: Guo, X.; Zhu, J.; Zou, X.; Huang, W.; Zhang, C.; Zhou, Z.; Wang, J.; Wang, H.; Zhang, H. Effect of Doping on the Bandgap of the Organic–Inorganic Hybrid Ferroelectric Material $[C_6N_2H_{18}]Bi_{1-x}Sb_xI_5$ (0.0 < x < 1.0). *Appl. Sci.* **2022**, *12*, 10454. https://doi.org/10.3390/app122010454

Academic Editor: Fabrice Goubard

Received: 9 September 2022
Accepted: 13 October 2022
Published: 17 October 2022

1. Preparation of organic-inorganic hybrid $[C_6N_2H_{18}]BiI_5$ and $[C_6N_2H_{18}]SbI_5$ Ferroelectric powder and ferroelectric film

1.1. Preparation of organic-inorganic Hybrid Ferroelectric powder $[C_6N_2H_{18}]BiI_5$:

BiI_3 (10.0 mmol, 5.90 g) powder was added to excess HI (45%, 100 ml) solution, heated, and stirred for more than 4 h, and the external heating temperature was maintained at about 90 ℃ until the powder was completely dissolved. Then $H_2N(CH_2)_6NH_2$ (1, 6-hexamethylenediamine; 10.0mmol, 1.16g) was added to the completely dissolved solution and heated and stirred for 24 h. A thermometer was inserted internally to keep the temperature at about 90 ℃. At this time, the external heating temperature was about 135 ℃. After the solution was completely reacted, it was heated and dried on a hot plate at 90 ℃ until the brick red crystal was precipitated. At this time, the ferroelectric material $[NH_3(CH_2)_6NH_3]BiI_5$ (HDA-BiI_5) needed in this experiment was obtained. Grind the crystals into powder and place them in a glass jar.

1.2. Preparation of organic-inorganic Hybrid Ferroelectric powder $[C_6N_2H_{18}]SbI_5$:

Firstly, an appropriate amount of HI solution was dropped into Sb_2O_3 (0.146g, 0.5mmol), and a clear SbI_3 solution was obtained by magnetic agitation. Then, 2-methyl-1,5-pentane diamine (0.117g, 1mmol) was added to the SbI_3 solution, heated, and stirred until completely dissolved. The fully reacted solution is heated and dried on a hot plate at 90 ℃ for about a week until red crystals are precipitated. The required ferroelectric material $[C_6N_2H_{18}]SbI_5$ is obtained at this time. Grind the crystals into powder and place them in a glass jar.

1.3. Preparation of organic-inorganic hybrid ferroelectric thin films:

The ground ferroelectric powder was dissolved in DMF solution at a ratio of 500 mg/0.4 mL, heated, and stirred for 4 h or ultrasonic equipment for 3 h, until the powder was completely dissolved and the solution turned dark brown. The completely dissolved solution was filtered through a 0.22 μm diameter filter to obtain the solution for spin coating. Place the cleaned and ozone-treated ITO based in the center of the homogenizer, turn on the vacuum pump, and make the base stick to it tightly. The sample was rotated at a rate of 6000 R.P.M. for 40 s. The sample was annealed for 30 min on a hot plate at 150 ℃ to complete the preparation of ferroelectric films.

2. Band gap calculation method

The UV-visible absorption spectrum data in Figure 4, through Kubelka - Munk formula calculation, can be obtained as shown in Figure 5 $(ahv)^{1/2}$~hv diagram. Where the abscissa represents energy, and its calculation formula is as follows:

$$E = hv = 1240 / \lambda \tag{3.1}$$

h is Planck's constant and v is the frequency of light. λ represents the wavelength and corresponds to the abscissa in Figure 5. A in the ordinate is the absorption coefficient of the material, and its calculation formula is as follows:

$$a = \ln(T/100)/d \tag{3.2}$$

Where, T is the transmittance of the material, whose value changes with the energy. d is the thickness of the material, which is uniformly set at 500 nm. After the above calculation, the relation diagram as shown in Figure 5 can be obtained. The optical band gap of the mixed ferroelectric film of each component can be obtained by making the tangent line as shown in the linear part of the curve.

3. Theoretical calculation method of the energy band of hybrid ferroelectric materials

Ab initio density generalized function theory simulations were performed in the CASTEP (Cambridge Serial Total Energy Package) code of Materials Studio-2019 with the help of the plane wave pseudopotential method. Super-soft pseudopotentials of the Vanderbilt type were used to describe electron-ion interactions. The GGA (Generalized Gradient Approximation) was used in the advanced form of the PBE (Perdew-Burke-Ernzerhof) to evaluate the exchange-correlation energy. The pseudo-atomic calculations take into account only the valence electrons. The influence of metal doping on the cubic $[C_6N_2H_{18}]BiI_5$ ferroelectric material was studied by constructing a 1*1*5 supercell containing 640 atoms. As a consequence, the metal-doped $[C_6N_2H_{18}]BiI_5$ material possessed the new chemical formula $[C_6N_2H_{18}]Bi_{1-x}Sb_xI_5$ ($0.0<x<1.0$). In the geometry optimization and electronic characterization study, SQS calculations were first performed with the VASP package to obtain randomly doped supercells. The energy band calculations were performed with PWmat, with truncation energy of 884 eV and k-point set to 1*1*1. The energy bandwidths of the ferroelectric material with different doping concentrations can be calculated and plotted in the energy band diagram in Figure 6.

