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Electronic Structure Governed by Displacement of Indium Site in In-S₆ Octahedra: LnOInS₂ (Ln=La, Ce, and Pr)

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Extremely large displacement of indium site in In-S₆ octahedra in LnOInS₂ (Ln=La, Ce, Pr) were found in synchrotron X-ray diffraction. LaOInS₂ with off-center indium in In-S₆ octahedra exhibited wider optical bandgap than those of CeOInS₂ and PrOInS₂ with on-center indium. Therefore, the electronic structure of LnOInS₂ is govern by the indium site with extremely large displacement. All the LnOInS₂ produced H₂ gas under visible light irradiation in the presence of sacrificial electron donors.

Introduction

Large atomic displacements from the equilibrium position in crystal structures are known to be key for designing functional materials such as thermoelectric materials,¹⁻⁴ superconductors,⁵⁻⁷ electrodes,⁸ and luminescent materials.⁹ For example, suppression of thermal conductivity by large atomic displacements is an effective strategy for designing thermoelectric materials.¹⁻⁴ Large displacement of chalcogenide site in BiCh₂-superconductors is regarded as a key for emergence of superconductivity.⁵⁻⁷ Conduction path in electrodes has been visualized by large atomic displacements.⁸ Nonetheless, the effect of large atomic displacements on the electronic structure has not been fully understood by the experimental results. For instance, 12CaO•7Al₂O₃ and CoSb₃ have cage structures, and have been extensively studied for use in developing various functional materials. H⁻ and In can be incorporated in these cage materials. H⁻ in 12CaO•7Al₂O₃:H⁻^{10,11} and indium in In_{0.125}Co₄Sb₁₂^{12,13} show large displacement in these cages, and hence are called as rattlers. The effect of these

rattlers on their thermoelectric and electronic properties has been supported by computationally predicted electronic structures.^{11,12} However, there is experimental difficulty to detect the states of these rattlers by X-ray photoemission spectroscopy (XPS). This is because the states contributed by these rattlers are much smaller than those by cages and the energy resolution of XPS is insufficient to distinguish between these contributions. Therefore, in order to design functional materials based on large atomic displacement, experimental study to bridge large displacement of atoms and its effect on the electronic structure is highly demanded.

Figure 1 Crystal structure of LaOInS₂ drawn by VESTA.¹⁴

In order to experimentally examine the correlation between atomic displacement and electronic structure, it is desirable to synthesize compounds containing rattlers as major components whose atomic displacement can be rationally controlled. The layered oxysulfide LaOInS₂¹⁵ would be a motif to examine the correlation between atomic displacement and electronic structures. Figure 1 shows the crystal structure of LaOInS₂.

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LaOInS₂ has alternately stacked oxide and sulfide layers. The sulfide layer is composed of In–S₆ octahedra, and In in the octahedral cage exhibit large anisotropic displacement parameters. These large atomic displacements would be controlled by the substitution of lanthanum in the La–O layer with smaller rare-earth elements; the decrease in the ionic radius probably results in an increase in the chemical pressure applied on the In–S₆ octahedra^{16,17}. Moreover, because indium is the major component of this compound and has a large scattering factor, synchrotron X-ray diffraction can help visualize the atomic displacement of indium in these compounds.

The electronic structure near the band gap of LaOInS₂ can be examined by their optical absorption. LaOInS₂ is reported to be a semiconductor photocatalyst with the band gap of ~2.64 eV. According to DFT calculations,¹⁵ the sulfur 3p states are located near the valence band maximum, and the indium 5s and 5p states form the bottom of the conduction band. Thus, the electronic structure near the bottom of the conduction bands of LaOInS₂ and its isostructural analogs can be evaluated by optical absorption and reflect a large displacement of In. The electronic structure should be sensitive to the atomic displacement of indium, although XPS analysis is not suitable for examining the electronic structure because of the absorption species present on the surface of these compounds.¹⁵

In this study, we revealed the relationship between the electronic structure and large displacements by means of structural analysis and optical absorption experiments. The newly synthesized CeOInS₂ and PrOInS₂ were characterized and compared with LaOInS₂. The on-center indium in CeOInS₂ and PrOInS₂ shifted their optical absorption edge to a lower energy as compared with that corresponding to the off-center indium in LaOInS₂.

