The Effect Of Cation Vacancy On The Properties Of $CsSnI_3$ Perovskite Based On The First Principle

Deng-hui Ji[a1] ,Cong-min Zhang[b1], Xing-ze Ge[c2], Xiu-ling Li[d3],Zhi-wei Zeng[e1] and Ming-zhe Hu[f1, *]

[1]Liupanshui Normal University, The Key Laboratory of Opto-electronic Information Technology of Liupanshui City,Engineering Research Center For Renewable resource recycling of Liupanshui City, Liupanshui City, 553004, People's Republic of China

[2]Ceramic Science Institute,China Building Materials of Academy,Beijing, 100024, People's Republic of China.

[3]Hebei Advanced Thin Films Laboratory, Department of Physics, Hebei Normal University, Shijiazhuang City, 050024, People's Republic of China

[f]mingzhe-hu@163.com

*Corresponding author

Keywords: Cation Vacancy, $CsSnI_3$Perovskite, The First Principle, Band Gap, Optical Properties.

Abstract. We used the CASTEP program to build seven configurations of cubic $CsSnI_3$ with cation vacancy at the A or B sites. The physical properties including geometric structure, electronic structure, states density and optical absorption properties has been calculated successfully by the generalized gradient approximation. The band structures show the $Cs_{1-x}SnI_3$ perovskites with self-doped at the A sites when x=0.00, 0.125, 0.50 have conductor performance, but the configuration with x=0.037 has the semiconductor performance, and all the $CsSn_{1-y}I_3$ perovskites with vacancy at the B sites when x=0.00, 0.037, 0.125, 0.50 have the semiconductor performance, too.

Introduction

The investigations of organo-metal perovskites [1] owing to their applications were widely concerned, such as perovskite solar cell photoelectric conversion field, topological insulator potential material, superconductors. The structure can be expressed as ABI3, A=monovalent cation, B=diavalent cation.CsSnI3 as a light absorber was extensively studied with rich optical properties [2-5].

Scaife et al. studied the structure of CsSnI3 perovskite material [6]. Hayatulla et al. studied the structural, electronic and optical properties of cubic perovskites CsSnI3 by the first principle calculations. It can be used in optical and optoelectronic devices in the spectrum range [7]. By local density approximation (LDA), Amreen Bano [8] et al. reported the dielectric and optical properties of the CsSnI3. There are three structures for the CsSnI3, α, β, and γ phases. Chonglong Yu et al.[9] reported the role of Cs atoms, and show that α structure is instable, and the β, and γ phases are stable ones, and they can be transformed reversibly. Christopher E. Patrick et al. used the standard harmonic theory of photons to demonstrate the critical role played by an harmonicity [10]. It has been found that SnI6 octahedra are stabilized against tilts and rotations by interacting with the re-normalized vibrations of the Cs ions. However, there must be defect in the material because the temperature is not 0K, so the investigation of the point defect is important.

Zewen Xiao et al. Calculated for Cs2SnI6 with the vacancy at the B sites by the projector-augmented wave (PAW) method [11]. The results indicate that the formation of the deep defects can be obtained by employing an I-rich synthesis condition, and the Cs2SnI6 perovskite can be as the photovoltaic and other semiconductor applications. The relationships between structure and property of ordered double perovskites Cs2SnI6 and Cs2TeI6 with vacancy at the B sites was given by Annalise E. Maughan et al.[12]. I-I contact distances decrease in carrier concentration and

mobility, and the defect level occurs deep within the band gap and thus localizes potential mobile charge carriers.

In this paper, we used the first principle to calculate the structural, density of states and optical properties of the CsSnI3 perovskite with vacancy at the A or B sites. The structural properties can be controlled by the vacancy at the A or B sites such as the cell volume decreases weakly firstly, and then increases linearly. In particular, the band gap decreases monotonically with the content of vacancy at the A sites increasing, from 0.00 eV to 2.001 eV. The Cs1-xSnI3 perovskites with self-doped at the A sites have conductor performance when x=0.00, 0.125, 0.50, but the configuration with x=0.037 has the semiconductor performance, and all the CsSn1-yI3 perovskites with vacancy at the B sites when x=0.00, 0.037, 0.125, 0.50 have the semiconductor performance.

