

Incorporation of rare earth elements in perovskites: The case of Neodymium incorporation in CaSnO₃

GOETHALS. J¹, FOURDRIN. C¹, TARRIDA. M¹,
HATERT. F², BEDIDI. A¹, ROSSANO. S¹

¹Laboratoire Géomatériaux et Environnement, 1 allée du
promontoire, 93160 Noisy le Grand

²Laboratoire de minéralogie, Allée du 6 août, B18, 4000 Liège

Synroc is a synthetic assembly of titanate phases to immobilize radioactive waste and perovskite is one of its major constituent ($\approx 25\%$). It is generally assumed that REE³⁺ and transuranic elements substitute Ca in CaTiO₃ perovskite of SYNROC owing to the proximity of their ionic radii. In this case, the mechanism of charge compensation can be explained either by partial replacement of Ti by Al, A site vacancies or titanium reduction to Ti³⁺ state. Several factors can affect the substitution mechanisms (such as the A/B cationic ratio, the percentage of REE³⁺ incorporation, the ionic radii of the REE³⁺, the atmosphere of synthesis...). In this study, we investigated the incorporation of Nd³⁺ in the CaSnO₃ perovskite, an analogue of CaTiO₃ with an orthorhombic structure *Pbnm*.

CaSnO₃ powder was synthesized by a conventional solid state route. The sintered CaSnO₃ was then mixed with Nd(OH)₃, pressed into pellet and sintered at 1550°C for 3 days. Samples with varying compositions (ranging from 5 to 60 wt% of Nd) were then analysed by XRD, SEM, EMPA and Raman spectroscopy. Incorporation of Nd in the perovskite phase was successful up to 50% wt. The evolution of the lattice parameters is following a Vegard's law. A phase transition from an orthorhombic *Pbnm* structure to a monoclinic *P2₁/n* structure is observed around Nd=30 wt%. The grain size of the ceramics globally increases with the Nd incorporation. Thus, crystals of the Nd 40 wt% and Nd 50 wt% samples were adapted for a single crystal XRD investigation. The results show that Nd substitutes Ca in the A site of the structure. The excess of positive charge on the A site due to the substitution of a divalent cation by a trivalent one is compensated by a migration of the calcium substituted on A site, to the Sn B site.

Depending on the different synthesis parameters, several crystallochemistry could be obtained due to the huge flexibility of the perovskite structure. Besides, the durability of those perovskites might be affected by the different substitutions mechanisms. Further studies on the CaTiO₃ doped perovskite are therefore necessary to apprehend its long-term behavior in SYNROC.