Results and discussion

Figure 2 Synchrotron X-ray diffraction pattern of LaOInS₂, CeOInS₂, and PrOInS₂ at 300 K.

Layered oxysulfides LnOInS₂ (Ln=La, Ce, and Pr) were synthesized by the reaction of LnOCl and NaInS₂. Figure 2 indicates X-ray diffraction pattern of LaOInS₂, CeOInS₂, and PrOInS₂ at 300 K. Synchrotron X-ray diffraction results indicated that CeOInS₂ and PrOInS₂ were isostructural with monoclinic LaOInS₂.¹⁵

Figure 3 Temperature dependence of lattice constants *a*, *b*, and *c* and volume of In–S₆ octahedra of LnOInS₂. Two type of In–S₆ octahedra in In₂S₃ (ICSD-151644) are shown for comparison.

Rietveld refinement of synchrotron XRD data were performed for further structural analysis. Even though only monoclinic cell can be fit with atomic positions of LnOInS₂, the refinements of β converged with 90° within the error. Therefore, all the LnOInS₂ were refined as monoclinic phases but β was fixed as 90°, according to the previous report about LaOInS₂.¹⁵ Since indium is a heavy atom and has a large atomic scattering factor, its probability density function of indium in LnOInS₂ can be determined. For initial Rietveld refinements of XRD patterns of LnOInS₂, the position of indium was settled in the central position of In–S₆ octahedral cage and second-order (harmonic) displacement parameters of indium (U_{11} , U_{22} , and U_{33}) were assumed, and U_{12} , U_{13} , and U_{23} were fixed as zero. These refinements converged with moderate refinement factors (R_{wp}); LaOInS₂: 8.58%, CeOInS₂: 9.88 %, and PrOInS₂: 9.29 % and derived larger thermal displacement of indium than that of the other atoms. Since U_{22} was extremely large for LaOInS₂ and PrOInS₂, In was expected to possess large atomic displacement along the *b* axis. In order to depict large atomic displacement of In, anharmonic displacement model was introduced. In this crystal structure model, indium was fixed at the central position of the In–S₆ Octahedron, and a fourth-order (anharmonic) atomic displacement parameter,¹⁸ D_{2222} , represented the thermal displacement of indium along the *b* axis. Rietveld refinements of the XRD patterns of LaOInS₂ and PrOInS₂, with fourth-order displacement parameter of indium, improved the refinement factors (LaOInS₂: 8.27 % and PrOInS₂: 9.24 %). Split models with two In sites were also employed for LaOInS₂ and PrOInS₂. The details of the refinements with site split and anharmonic displacement models are summarized in supporting document. These models suggested that the atomic position derived by these two-site model were same as the position of maximum probability density derived by the model

with fourth-order (anharmonic) atomic displacement parameter. Thus, we conclude that both models are comparable although here we explained the results by using the model with anharmonic atomic displacements. On the other hand, for CeOInS₂, the refinement of XRD pattern with harmonic displacement parameters converged with U less than $0.1 \text{ \AA}^2$. Furthermore, the fourth-order term D_{2222} converged with negative probability density although its refinement factor improved. The position of In with the split model of CeOInS₂ converged into central position of In–S₆ octahedra within the statistic error. Thus, the XRD pattern of CeOInS₂ was refined by a simple model without the fourth-order atomic displacement parameters and split In site.

Figure 3 shows the temperature dependence of lattice constants. The Rietveld profiles of LaOInS₂, CeOInS₂, and PrOInS₂ are shown in Figure S2. The details of the refinement are summarized in Table S2, Table S3, and Table S4. The lattice constants a and b decreased upon the substitution of La by Ce and Pr, while the lattice constant c increased. A decrease in temperature from 450 K to 300 and 150 K decreased the lattice constants and increased the difference between the lattice constants a and b . The volume of In–S₆ octahedron is also shown in Figure 3. This volume was significantly larger than those of In–S₆ octahedra found in In₂S₃ (ICSD-151644), indicating that octahedral cages were expanded by Ln–O layers.

Figure 4 Probability density functions of indium in the ab plane of LaOInS₂ at 150, 300, and 450 K were derived from the Rietveld analysis using Jana2006 program.¹⁹ $V(\text{In-S}_6)$ represents the volume of In–S₆ octahedra.

