Composition and crystal chemistry of hydrothermally synthesized rare earth fluorocarbonate minerals

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Behavior of rare earth elements in geosphere is a good indicator of the geochemical conditions and processes. Crystal chemistry of rare earth minerals may have essential key to understand the relationship between rare earth element species and mineralogical and geochemical behavior of the rare earth elements. In this study, we carried out hydrothermal synthesis experiments of rare earth fluorocarbonate minerals. The starting materials of the experiments are reagent mixture of La, Nd or Gd fluoride and carbonate and $CaCO_3$. Experimental conditions are at water vapor pressure from 100^{o}C to 300^{o}C with sealed vessels, and at 100MPa from 300^{o}C to 500^{o}C with cold seal hydrothermal synthesis reactors. Run durations are from 6 days to 126 days. Run products are observed by SEM and analyzed by powder X-ray diffractometer.

In the run products, REE fluoride crystals are substituted by bastnaesite ($REE(CO_3)F$). Bastnaesite crystals contain substantial amount of CaO component. Semi-quantitative analysis of CaO wt.% shows negative correlation to the experimental temperatures from approximately 3% to 0.5% on Nd and Gd-bastnaesite. However, bastnaesites produced in La series have less than 0.5wt.% of CaO in all temperatures.

Powder X-ray diffraction revealed that cell dimensions of Nd and Gd-bastnaesite expand with run temperature. However, cell dimensions of La-bastnaesite shrinks with temperature. Full Width at Half Maximum (FWHM) of d_{110} peaks decrease with temperature in all three REEs, but those of d_{002} peaks show different behavior. FWHM of La-bastnaesite d_{110} peak decreases like d_{002} peak. However, those of Nd and Gd-bastnaesite show the maximum at approximately 300^{o}C.

Six-coordinated Ca^{2+} ion has ionic radii between La^{3+} and Nd^{3+}. Characteristics of cell dimensions of synthesized bastnaesite shows effects from crystallization depending on run temperature and disturbance from CaO component.