論 文 の 要 旨

題 目 Synthesis, Structural Characterization, and Thermal Transformation of Methylammonium Isopolyoxometalates, and their Application as Staining Reagent for SARS-CoV-2 Observation

(メチルアンモニウムイソポリオキソメタレートの合成、構造解析、加熱による構造変換、および SARS-CoV-2 観察のための染色試薬としての応用)

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Polyoxometalates are anionic polynuclear metal–oxo molecules of early transition metals, such as W, Mo, V, and Nb, formed between metal oxides (WO_3 or MoO_3) and monometalates ($[WO_4]^{2-}$ or $[MoO_4]^{2-}$). The primary goal of this dissertation was to synthesis of alkylammonium isopolyoxometalates and their crystal transformation by heat treatment. Methylammonium monomolybdate, methylammonium vanadate, and methylammonium paradodecatungstate were prepared by the reaction of methylamine solution with MoO_3, V_2O_5, and WO_3 or H_2WO_4, respectively.

Methylammonium monomolybdate, $(CH_3NH_3)_2MoO_4$ contained monomeric $[MoO_4]^{2-}$ and two methylammonium counter cations, which crystallized in the space group *Pnma*. Solid state heating of the $(CH_3NH_3)_2MoO_4$ in air released water and methylammonium to produce several methylammonium isopolymolybdates such as $(CH_3NH_3)_8[Mo_7O_{24}\text{-}MoO_4]$, $(CH_3NH_3)_6[Mo_7O_{24}]$, $(CH_3NH_3)_8[Mo_{10}O_{34}]$, and $(CH_3NH_3)_4[Mo_8O_{26}]$, and molybdenum oxides such as hexagonal MoO_3 and orthorhombic MoO_3 which were confirmed by single crystal XRD, powder XRD, IR, Raman, and elemental analysis.

The asymmetric unit of methylammonium vanadate, $(CH_3NH_3)[VO_3]$ contained four methylammonium cations and a “snake-like” $([VO_3]_4)^{4-}$ anion chain along the *c*-direction in the $Pna2_1$ space group. The solid-state thermal structure transformation of methylammonium vanadate, $(CH_3NH_3)[VO_3]$, from -150 °C to 350 °C is reported. A reversible structural transformation due to the change in the direction of the methylammonium cations in the crystal packing was observed between −150 and −100 °C, which is also confirmed by the reversible profiles observed in differential scanning calorimetry. The methylammonium vanadate is stable until at ca. 100 °C and further heating releases methylamine and water and V_2O_5 is formed at ca. 275 °C .

Methylammonium paradodecatungstate, $(CH_3NH_3)_{10}[H_2W_{12}O_{42}]\cdot nH_2O$, contained $[H_2W_{12}O_{42}]^{10-}$ anion, ten methylammonium cations, and lattice water. The $[H_2W_{12}O_{42}]^{10-}$ anion consists of two HW_3O_{13} groups containing three edge-sharing WO_6 octahedra and two W_3O_{14} groups having two edge-sharing connections. Some lattice water was released by drying the produced material at 70 °C, but this did not affect the $[H_2W_{12}O_{42}]^{10-}$ structure, although there was a decrease in the unit cell volume. By adding water, the loss of lattice water and structural changes were reversed. CH_3NH_2 and H_2O were released by heating methylammonium paradodecatungstate at more than 150 °C, and the amorphous phase was observed as an intermediate product and monoclinic WO_3 as the final product.

Negative staining is a valuable technique for viewing the detailed morphology and size of the intact virus. The primary distinction between members of viral families is their morphology, so viral morphology is crucial to the study of virology. In this dissertation, we evaluate the performance of synthesized methylammonium molybdate, tungstate, and vanadate as staining reagents for transmission electron microscopy observation of SARS-CoV-2. The results show that methylammonium polyoxometalates are a potential negative staining agent for observing the spike protein of coronaviruses. Based on the contrast and sharpness of the stained particles, methylammonium heptamolybdate was found to be an excellent staining agent for observing the SARS-CoV-2 delta variant.