Figure 4 shows the crystal structure and the probability density function of indium in the ab plane of LaOInS₂. The probability density functions of indium between 150 and 450 K showed two maxima at the off-center positions and a local minimum at the center of the In–S₆ octahedra. As the temperature decreased from 450 to 150 K, the volume of the

In–S₆ octahedra decreased by approximately 1.1 %. The decrease in temperature increased the distance between the center and the maxima from 0.34 to 0.46 Å, and decreased the probability density at the center from 1.11 to 0.72 Å^{–3}. Assuming that the magnitude of atomic displacement continuously changes with temperature, indium can be expected to exhibit a large atomic displacement even at 0 K. Hence, the atomic displacement parameters for indium are anomalous.¹⁵ Larger atomic displacement of In in LaOInS₂ was also supported by In K-edge X-ray Absorption Fine Structure (XAFS) (Figure S6). The probability density functions of CeOInS₂ and PrOInS₂ at 150, 300, and 450 K are shown in Figure S3 and Figure S4, respectively. The probability density function of PrOInS₂ at 450 K showed one maximum at the center of the In–S₆ octahedra. At 150 and 300 K, the functions had two maximum points, and the maxima were slightly off-centered at lower temperature. In CeOInS₂, the probability density function of indium at the center of the In–S₆ octahedra was the maximum in the temperature range between 150 and 450 K. The indium atoms in CeOInS₂ and PrOInS₂ were also considered to show large displacement even at 0 K. In other words, we found abnormal displacements of indium in LaOInS₂, CeOInS₂, and PrOInS₂.

Figure 5 Probability density functions of indium in LaOInS₂, CeOInS₂, and PrOInS₂ along the b axis and volumes of In–S₆ octahedra.

Figure 5 shows the probability density functions along the b axis of LaOInS₂, CeOInS₂, and PrOInS₂ at 300 K. The probability density of indium at the center of the In–S₆ octahedra in LaOInS₂ was located at the off-center positions, whereas the probability densities at the center of the In–S₆ octahedra were the maximum in CeOInS₂. The probability density at the center in PrOInS₂ was close to maximum although two maximums appeared in off-center positions. Higher probability density in off-center position can be understood by longer lattice parameter of b -axis (Figure 3: CeOInS₂ < PrOInS₂ < LaOInS₂). The distance from sulfur to center of the In–S₆ octahedron on ab plane were 2.8895(4) Å for LaOInS₂, 2.8235(3) Å for CeOInS₂, and 2.8406(3) Å for PrOInS₂. These distance are much larger than the sum of ionic radii of In³⁺ and S^{2–} (2.64 Å), and shifting of In atom from the center of octahedron would be favorable to

shorter bond lengths between In and S. Similar shifting of Bi^{3+} are also proposed in structurally-related LaOBiS_2 and LaOBiSe_2 .²⁰

Although ionic radius of Ce^{3+} is larger than Pr^{3+} ,²¹ the lattice parameters a and b of CeOInS_2 were shorter than that of PrOInS_2 . In order to explain these results, the valence state of Ce was examined by XAFS. The Ce L_3 -edge XAFS spectra of CeOInS_2 is shown in Figure 6. Although Ce^{3+} was dominant in CeOInS_2 , Ce^{4+} was also detected. The fraction of Ce^{4+} was estimated to be 10 % from linear combination fitting of the spectra of Ce_2S_3 and CeO_2 . Since the ionic radius of Ce^{4+} is smaller than that of Ce^{3+} and Pr^{3+} ,²¹ the smaller lattice constants a and b of CeOInS_2 than those of PrOInS_2 can be explained by the existence of Ce^{4+} .

Figure 6 Ce L_3 -edge XAFS spectra of CeOInS_2 . Ce_2S_3 and CeO_2 are references of Ce^{3+} and Ce^{4+} cation, respectively.

Figure 7 Tauc plot of diffuse reflectance of LnOInS_2 at 300 K.

Figure 7 shows the Tauc plots derived from diffuse reflectance measurements of LnOInS_2 at 300 K by assuming their direct transition. The optical absorption gaps of LaOInS_2 , CeOInS_2 , and PrOInS_2 were determined to be 2.67, 2.41, and 2.43 eV, respectively.

Figure 8 Crystal structure models of LaOInS_2 , electronic structures, and absorption coefficients calculated by the DFT method.