COMPUTATIONAL METHODS

The Configuration Found

The relevant parameters of structure of CsSnI3 was obtained by the reference pattern with ICDD=01-080-2140 and ICSD=069997, the space group is Pm-3m, the number is 221, the lattice parameters are a=b=c=6.2190 Å. The initial fractional coordinates of Cs, Sn and I are (0.5000, 0.5000, 0.5000), (0.0000, 0.0000, 0.0000), and (0.5000, 0.0000, 0.0000), respectively.

Calculation Methods

The cubic perovskite Cs1-xSn1-yI3 (x, y=0.00, 0.037, 0.125, 0.50) were calculated by the plane-wave pseudopotential density functional theory (DFT) method [13] using as implemented in the Cambridge Serial Total Energy Package (CASTEP) program, and the Perdew Burke and Ernzerhof (1996) version (PBE) exchange correlation functional was employed. The cutoff energy was set as 250 eV, and the ultrasoft pseudopotentials were used to describe the electron-ion interaction. Parameters for the convergence tolerance were 1.0×10-6 eV/atom, and the maximum SCF cycles is 1000, electronic is set as density mixing with change 0.5 and spin 2.0. A Gaussian smearing scheme was used with 0.1 eV for the smearing width. A 2×2×2 k-point mesh is carried out the supercell with 135 atoms in reciprocal space. The state density is set as fine level with 4×4×4 k-point mesh, empty band is set as 12, and the PDOS is calculated.

Results and Disscussion

Optimized Structure of $CsSnI_3$ Perovskite with Cation Vacancy.

The optimized structures of cubic perovskite Cs1-xSn1-yI3 (x, y=0.00, 0.037, 0.125, 0.50) are shown in Table 1. All the lattice parameters and cell volumes increase firstly, and then decrease, with the x or y decreasing. Inflection points are x=0.037, y=0.125, which indicates that the effect of vacancy at the A sites is greater than that at the B sites for crystal structure.

Table 1. Optimized structure of perovskite Cs1-xSn1-yI3 (x, y=0.00, 0.037, 0.125, 0.50) such as lattice parameters a, b and c, cell volumes V. Unites are [Å], [Å3]

Structural parameters	*x*=*y*=0.00	*x*=0.037	*x*=0.125	*x*=0.50	*y*=0.037	*y*=0.125	*y*=0.50
a[Å]	6.0689	6.1174	6.1111	4.7624	6.1540	6.5401	5.4144
b[Å]	6.0689	6.1174	6.1111	4.7624	6.1540	6.5401	5.4144
c[Å]	6.0689	6.1174	6.1111	4.7624	6.1540	6.5401	5.4144
V[$Å^3$]	223.5285	228.9242	228.2273	108.0100	233.0652	279.7444	158.7305

Optimized Band Structure of $CsSnI_3$ Perovskite with Cation Vacancy

The optimized band structures of perovskite $Cs_{1-x}Sn_{1-y}I_3$ (x, y=0.00, 0.037, 0.125, 0.50) are shown in Fig.1. The Fermi level is 0 eV. The perovskite $Cs_{1-x}Sn_{1-y}I_3$ with x=0.037, y=0.037, y=0.125 y=0.50, have forbidden band structures, others do not have the band gap, whose configurations with band gap can be as the photoelectric conversion material. It notes that the band gap monotonically increases with the content of vacancy at the B sites, whose value changes to 2.001 eV from 0.0000 eV. The total density of state shows that s and p electrons located at the 0 eV inducing sp orbit hybridization, which dominant the electrical properties. 3d electrons of Pb cations below -20eV do not permit orbit hybridization.

