

論文 / 著書情報  
Article / Book Information

題目(和文)	結晶性八面体型モリブデンクラスター化合物の光電子機能化に向けた探索
Title(English)	Exploration of Crystalline Octahedral Molybdenum Cluster Compounds for Optoelectronic Functionalization
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

## 論文要旨

THESIS SUMMARY

専攻 : Department of	材料工学	専攻	申請学位 (専攻分野) : Academic Degree Requested	博士 (工学)
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

**[Section 1]** This thesis presents new research on the utilization of building blocks such as ionic molecules or clusters as virtual elements to build crystalline solids. In particular, this study has focused on the octahedral molybdenum cluster complex,  $[\text{Mo}_6\text{X}_8\text{X}_6]^{2-}$  (X: halogen, i: inner, a: apical), as a candidate for a virtual element. The  $[\text{Mo}_6\text{X}_8\text{X}_6]^{2-}$  complex consists of an octahedron of six Mo(II) ions and 14 halogen ligands where face-capped 8 inner sites ( $\text{X}^i$ ) and terminal-capped 6 apical sites ( $\text{X}^a$ ) are arranged. This kind of cluster complex exhibits interesting optoelectronic features such as luminescence, photocatalytic and redox behavior, and which are tunable by substituting  $\text{X}^i$ s and  $\text{X}^a$ s the halogen species. Until now, the fundamental features of these crystalline solids built with the  $[\text{Mo}_6\text{X}_8\text{X}_6]^{2-}$  complex have been really unclear. This thesis explains the composition-structures-properties relationship of the  $[\text{Mo}_6\text{X}_8\text{X}_6]^{2-}$  compound system with  $\text{Cs}^+$  ion as counter cations through the use of both experiments and theoretical calculations.

**[Section 2]** Crystal structures and optoelectronic characteristics of  $\text{Cs}_2[\text{Mo}_6\text{X}_8\text{X}_6]$  with various halogen specie combinations have been calculated by the density functional theory (DFT) method. Based on crystalline structural studies, total energy calculations of trigonal-phase  $\text{Cs}_2[\text{Mo}_6\text{X}_8\text{X}_6]$  compounds were performed, and particularly relative structural stabilities of two trigonal-phase polymorphs, i.e., centrosymmetric *P*-31c and non-centrosymmetric *P*31c space groups were investigated. The difference between the total energies of two polymorphs was relatively small, indicating that these polymorphs possibly exist in the  $\text{Cs}_2[\text{Mo}_6\text{X}_8\text{X}_6]$  compound system but it was difficult to compare their relative structural stability by DFT calculations alone. According to electron orbital analyses and effective charge analyses,  $\text{X}^i$  was very covalent and neutrally charged in contrast,  $\text{X}^a$  was very ionic and significantly negatively charged, which indicates that  $\text{X}^a$  should be selectively substitutable. The band structure calculations show that band gap energy of the  $\text{Cs}_2[\text{Mo}_6\text{X}_8\text{X}_6]$  compounds varied over the entire visible absorption range. Hence, the DFT calculations predict that optical properties of the  $\text{Cs}_2[\text{Mo}_6\text{X}_8\text{X}_6]$  should be controllable by halogen substitution.

**[Section 3]** In order to study intrinsic crystal structures and optical properties of the metal-cluster-based compounds, a standardize procedure to obtain high-purity  $\text{Cs}_2[\text{Mo}_6\text{Cl}_{14}]$  has been investigated. For this purpose,  $\text{Cs}_2[\text{Mo}_6\text{Cl}_{14}] \cdot \text{H}_2\text{O}$  and  $\text{Cs}_2[\text{Mo}_6\text{Cl}_{14}]$  were used as precursors where water molecules were removed by dispersing the precursors in hydrophilic alcohol solvents such as MeOH, EtOH, and 1-PrOH. Consequently, dehydrated  $\text{Cs}_2[\text{Mo}_6\text{Cl}_{14}]$  was obtained by recrystallization with EtOH or 1-PrOH regardless of the precursor composition. In contrast, the sample recrystallized with MeOH resulted in a monoclinic form similar to  $\text{Cs}_2[\text{Mo}_6\text{Cl}_{14}] \cdot \text{H}_2\text{O}$  even using the anhydrous precursor. Powder X-ray diffraction (XRD), thermal desorption spectroscopy and Fourier transform spectroscopy suggest that obvious water impurities were not observed in the sample recrystallized with 1-PrOH as solvent. Furthermore, time-resolved photoluminescence (TRPL) study shows that emission lifetime of  $\text{Cs}_2[\text{Mo}_6\text{Cl}_{14}]$  recrystallized with EtOH or 1-PrOH was enhanced compared to that of water-contaminated samples. Hence, the purification procedure is effective to obtain high-purity  $\text{Cs}_2[\text{Mo}_6\text{Cl}_{14}]$ , with enhanced luminescence performance.