In this case, a convergence test was performed on the truncation energy, which was calculated for X*13.6eV. As shown in Figure S5, the total energy of the supercell is calculated by first giving the system a lower X value of 25 and gradually increasing the X value. If the total energy of the supercell converges to a stable value, the system converges, and the corresponding X value is the truncation energy of X. From Figure S5, we can see that the supercell converges at 85, but because the computational capacity of the server is limited to calculate such a large-scale system, we set the X value at 65, which is similar to the total energy at 85. At this point, the truncation energy is derived to be 884 eV.

4. Supporting Figures

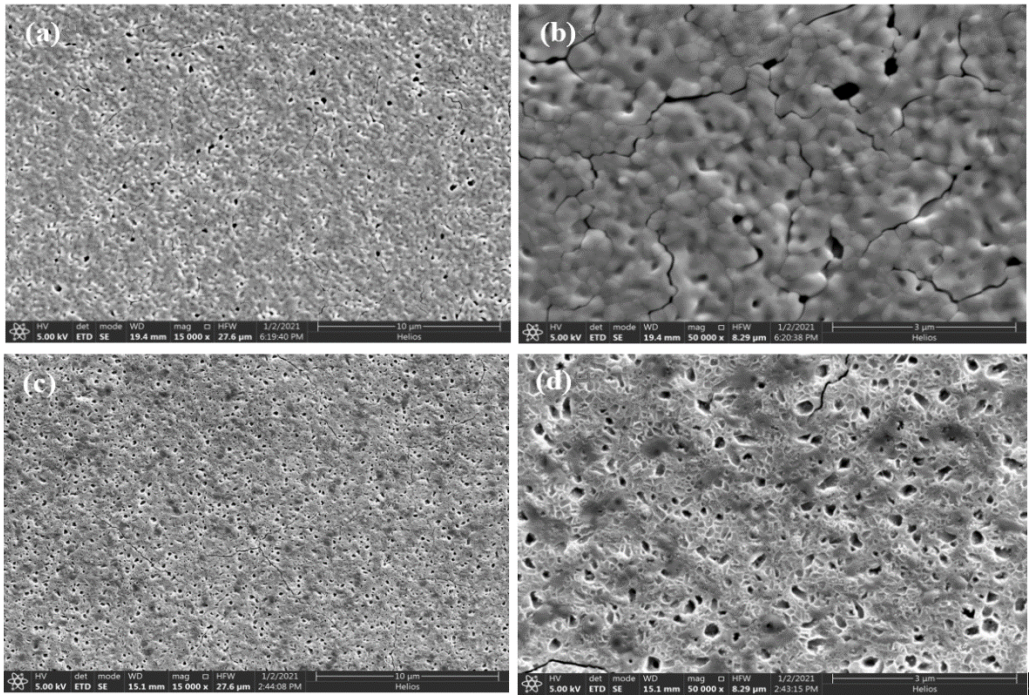

Figure S1. Top view of a single organic-inorganic hybrid ferroelectric film by SCANNING electron microscopy. (a) and (c) are HDA-BiI_5 and $[C_6N_2H_{18}]SbI_5$ ferroelectric films, respectively. (b) and (d) are enlarged images of (a) and (c), respectively.

