Low-temperature synthesis of britholite-(La) by co-precipitation method and its properties

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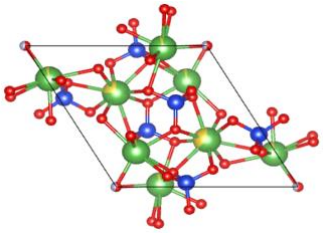
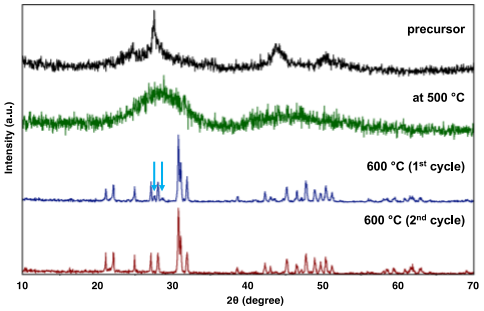


The structure of britholite-(La)

Since Nakayama et al. reported that apatite-type structures of compositions $Ln_{10-x}Si_6O_{26+y}$ (Ln = La Sm, Nd, Dy, Gd, x = 8 to 11) materials exhibited high ionic conductivity,[1] rare-earth apatite material with high conductivity have been investigated to develop new electrolytes working at intermediate temperature. Ito et al. first synthesized britholite-(La) crystals considered to be of composition $Na_2La_8Si_6O_{24}F_2$, which is a *pseudo*-hexagonal P21 sub-symmetry of the P63/m apatite in a study of silicate apatite structures.[2] In general, the preparation of apatite requires a high calcination temperature of more than 1000 °C, which consumes a lot of energy for the preparation of apatite-based materials. In this study, we developed a low-temperature preparation method of britholite-(La).



PXRD of britholite-(La) obtained by co-precipitation method.

The raw material was prepared by coprecipitation method in water. In the presence of lanthanum nitrate ($La(NO_3)_3 \cdot 6H_2O$) and sodium fluoride (NaF), an aqueous solution of sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$) was added. The thus-formed solid was calcined at 600 °C twice to afford britholite-(La). The formation of apatite structure was confirmed by powder X-ray diffraction (PXRD) analysis. In addition, it was found that Bi, Fe and Ce can be doped at the La site with maintaining britholite structure. The ion conductivity measurement of pristine britholite-(La) showed considerably high conductivity of 1.17×10^{-3} S cm^{-1}.

Previous work

$La_2O_3 + SiO_2$ —(NaF flux, 1350 °C to 950 °C)→ Transparent crystals $Na_2La_8Si_6O_{24}F_2$

This work

$La(NO_3)_3 + NaF$ —(Na_2SiO_3 solution, Dropwise)→ The as-prepared white powder —(Calcine, 600 °C, 4h in air)→ Britholite-(La)

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2) I. Ito, Am. Mineral. **1968**, *53*, 890.

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