

論文 / 著書情報
Article / Book Information

題目(和文)	Exploration of Crystalline Octahedral Molybdenum Cluster Compounds for Optoelectronic Functionalization
Title(English)	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
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第10619号, 授与年月日:2017年9月20日, 学位の種別:課程博士, 審査員:CROSS JEFFREY SCOTT,篠崎 和夫,矢野 哲司,宮内 雅浩,大場史康,大橋 直樹
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第10619号, Conferred date:2017/9/20, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

Thesis Outline

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Outline

Section 1. Introduction

Recently, new kinds of materials utilizing ionic molecules or clusters as building blocks have attracted a lot of attention, because of their unique structures and effective optoelectronic functionalities. In these materials, materials functionalities are expectedly controllable by variation of the building blocks. As influenced by previous investigations, the author has focused on octahedral molybdenum cluster complex, $[\text{Mo}_6\text{X}_8^i\text{X}_6^a]^{2-}$, as a candidate of elements for construction of novel crystalline compounds with optoelectronic functionalities. The $[\text{Mo}_6\text{X}_8^i\text{X}_6^a]^{2-}$ complex is a very large (~ 1 nm) anionic complex, consisting of a Mo(II)_6 cluster core and 14 halogen ions (X^i and X^a) surrounding the core. It is well known that the $[\text{Mo}_6\text{X}_8^i\text{X}_6^a]^{2-}$ complex can absorb visible light and then exhibit red luminescence. Since optical properties and atomic characteristics such as ionic radius and effective charges of the complexes are expected to depend on their halogen compositions, substitution of X^i s and X^a s possibly enables us to control the optical properties and realize functionalization based on crystal symmetry. In this context, the thesis has focused on a $[\text{Mo}_6\text{X}_8^i\text{X}_6^a]^{2-}$ -based compound system, $\text{Cs}_2[\text{Mo}_6\text{X}_8^i\text{X}_6^a]$, and explored crystal structures and optical properties of the compound system through the use of experimental and theoretical calculation studies.

Section 2. Theoretical calculation of $\text{Cs}_2[\text{Mo}_6\text{X}_8^i\text{X}_6^a]$

Crystal structures and electronic properties of $\text{Cs}_2[\text{Mo}_6\text{X}_8^i\text{X}_6^a]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were calculated by density functional theory (DFT). Consequently, how halogen species and their coordination sites affect electronic structures of $\text{Cs}_2[\text{Mo}_6\text{X}_8^i\text{X}_6^a]$ was clarified. With crystal structure studies, determination of presence or absence of inversion center in the crystal structure was attempted through comparison of total energies of two trigonal polymorphs (i.e., $P31c$ and $P-31c$ symmetry). However, it was difficult to determine which phase is more stable, because of the very small differences in total energies of two polymorphs.

Section 3. Effects of impurity intercalation and purification of $\text{Cs}_2[\text{Mo}_6\text{Cl}_{14}]$

An efficient purification procedure of metal-cluster compounds was studied in order to investigate their intrinsic crystal structures and physical and chemical characteristics. In this study, purification of $\text{Cs}_2[\text{Mo}_6\text{Cl}_{14}]$ was focused and impurities interaction was removed by recrystallization in some hydrophilic alcohol solvents where $\text{Cs}_2[\text{Mo}_6\text{Cl}_{14}]$ powders were dispersed. As a result, it is found that 1-propanol is particularly suitable as a solvent for purification of $\text{Cs}_2[\text{Mo}_6\text{Cl}_{14}]$ and the purification treatment made the luminescence lifetime much longer than that of water-contaminated samples.

Section 4. Synthesis of halogen-substituted $\text{Cs}_2[\text{Mo}_6\text{X}_8^i\text{X}_6^a]$ compounds

Metal-cluster compounds with single halogen specimen ($\text{X}^i = \text{X}^a$) and different halogen species ($\text{X}^i \neq \text{X}^a$) were synthesized using solid-state reactions and ion-exchange reactions in solutions to substitute X^a s to different halogens. Crystalline phases and halogen compositions of synthesized compounds were characterized by

X-ray diffraction and X-ray photoemission spectroscopy. Those measurements reveal that most of the X^as of ternary Cs₂[Mo₆X₁₄] can be substituted by the ion-exchange reactions.

Section 5. Crystal structure and optical properties of Cs₂[Mo₆X₈ⁱX₆^a]

Crystal structures and optical properties of the Cs₂[Mo₆X₈ⁱX₆^a] compounds synthesized in the previous section were characterized. Particularly, second harmonic generation (SHG) measurements suggest that some quaternary trigonal-phase compounds such as Cs₂[Mo₆Cl₈ⁱBr₆^a], Cs₂[Mo₆Cl₈ⁱI₆^a] and Cs₂[Mo₆Br₈ⁱI₆^a] exhibited clear SHG signals under excitation with a high-intensity infrared pulsed laser. This result indicates that the Cs₂[Mo₆X₈ⁱX₆^a] compound system can potentially be functionalized in terms of optical and electrical properties on the basis of crystal symmetry.

Section 6. General conclusions

Result of each section was listed and technical concepts to utilize the [Mo₆X₈ⁱX₆^a]²⁻ complexes for construction of crystalline compounds were summarized. Finally, remaining issues and future prospects which were identified in this study are described.