Topotactic Synthesis of Ca_2MnO_4 Ruddlesden-Popper Perovskite Polyhedra

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Introduction

In developing novel functional ceramic materials, independent controls over the crystalline phase and the morphology are important. As a major strategy to achieve the morphological control, the solution processes have been extensively studied for various ceramics. In the previous report, cubic microparticles of $Ca_3Al_2(OH)_{12}$ hydrogarnet were prepared via a solution process, and the topotactic transformation followed by selective removal of CaO gave rise to porous mayenite microcubes.[1] It was also revealed that the porous $SrFeO_{3-\delta}$ perovskite particles can be obtained from the $Sr_3Fe_2(OH)_{12}$ hydrogarnet precursor by the similar approach.[2] However, the appropriate combination of two types of cations, divalent and trivalent, as well as suitable ionic radii are required to synthesize targeted hydrogarnets. In this study, we aimed to extend the range of compounds that can be prepared by using carbonate solid solutions as a precursor for topotactic synthesis. $Ca_xMn_{1-x}CO_3$ solid solution with polyhedral shape was prepared by hydrothermal synthesis, and Ca_2MnO_4 Ruddlesden-Popper perovskite polyhedra were obtained by selective removal of CaO after calcination.

Experimental Procedures

The precursor $Ca_xMn_{1-x}CO_3$ particles were prepared by the hydrothermal synthesis. First, given amounts of $Ca(CH_3COO)_2{\cdot}H_2O$ and $Mn(CH_3COO)_2{\cdot}4H_2O$ were dissolved in a mixed solvent of diethylene glycol and distilled water followed by the addition of N,N-dimethylethylenediamine and ammonium carbonate. The resultant slurry was transferred into a Teflon-lined stainless steel autoclave and heated at 100 ºC for 16 h. The product was separated by centrifugation, washed with distilled water and dried at 60 ºC for 24 h. The dried powder was calcined in air at 700 ºC for 1 hour, and porous Ca_2MnO_4 polyhedral particles were obtained by selectively removing the CaO byproduct. The samples were characterized by powder X-ray diffraction (XRD), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) and N_2 adsorption-desorption measurements.

Results and Discussion

Figure 1 shows the SEM-EDX elemental mapping images of the carbonate precursor prepared with a Ca/Mn ratio of 7/3. The particles exhibited polyhedral morphology with uniform shapes. Elemental mapping revealed that Ca and Mn were homogeneously distributed within each particle, suggesting the formation of $Ca_xMn_{1-x}CO_3$ solid solution. Figure 2 shows the XRD patterns of the $Ca_xMn_{1-x}CO_3$ precursor and the calcined samples. After calcination above 700 ºC, the peaks of $Ca_xMn_{1-x}CO_3$ disappeared, and new peaks assigned to Ca_2MnO_4 and CaO appeared, showing decomposition into these phases. Figure 3 presents the XRD patterns of the samples after calcination and after removal of the secondary phase. While the calcined sample contained both Ca_2MnO_4 and CaO, single-phase Ca_2MnO_4 was successfully obtained after the selective CaO removal.

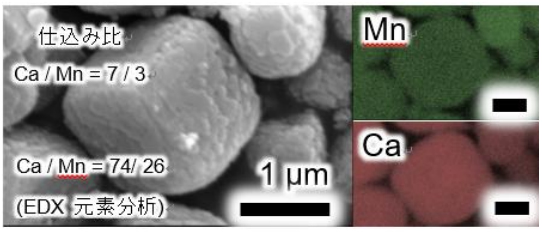

Fig. 1 SEM and EDX elemental mapping images of the $Ca_xMn_{1-x}CO_3$ particles.

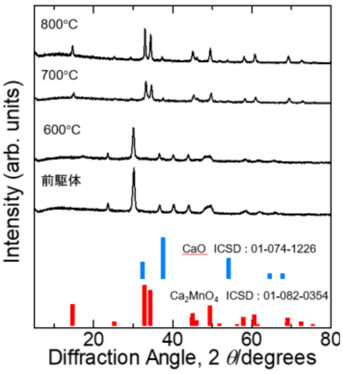

Fig. 2 XRD patterns of the $Ca_xMn_{1-x}CO_3$ particles and the calcined sample

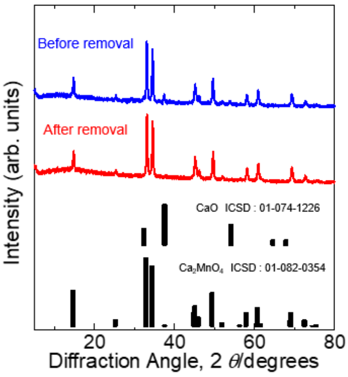

Fig. 3 XRD patterns of the calcined sample and removed CaO.

References

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