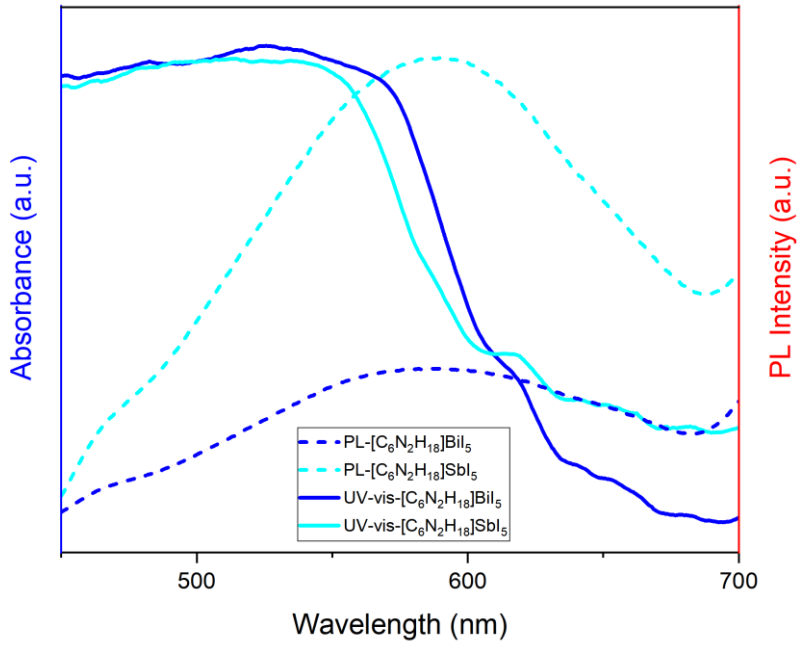

Figure S2. UV-vis absorption spectra and photoluminescence spectra of organic-inorganic hybrid ferroelectric thin films.

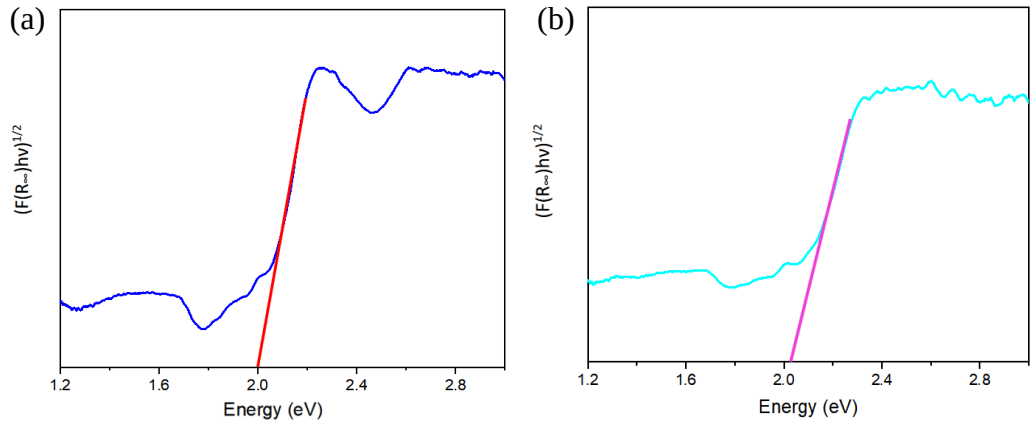

Figure S3. $(ahυ)^{1/2}$~hυ relation of organic-inorganic hybrid ferroelectric thin films. (a) HDA-BiI_5; (b) $[C_6N_2H_{18}]SbI_5$.

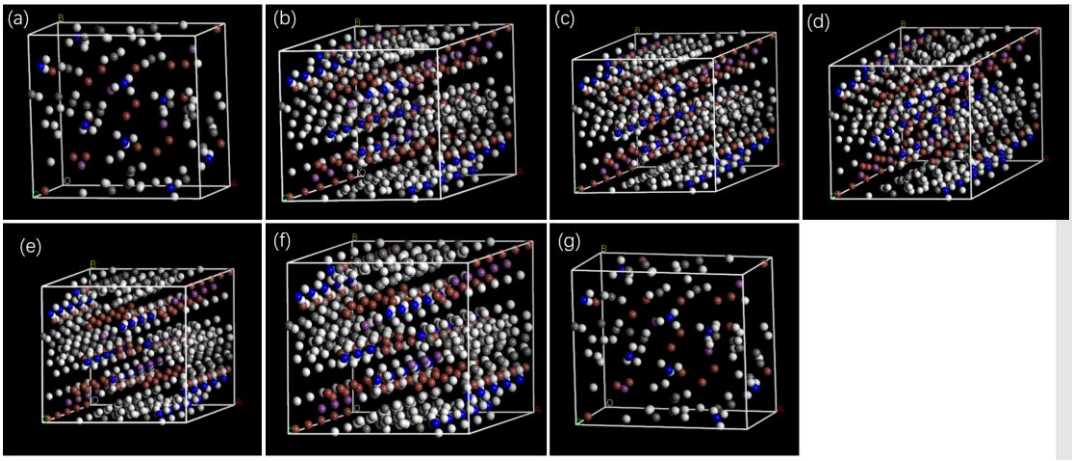

Figure S4. Optimized supercell diagram. (a)HAD-SbI_5. (b)0.2Bi+0.8Sb. (c)0.4Bi+0.6Sb. (d)0.5Bi+0.5Sb. (e)0.6Bi+0.4Sb. (f)0.8Bi+0.2Sb. (g)HAD-BiI_5.

25	-341239.49618651
35	-342504.30174652
45	-342652.73231736
55	-342694.75859558
65	-342707.06979927
75	-342709.77640782
85	-342710.02844336
95	-342710.17265612
105	-342710.34599070
115	-342710.49113888

Figure S5. Results of truncation energy convergence calculation.