The probability density of indium in LaOInS_2 was low at the center of the In-S_6 octahedra and spread along the b axis, while that in CeOInS_2 and PrOInS_2 was distributed at the center of the In-S_6 octahedra. The optical absorption gap of LaOInS_2 was approximately 0.3 eV larger than that of CeOInS_2 and PrOInS_2 . These differences suggest that optical absorption of LnOInS_2 is controlled by the atomic displacement of indium. The influence of the displacement of indium on absorption was also investigated by density functional theory (DFT) calculation. The split models with the on-center or off-center indium sites in the

In-S₆ octahedra were used. Figure S7 and Table S7 show the structure models with several arrangements of indium atoms and the calculation results, respectively. We assumed the static distribution of indium in several models. XRD only reflects the average structure, so the statistic or dynamic displacement has not been clarified. Although DFT calculations supported the fact that the optical absorption is sensitive to the indium position as below, these calculations were based on structural models with limited supercells. The ordering of the indium positions and dynamics of indium would also affect the electronic structure, and further study in this regard is necessary. Nonetheless, the results showed that the bandgaps depend on the position of indium. The simulation models, electronic structures, and absorption coefficients are shown in Figure 8. The PBE-GGA method was employed for structure optimization, and the HSE06 method was used for the calculation of the electronic structure and absorption coefficients. The electronic structure of the on-center and off-center models were similar, and the valence band maximum and conduction band minimum were all dominated by sulfur and indium, respectively. The energy level of absorption edge of the model with off-center indium sites was 2.60 eV, which was 0.15 eV higher than that of on-center model. In both models, the bond between indium and the nearest sulfur was parallel to the *c* axis. Furthermore, the hybridization of the indium 5p and sulfur 3p orbitals was decreased by the displacement of indium. Consequently, the energy difference of the hybridized orbitals increased and the optical absorption edge, which corresponds to the band edge, shifted toward shorter wavelengths.

Experimental results showed that the probability densities of indium at the center of the In-S₆ octahedra in LaOInS₂ were lower, and the optical band gaps were about 0.3 eV wider than that of CeOInS₂ and PrOInS₂. Computational results showed that the absorption edge of LaOInS₂ was affected by the thermal displacement of indium in the In-S₆ octahedra; the off-center models showed an absorption edge with higher energy than the center models. These results indicate that the optical absorption of LnOInS₂ can be modulated by the large thermal displacement of indium. Synchrotron X-ray diffraction showed that the potential curve for indium in LaOInS₂ had two minima at the off-center positions that were about 0.5 Å apart from the center of the In-S₆ octahedra. The energy barrier between two off-center positions was about 14 meV (Figure S5). Since the product of the Boltzmann constant and temperature at 300 K (25 meV) is higher than the energy barrier, indium would dynamically move between the two off-center positions. Although further investigation of dynamic displacement is necessary, our results show that LaOInS₂ is a suitable motif to show the correlation between atomic displacement and electronic properties and help us understand how the atomic displacement affects the properties of solid-state compounds.

Finally, photocatalytic activities of LnOInS₂ for H₂ evolution were examined. As shown in Figure 9, all of the LnOInS₂ produced H₂ upon visible light. The amount of H₂ evolved from the Pt-loaded CeOInS₂ and PrOInS₂ samples were less than 10% of that from Pt-loaded LaOInS₂ sample. The lower activities of Ce- and Pr-analogues may be explained by the existence of 4f electrons, which can increase the electron-hole recombination rates.²²²³

Figure 9 Time courses of H₂ evolution on Pt-loaded LnOInS₂ under visible light irradiation (420 < λ < 800 nm). Reaction conditions: catalyst, 50 mg; aqueous Na₂S (10 mM) + Na₂SO₃ (10 mM) solution; light source, xenon lamp (300 W) with a cutoff filter (L-42); reaction vessel, Pyrex top-irradiation type.

Conclusions

In summary, we found that the optical absorption correlated with the electronic structure of LnOInS₂ depended on the abnormally high displacement of indium. The probability density function of indium at the center of In-S₆ octahedra was low in LaOInS₂, but high in CeOInS₂ and PrOInS₂. The optical band gap of LaOInS₂ was about 0.3 eV wider than that of CeOInS₂ and PrOInS₂. The optical absorption was demonstrated to be sensitive to the indium position by computational calculations. These experimental and computational results confirm the electronic structure modulation by the atomic displacements of indium, and will deepen our understanding toward the development of new functionalities controlled by atomic displacement.

