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| 学位論文題目 | Studies on flux growth of inorganic oxide-based ion exchange crystals with two- or three-dimensionally nanostructured channels (二次元および三次元ナノ空間構造をもつ無機イオン交換結晶のフラックス育成に関する研究) |
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論 文 内 容 の 要 旨

“Materials” are identified as substances in the condensed states that show performances and are intended to be used for certain applications. Usually, materials are preferred to describe as a set of “composition + structure”, wherein the “structure” including crystallinity, nanostructure, and morphology of the material which is strongly affected by the preparation method. A flux growth technique is a powerful method to grow idiomorphic crystals below the melting point of the solutes. Herein I focuses on the flux growth of inorganic oxide materials with high crystallinities, specific ion exchangeable nanostructural channels, well-developed crystal facets, and appropriate appearance morphologies and understanding their growth manner from fluxes.

In **Chapter 1**, factors that affect the performance of material, flux growth method, and my overall research objective are summarized.

Chapter 2 deals with the low-temperature growth of idiomorphic $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ single crystals from LiOH flux. The $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ crystals were grown at 500 °C from LiOH flux and transformed into $\text{Li}_7\text{La}_3\text{Ta}_2\text{O}_{13}$ at 700 °C. Pseudo-perovskite-type $\text{LiLa}_2\text{TaO}_6$ phase, initially formed during the holding at 500 °C, was efficiently transformed into $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ phase with increase in holding time. The growth of $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ crystals was independent of the cooling rate, but was affected by flux type and solute concentration. A low solute concentration (1 or 5 mol%) was the key to obtain well-dispersed and idiomorphic single crystals. All the results indicate that formation and growth of $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$ single crystals are not only controlled by a general flux growth process, but also involve chemical reactions between solutes and LiOH flux. Finally, high-resolution transformation electron microscopy image and selected area diffraction pattern highlighted products with high crystallinity and well-developed {110} and {211} facets.

In **Chapter 3**, the flux growth of $\beta\text{-Li}_2\text{TiO}_3$ crystals is studied comprehensively under different conditions, and the efficient anisotropic growth of {001}-faceted $\beta\text{-Li}_2\text{TiO}_3$ single crystals is demonstrated using the Na_2SO_4 flux method. In the Na_2SO_4 flux at 1000 °C, the optimal solute concentration is 20 mol% for growing large (~15.0 μm in lateral size), platy, and faceted $\beta\text{-Li}_2\text{TiO}_3$ crystals. Observations from varying the holding time indicated that these crystals were

anisotropically grown. TEM images with clear electron diffraction spots revealed that the flux-grown platy β - Li_2TiO_3 are single crystals with $\{001\}$ dominated facets. This anisotropic crystal growth could be attributed to the concerted effects of the preferential attachment of sodium cations on the $\{001\}$ faces, and efficient dissolution of β - Li_2TiO_3 crystals as well as the solvation of the resulting O^{2-} ions in the oxysalt flux.

Chapter 4 presents a combined experimental and computational study of KTiNbO_5 (KTN) as a selective and durable adsorbent for Sr^{2+} ions. KTN grown from nitrate flux at 500–600 °C (KTN_{flux}) has a zigzag layered gallery space. Structural analysis indicates that KTN_{flux} crystals are platy with surface areas of 48–86 $\text{m}^2\cdot\text{g}^{-1}$. These areas are ~ 50 times larger than those of KTN prepared by solid-state reaction at 1100 °C as a result of efficient, anisotropic crystal growth. Sr^{2+} adsorption experiments indicate that the Sr^{2+} ion-exchange capacity of KTN_{flux} is ~ 1.04 $\text{mmol}\cdot\text{g}^{-1}$, and most of the ion-exchange sites are homogeneous. Kinetic analysis shows that the Sr^{2+} ion-exchange rate on KTN_{flux} is one order of magnitude higher than that on KTN_{SSR} . The $[\text{Na}^+]$ concentration dependence of the distribution coefficient K_d for Sr^{2+} indicates that KTN_{flux} shows high affinity for Sr^{2+} and remarkable durability, and $K_d > 1.26 \times 10^4$ $\text{mL}\cdot\text{g}^{-1}$ even at $[\text{Na}^+] = 0.1$ $\text{mol}\cdot\text{L}^{-1}$. The origin of the high selectivity for Sr^{2+} was studied by density functional theory. The calculations indicate that the high preference for Sr^{2+} is due to confinement within subnanometer-sized pockets built from oxygen species of both the anionic metalate frameworks and intercalated water molecules, forming monocapped heptahedra or octahedra that resemble the active sites of enzymes.

In **Chapter 5**, the conclusions from the present research as well as future perspectives are summarized.