**[Section 4]** The section reports on the synthesis of ternary  $\text{Cs}_2[\text{Mo}_6\text{X}_{14}]$  and quaternary  $\text{Cs}_2[\text{Mo}_6\text{X}_8\text{X}_6]$  ( $\text{X}^i \neq \text{X}^a$ ). First, the ternary compounds were synthesized through solid-state reactions and subsequently quaternary ones were synthesized from the ternary precursors through ion-exchange of  $\text{X}^a$  using  $\text{AgBF}_4$  as intermediates. X-ray photoemission measurements indicate that almost all  $\text{X}^a$  halogens in  $\text{Cs}_2[\text{Mo}_6\text{X}_{14}]$  was substituted to different ones by the ion-exchange reactions. X-ray diffraction measurements show that most of compounds prepared in this study exhibited the trigonal phase (i.e., *P*31c or *P*-31c space group), but  $\text{Cs}_2[\text{Mo}_6\text{Br}_8\text{Cl}_6]$  exhibited the monoclinic phase, indicating a stable crystalline phase that potentially varies according to ( $\text{X}^i$ ,  $\text{X}^a$ ) combinations.

**[Section 5]** Optical properties of prepared  $\text{Cs}_2[\text{Mo}_6\text{X}_8\text{X}^a_6]$  were characterized by UV-visible diffuse reflection (UV-vis), PL and TRPL studies and second harmonic generation (SHG) measurement with a high-intensity infrared pulse. The UV-vis measurement indicates that band gap energies of the compounds varied with the atomic number of X, of which behavior was well matched with prediction by DFT. However, PL spectra were very insensitive to halogen substitution, indicating that the emissive state of the  $[\text{Mo}_6\text{X}_8\text{X}^a_6]^{2-}$  complex does not correlate with its band gap energy and is strongly dominated only by the  $\text{Mo}_6$  cluster. On the other hand, luminescence lifetime was obviously decreased with the atomic number of X, and the lifetime values can be associated with the effective charge of Mo. Furthermore, the SHG measurement shows that clear SHG signal was detected from trigonal-phase  $\text{Cs}_2[\text{Mo}_6\text{Cl}_8\text{Br}^a_6]$ ,  $\text{Cs}_2[\text{Mo}_6\text{Cl}_8\text{I}^a_6]$ , and  $\text{Cs}_2[\text{Mo}_6\text{Br}_8\text{I}^a_6]$ , suggesting that they did not possess an inversion center in the lattice. Hence, this indicates that these compounds are possibly functionalized as piezoelectric and pyroelectric materials. From structural refinement of them with the XRD data, a possible reason why the inversion center disappeared in these quaternary trigonal phases is proposed to be presence of a disorder and additional interstitial sites of  $\text{Cs}^+$  ions and displacement of them along *c*-axis.

**[Section 6]** The thesis has summarized the results of each sections and composition-structures-properties relationship of the  $\text{Cs}_2[\text{Mo}_6\text{X}_8\text{X}^a_6]$  compound system through comparison of the DFT calculations and experimental observations. Finally, future prospects to utilize the  $[\text{Mo}_6\text{X}_8\text{X}^a_6]^{2-}$  complex as virtual elements of crystalline solids is generally discussed. Through these discussions, the thesis shows a pathway for exploring new functional crystalline materials.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).

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