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
著者(和文)	斎藤典生
Author(English)	Norio Saito
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,篠﨑 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)	審査の要旨
Type(English)	Exam Summary

（博士課程）

論文審査の要旨及び審査員

報告番号	甲第　　号		学位申請者氏名		齋藤　典生	
論文審査 審査員		氏　名	職　名		氏　名	職　名
	主査	Jeffrey S. Cross	教授	審査員	大橋　直樹	拠点長
	審査員	篠﨑　和夫	教授			
		矢野　哲司	教授			
		宮内　雅治	教授			

論文審査の要旨（2000 字程度）

The thesis written in English is entitled, Exploration of Crystalline Octahedral Molybdenum Cluster Compounds for Optoelectronic Functionalization（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）is summarized below in 6 sections.

[Section 1] The thesis has been devoted to build a new concept to utilize 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, $[Mo_6X^i_8X^a_6]^{2-}$ (X: halogen, i: inner, a: apical), as a candidate for virtual elements. The $[Mo_6X^i_8X^a_6]^{2-}$ complex consists of an octahedron of six Mo(II) ions and 14 halogen ligands where face-capped 8 inner sites (X^i) and terminal-capped 6 apical sites (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 X^is and X^as to different ones. Until the present, fundamental features of crystalline solids built with the $[Mo_6X^i_8X^a_6]^{2-}$ complex have been really unclear. Then, this thesis explores the composition-structures-properties relationship of the $[Mo_6X^i_8X^a_6]^{2-}$ compound system with Cs^+ ion as counter cations through the use of both experiments and theoretical calculations.

[Section 2] Crystal structures and optoelectronic characteristics of $Cs_2[Mo_6X^i_8X^a_6]$ with various halogen combinations have been calculated by the density functional theory (DFT) method. With crystal structure studies, total energy calculations of trigonal-phase $Cs_2[Mo_6X^i_8X^a_6]$ compounds were performed, and particularly relative structural stabilities of two trigonal-phase polymorphs, i.e., centrosymmetric *P*-31*c* and non-centrosymmetric *P*31*c* space groups were investigated. As a result, a difference between total energies of two polymorphs was very small, indicating that these polymorphs possibly exist in the $Cs_2[Mo_6X^i_8X^a_6]$ 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, X^i was very covalent and neutrally charged and in contrast X^a was very ionic and significantly negatively charged, which indicates that X^a should be selectively substitutable. The band structure calculations show that band gap energy of the $Cs_2[Mo_6X^i_8X^a_6]$ compounds varied over entire visible absorption range. Hence, the DFT calculations predict that optical properties of the $Cs_2[Mo_6X^i_8X^a_6]$ 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 $Cs_2[Mo_6Cl_{14}]$ has been investigated. For this purpose, $Cs_2[Mo_6Cl_{14}]$•H_2O and $Cs_2[Mo_6Cl_{14}]$ were used as precursors and water insertion was removed by dispersing the precursors in hydrophilic alcohol solvents such as MeOH, EtOH, and 1-PrOH. Consequently, dehydrated $Cs_2[Mo_6Cl_{14}]$ was obtained by recrystallization with EtOH or 1-PrOH regardless of precursor composition. In contrast, the sample recrystallized with MeOH resulted in a monoclinic form similar to $Cs_2[Mo_6Cl_{14}]$•H_2O even using the anhydrous precursor. Powder X-ray diffraction (XRD), thermal desorption spectroscopy and Fourier transform spectroscopy suggest that obvious water insertion was not observed in the sample recrystallized with 1-PrOH as solvent. Furthermore, time-resolved photoluminescence (TRPL) study shows that emission lifetime of $Cs_2[Mo_6Cl_{14}]$ 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 $Cs_2[Mo_6Cl_{14}]$, leading to enhancement of luminescence performance.

[Section 4] The section reports synthesis of ternary $Cs_2[Mo_6X_{14}]$ and quaternary $Cs_2[Mo_6X^i_8X^a_6]$ ($X^i \neq X^a$). First, the ternary compounds were synthesized through solid-state reactions and subsequently quaternary ones were synthesized from the ternary precursors through ion-exchange of X^a using $AgBF_4$ as intermediates. X-ray photoemission measurements indicate that almost X^a of $Cs_2[Mo_6X_{14}]$ 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*31*c* or *P*-31*c* space group), but $Cs_2[Mo_6Br^i_8Cl^a_6]$ exhibited the monoclinic phase, indicating stable crystalline phase possibly varies according to (X^i, X^a) combinations.

[Section 5] Optical properties of prepared $Cs_2[Mo_6X^i_8X^a_6]$ 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 $[Mo_6X^i_8X^a_6]^{2-}$ complex does not correlate with its band gap energy and is strongly dominated only by the 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 $Cs_2[Mo_6Cl^i_8Br^a_6]$, $Cs_2[Mo_6Cl^i_8I^a_6]$, and $Cs_2[Mo_6Br^i_8I^a_6]$, suggesting that they did not possess an inversion center in the lattice. Hence, This evidences 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 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 $Cs_2[Mo_6X^i_8X^a_6]$ compound system through comparison the results of DFT calculations and experimental observations. Finally, future perspectives to utilize the $[Mo_6X^i_8X^a_6]^{2-}$ complex as virtual elements of crystalline solids is generally discussed. Through these discussion, the thesis shows a pathway for exploring new functional crystalline materials.

The committee members agreed that the above thesis satisfies the requirements for the conferment of the doctoral degree in Engineering.