Experimental

Synthesis

LnOInS₂ was synthesized from NaInS₂ and LnOCl. NaInS₂ was obtained by heating NaSH·nH₂O (Sigma-Aldrich) and In(NO₃)₃·nH₂O (Kanto Chemical) at 200 °C in a Teflon-coated autoclave. LnOCl was prepared by heating of lanthanoid

chlorides at 650–820 °C for 34 h. $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (Wako) and $\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$ (Junsei Chemical) were heated in a flow of N_2 . $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (Junsei Chemical) was heated in a flow of H_2 (4%) and Ar. Then, LnOInS_2 was synthesized in an evacuated quartz tube by the metathesis reaction of LnOCl and NaInS_2 at 850 °C. After cooling, the obtained powders were washed by distilled water to remove the NaCl byproduct.

Characterization

Synchrotron X-ray diffraction profiles were measured at 150, 300, and 450 K at the BL02B2 beam line at SPring-8 (Proposal Numbers: 2017B1211, 2018A0074, 2018B1246, and 2019A1114). The wavelength of the incident X-ray used for presented refinements was 0.495274 Å. The diffraction data was collected using a high-resolution one-dimensional semiconductor detector, multiple MYTHEN system.²⁴ The X-ray diffraction data were analyzed by the Rietveld method using the Jana2006 program,¹⁹ and the crystal structure was drawn using the VESTA program.¹⁴ We depicted the probability density function of *ab* plane locating indium site, which is averaged along the *c* axis in the range of 0.8 Å with 0.05 Å intervals. The potential curves for indiums in LaOInS_2 and PrOInS_2 were calculated from respective probability density functions.²⁵ The valence of cerium was estimated by X-ray absorption fine structure (XAFS) spectroscopy analysis at the beam line BL11S2 of Aichi Synchrotron Radiation Center (Proposal Number: 201801025). The diffuse reflectance spectra of LnOInS_2 were measured from 200 nm to 850 nm using a UV-vis spectrophotometer (JASCO V-750) at room temperature. The optical band gaps of LaOInS_2 , CeOInS_2 , and PrOInS_2 were calculated assuming their direct band gaps.

Computational

Projected density of states (pDOS) and optical absorption coefficient were calculated by density functional theory (DFT) using the VASP package^{26,27} with the PBE and HSE06 method^{28,29} the projector augmented wave (PAW) method³⁰ with energy cutoff of 400 eV were utilized. The convergence criteria for all calculations set for the electronic self-consistent iterations and forces with 10^{-5} eV and 0.02 eV/Å respectively. The Gamma-point-centered Monkhorst–Pack (MP) ($5 \times 5 \times 2$) k-mesh scheme³¹ was employed for structure optimization and density of states (DOS) and dielectric function calculations. The imaginary part ($\epsilon_{\text{Im}}(\omega)$) of the frequency dependent dielectric matrix (ϵ) is determined for the calculation of absorption coefficient and bandgaps by a summation over empty states using the converged ground state.¹⁵

Photocatalytic reactions

Photocatalytic H_2 evolution reaction was conducted at room temperature using a top-irradiation type cell that was connected to a closed gas circulation system made of glass. 50 mg of sample was dispersed in aqueous Na_2S (10 mM) and Na_2SO_3 (10 mM) mixed solution (140 mL). A Pt cocatalyst (0.75 wt%) was loaded onto LnOInS_2 by an in-situ photodeposition method using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Kanto Chemical) as the precursor. After outgassing the reactant solution by a vacuum pump, Ar

gas (ca. 5 kPa) was introduced into the reaction system and the solution was irradiated under a 300 W Xe lamp (Cermex, PE300BF) with an output current of 20 A. The irradiation wavelength was fitted by the combination of a cold mirror (CM-1), cutoff filter (L-42) and water filter ($\lambda > 420$ nm). The evolved gases during the preparation process were analysed by a gas chromatography (GL Sciences, GC-3200 with TCD detector; argon carrier gas).

Conflicts of interest

There are no conflicts to declare.

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