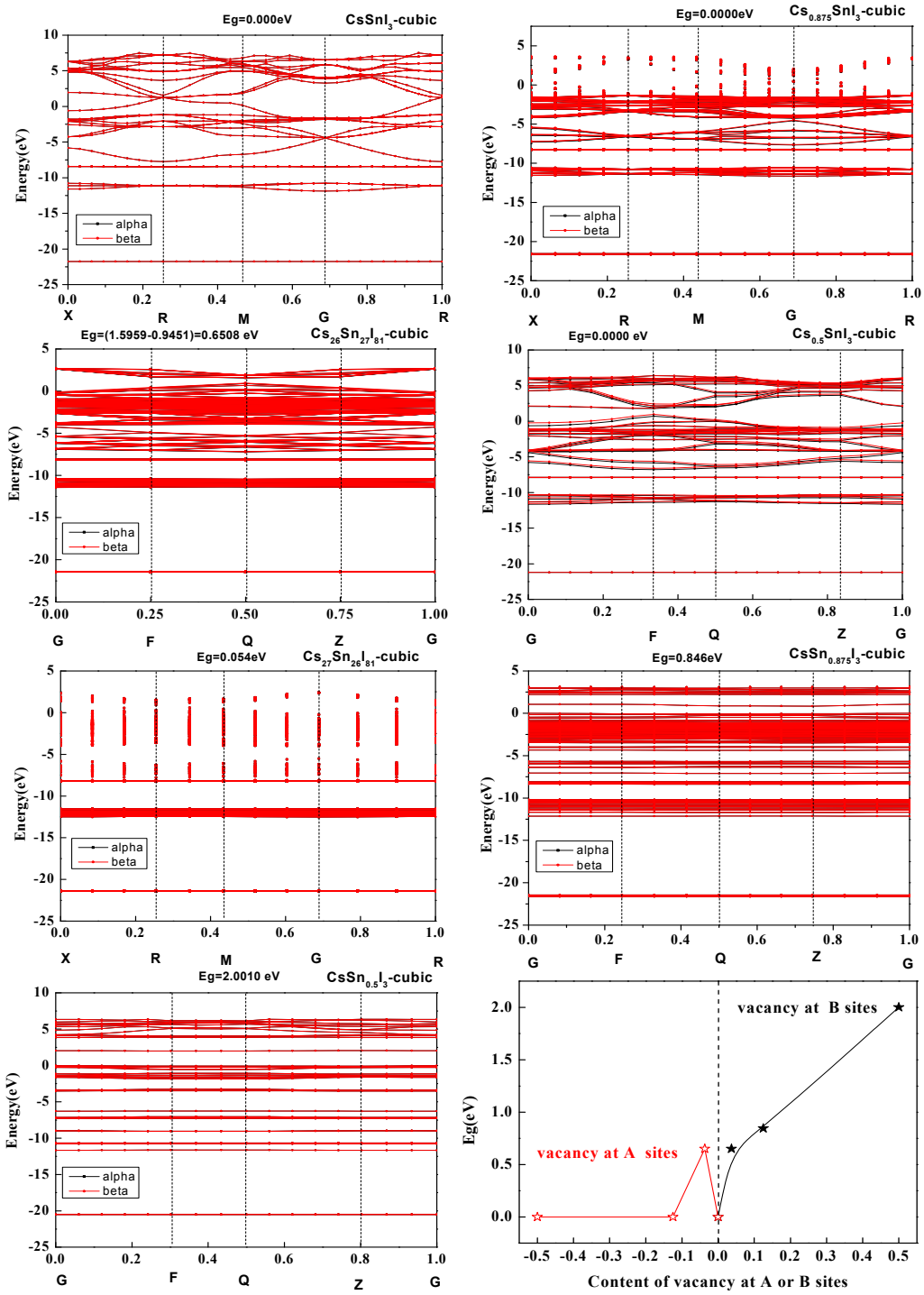

Fig.1 Energy band structures of perovskite $Cs_{1-x}Sn_{1-y}I_3$ (x, y=0.00, 0.037, 0.125, 0.50), and the curve of band gap (E_g) *vs* the content of cation vacancy at the A or B sites.

Results and Disscussion

We calculated the geometries, band structure, and state density of inorganic perovskite with $Cs_{1-x}Sn_{1-y}I_3$ (x, y=0.00, 0.037, 0.125, 0.50) by the first-principles based on density-functional theory-GGA calculations. For the structural properties, the vacancy at the A or B sites controls the cell volume decreases weakly firstly, and then increases linearly. In particular, the band gap decreases monotonically with the content of vacancy at the A sites increasing, from 0.000 eV to 2.001 eV. The $Cs_{1-x}SnI_3$ perovskites with vacancy at the A sites with x=0.037, and all the $CsSn_{1-y}I_3$ perovskites with vacancy at the B sites with x=0.00, 0.037, 0.125, 0.50 are semiconductor.

