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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, $[Mo_6X^i_8X^a_6]^{2-}$, as a candidate of elements for construction of novel crystalline compounds with optoelectronic functionalities. The $[Mo_6X^i_8X^a_6]^{2-}$ 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 $[Mo_6X^i_8X^a_6]^{2-}$ 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^is and X^as possibly enables us to control the optical properties and realize functionalization based on crystal symmetry. In this context, the thesis has focused on a $[Mo_6X^i_8X^a_6]^{2-}$-based compound system, $Cs_2[Mo_6X^i_8X^a_6]$, 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 $Cs_2[Mo_6X^i_8X^a_6]$

Crystal structures and electronic properties of $Cs_2[Mo_6X^i_8X^a_6]$ (X = Cl, Br, I) were calculated by density functional theory (DFT). Consequently, how halogen species and their coordination sites affect electronic structures of $Cs_2[Mo_6X^i_8X^a_6]$ 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., *P*31*c* and *P*-31*c* 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 $Cs_2[Mo_6Cl_{14}]$

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 $Cs_2[Mo_6Cl_{14}]$ was focused and impurities interaction was removed by recrystallization in some hydrophilic alcohol solvents where $Cs_2[Mo_6Cl_{14}]$ powders were dispersed. As a result, it is found that 1-proponol is particularly suitable as a solvent for purification of $Cs_2[Mo_6Cl_{14}]$ and the purification treatment made the luminescence lifetime much longer than that of water-contaminated samples.

Section 4. Synthesis of halogen-substituted $Cs_2[Mo_6X^i_8X^a_6]$ compounds

Metal-cluster compounds with single halogen specimen ($X^i = X^a$) and different halogen species ($X^i \neq X^a$) were synthesized using solid-state reactions and ion-exchange reactions in solutions to substitute X^as 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 $Cs_2[Mo_6X_{14}]$ can be substituted by the ion-exchange reactions.

Section 5. Crystal structure and optical properties of $Cs_2[Mo_6X^i_8X^a_6]$

Crystal structures and optical properties of the $Cs_2[Mo_6X^i_8X^a_6]$ compounds synthesized in the previous section were characterized. Particularly, second harmonic generation (SHG) measurements suggest that some quaternary trigonal-phase compounds such as $Cs_2[Mo_6Cl^i_8Br^a_6]$, $Cs_2[Mo_6Cl^i_8I^a_6]$ and $Cs_2[Mo_6Br^i_8I^a_6]$ exhibited clear SHG signals under excitation with a high-intensity infrared pulsed laser. This result indicates that the $Cs_2[Mo_6X^i_8X^a_6]$ 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 $[Mo_6X^i_8X^a_6]^{2-}$ complexes for construction of crystalline compounds were summarized. Finally, remaining issues and future prospects which were identified in this study are described.