Project No. 02213 / Grant No. JPMXP0621467974

Report form of Joint Research Project at ZAIKEN (FY2022)

Title of Project	**Design of the stable light absorption layer for inorganic perovskite solar cell**		
Priority Area	**I-B, III-B, I-C, III-C**		
Continuation of 2021 joint project			
Name of Main Applicant	**Farhod Rahimi**		
Institution	**National Academy of Sciences of Tajikistan**	**title**	**President (Professor)**

Aim of the research project

Lead-halide perovskites have attracted great attention these days due to their potential applications for the light absorption layers of the next generation solar cells and for light emitting devices. There are some stable polymorphs depending upon the temperature in the lead-halide perovskites, i.e., α-, δ- and γ-phases. Among them, α- and γ-phases with cubic and orthorhombic structured perovskites, respectively, have good optical property for the above applications, while δ-phase with orthorhombic non-perovskite structure is not suitable for such purpose. Some of them crystallizes in δ-phase at ambient condition, e.g., $CsPbI_3$, though such materials with α- or γ-phases are quite good for solar cells. Hence, a lot of attempts have been done to stabilize the α- and/or γ- phases at room temperature by anion and cation mixings. In the current study, influence of cation and anion mixings on the phase stability and on the electronic structures of the lead-halide perovskites are investigated by using the first-principles calculations within a density functional theory (DFT) level, which will be applied to the development of new stable and efficient light absorbing materials for the next generation solar cells.

Contents and results of the research

We have performed first-principles calculations for a series of $CsBX_3$, where B is a mixture of Pb and Sn and X is a mixture of Cl, Br and I, to investigate phase stabilities and electronic structures. These calculations are not limited to the organic perovskites, but those for organic-inorganic hybrid perovskites are performed, in which MA (methyl-ammonium ion) and FA (form amidine ion) are chosen for A site cation instead of and mixture of Cs.
Purpose of the current calculations is to find the stable perovskites with desired optical property under operating condition of the solar cells. Then we focused on the following two points, i.e., 1) free energy at finite temperature, and 2) electronic density of states.

1) Free energy at finite temperature
The total electronic energy calculated by the first principles calculations can provide us the phase stability of the perovskites only at 0 K. Combining the static first-principles calculations with direct method to calculate phonon density of states, we can obtain Helmholtz free energy at finite temperature, which enables us to examine phase stability of the perovskites. We have calculated free energy for a series of inorganic cesium halide perovskites using vasp with a conventional GGA-PBE functional for electron-electron correlation and phonopy code to obtain phonon density of states. $CsPbI_3$ crystallizes in δ-phase at room-temperature, which is not photo-active for visible light, and transforms to the cubic structured photo-active α-phase beyond approx. 600 K. Our current calculations indicate that the free energy of the α-phase becomes lower beyond 490 K. At this stage, the phase transition temperature is still lower than experiments, other electron-electron correlation functionals are under testing to show better agreements with experiments.

2) Electronic density of states
For the solar cell applications, it is desired to have suitable photo-absorption ability in the light absorbing layer, here perovskites, of the solar cells. To evaluate such ability, one important parameter is an electronic band gap, which can be obtained from the results of the first-principles calculations. We have performed band structure calculations for a series of Cs halide perovskites, say $CsBX_3$, where B = Pb, Sn and Ge, and X = Cl, Br and I. In addition, anion mixed models were also constructed, whose band gaps were also calculated.

Combining the calculated results of phase stability and band gap, we have searched the suitable photo-absorbing layer perovskites and started synthesis of the recommended materials with spin coating method, which are in progress in the research group of Professor Yamamoto in Waseda University.

Outputs of the project (publications, presentations, patents)

Presentation & Proceedings:
Umar Zafari, Mehrdod Subhoni, Farhod Rahimi and Tomoyuki Yamamoto, Proceedings of the international conference "The role of physics in the development of science, education and innovation", TNU, Dushanbe, 10/27/2022.