Acknowledgment

This work was supported by Joint Funds of department of Science and Technology of Guizhou Province, LiuPanshui Administration of Science and Technology and LiuPanshui Normal University under Contract No.[2014]7449, Research Foundation for Advanced Talents of LiuPanshui Normal University (Grant No. LPSSYKYJJ201404 and LPSSYKYJJ 201403), the Key Project of the Education Department of Guizhou Province (No.2015379 and 2013174), the National Science Foundation of China under Contract (No 51567017 and 61076049), the Key Laboratory of Opt-electrical Information Technology of Liupanshui City (No. 5202020142 0205), the Recruitment Program of Guizhou University granted 2012032, the MIT Creative Team of Liupanshui Normal University No.LPSSYKJTD201402, the Physical Electronic Key Discipline of Guizhou Province No. ZDXK201535, the Outstanding Young Scientist Cultivation Program of Guizhou Province No.201522 and the Joint Science Foundation of Liupanshui City and Guizhou Province No. LH20147448.

References

[1] S. Liu, F. Zhang, N. Z. Koocher, H. Tanaka, F.Wang and A. M. Rappe, Ferroelectric Domain Wall Induced Band Gap Reduction and Charge Separation in Organometal Halide Perovskites, J. Phys. Chem. Lett. 6 (2015) 693-699.

[2] C. C. Stoumpos, C. D. Malliakas, and M. G. Kanatzidis, Semiconducting tin and lead iodide perovskites with organic cations: phase transitions, high mobilities, and near-infrared photoluminescent properties, Inorg.Chem. 52 (2013) 9019-9038.

[3] C. Yu, Z. Chen, J. J. Wang, W. Pfenninger, N. Vockic, J. T. Kenney, and K. Shum, Temperature dependence of the band gap of perovskite semiconductor compound $CsSnI_3$, J. Appl. Phys. 110 (2011) 063526.

[4] Z. Chen, C. Yu, K. Shum, J. J.Wang,W. Pfenninger, N. Vockic, J. Midgley, and J. T. Kenney, Photoluminescence study of polycrystalline $CsSnI_3$ thin films: Determination of exciton binding energy, J. Lumin. 132 (2012) 345-349.

[5] Ling-yi Huang and Walter R. L. Lambrecht, Electronic band structure, phonons, and exciton binding energies of halide perovskites $CsSnCl_3$, $CsSnBr_3$, and $CsSnI_3$, PHYSICAL REVIEW B 88 (2013) 4977-4984.

[6] D. Scaife, P. Weller, W. Fisher, Crystal preparation and properties of cesium tin(II) trihalides, J. Solid State Chem.9 (1974) 308-314.

[7] Hayatullaha, G. Murtazab, S. Muhammada, S. Naeemb, M.N. Khalidb and A. Manzar, Physical Properties of $CsSnM_3$ (M = Cl, Br, I):A First Principle Study, ACTA PHYSICA POLONICA A, 124 (2013) 102-107.

[8] Amreen Bano, Preeti Khare and N. K. Gaur. First-Principles Calculation For Phonon And Optoelectronic Properties Of $CsSnI_3$. AIP Conference Proceedings 1731 (2016) 090001.

[9] Chonglong Yu, Yuhang Ren, Zhuo Chen, and Kai Shum, First-principles study of structural phase transitions in $CsSnI_3$. J. Appl. Phys 114 (2013) 163505.

[10] Christopher E. Patrick, Karsten W. Jacobsen, and Kristian S. Thygesen. Anharmonic stabilization and band gap renormalization in the perovskite $CsSnI_3$. PHYSICAL REVIEW B 92 (2015) 201205(R).

[11] Zewen Xiao, Yuanyuan Zhou, Hideo Hosono, Toshio Kamiya, Intrinsic defects in photovoltaic perovskite variant Cs_2SnI_6 , Physical Chemistry Chemical Physics, 17 (2015) 189000-189003.

[12] Annalise E. Maughan, Alex M. Ganose, Mitchell M. Bordelon, Elisa M. Miller, David O. Scanlon, and James R. Neilson, Defect Tolerance to Intolerance in the Vacancy-Ordered Double Perovskite Semiconductors Cs_2SnI_6 and Cs_2TeI_6.J. Am. Chem. Soc. 138 (2016) 8453-8464.

[13] V. Milman, B. Winkler, J.A. White, C.J. Packard, M.C. Payne, E.V. Akhmatskaya, R.H. Nobes, Electronic structure, properties, and phase stability of inorganic crystals: A pseudopotential plane-wave study, International Journal of Quantum Chemistry 77 (2000) 895-910.