STEPS Students Report

Shodruz Umedov (M1)
Faculty of Materials Science, MSU

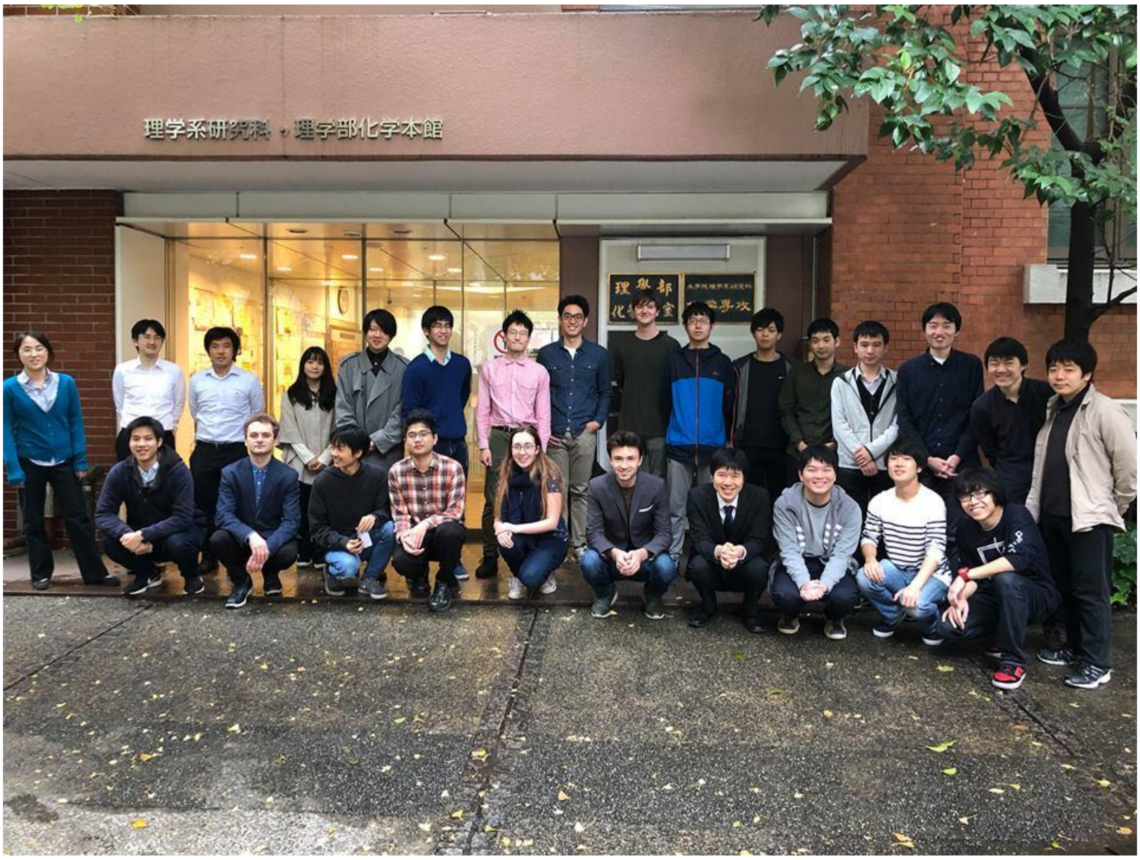
Currently, renewable solar energy is being actively used. Among the converters of solar energy, photovoltaic devices have more interest. The most promising are photoelectrochemical cells, in which oxide semiconductors with a wide band gap are used, and they are called Gretzel cells or hybrid solar cells. The great interest for using in the Gretzel cells as a light-harvesting component represents complex iodides with a perovskite like structure. Previously, tin-based iodides have been studied in the +2 (γ-$CsSnI_3$) oxidation state, which is not stable. The complexity of synthesizing and creating the architecture of cells is associated with the need to use an inert atmosphere and the absence of moisture, and therefore it has been suggested to use perovskite-like structures of the composition Cs_2SnI_6 (Iodostannate (IV) cesium) containing tin in oxidation state +4, which has resistant to air and moisture. Cs_2SnI_6 is the direct-gap semiconductor of p-type with a bandgap of ~ 1.6 eV and is the promising material in solar cells that can be replaced a lead-based perovskite, which is toxic. Many scientific articles have been published about the improvement of the properties of Cs_2SnI_6 and it using in solar cells, but the problems of stability and high efficiency of these cells are still relevant. These problems mostly depend on the light-harvesting component, namely on Cs_2SnI_6.

The aim of my work is the synthesis and study of the properties of new materials based on Cs_2SnI_6 which could be a decision to the above problems and not only. Analysis of literature sources and possible quasi-chemical equilibria has shown that doping the Cs_2SnI_6 compound with another metal (a metal whose atomic radius and electronegativity are approximately equal to the atomic radius and electronegativity of tin) initiate the appearance of donor levels in the bandgap and increase the electronic conductivity of the materials. Indium (In) is a good candidate for this role. Cs_2SnI_6 doped with indium with different ratios (1, 5, 9, 15, 30, 50, 90, 95, 99 and 100%) and obtained solid solutions. Above 15% substitution of tin atoms with indium in diffractograms, reflexes are formed related to the phase $CsInI_4$ and above 90% pure $CsInI_4$ phase is formed.

Synthesized samples at the Lomonosov Moscow State University, I brought to the Professor Ohkoshi laboratory for studying their properties. In the laboratory of Prof. Ohkoshi, under the guidance of Dr. Koji Nakabayashi, I investigated my samples with Low-temperature Electron Spin Resonance (ESR) method and Terahertz time-domain spectroscopy (THz-TDS).

The ESR method provides unique information about paramagnetic centers. It uniquely distinguishes impurity ions that are isomorphically included in the lattice from microinclusions. In this case, complete information is obtained about a given ion in a crystal: valence, coordination, local symmetry, hybridization of electrons, how many and in what structural positions of electrons, and detailed information about the chemical bond. And, very importantly, the method allows to determine the concentration of paramagnetic centers in regions of a crystal with a different structure. In order to obtain this information, 8 samples with different composition of doping were analyzed by the ESR method and observed how the resonance intensity changes when the compounds are cooled to low temperatures. The temperature decrease was reproduced with the following intervals: 300 Kelvin (K)-250K-200K-150K-100K-50K-30K-20K-15K-10K and 4.2K (cooling agent - liquid helium). The maximum intensity of the spectra of all samples were observed at 4.2 K. Resonance absorption was observed at a magnetic field (H) of 320.4 mT and shifted to 320.85 mT (for $CsInI_4$) with an increase the indium concentration to 100%. The gyromagnetic ratio or g-factor was calculated from the ESR spectrum at each temperature.

THz-TDS measurement were used for analyzing of the local environment of a heavy cesium atom in a perovskite structure, for analyzing tin and indium atoms vibration modes if they exist (assuming that they are also heavy atoms) and also as well as to study of $Sn\text{-}I$ bonds vibration, if any, in the frequency region of 0–8 THz. In the Cs_2SnI_6 structure, cesium atoms are located in octahedral voids and should vibrate slowly and to resonate with a low-frequency terahertz light. All obtained samples were measured by THz-TDS method and characteristic THz-light absorption spectra were obtained.


理学系研究科・理学部化学本館