

Study of structure and durability of CaTiO₃ doped with rare earth elements

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SYNROC is a ceramic composed of several titanate phases designed to immobilize radioactive waste. CaTiO₃ perovskite is one of its major components and many studies demonstrated that, in CaTiO₃, Ca can be substituted by trivalent Rare Earth Elements (REE) thanks to their close ionic radii. In a study on a Nd-doped CaSnO₃ perovskite a new substitution mechanism was revealed Nd substitutes the Ca on the Ca site and the excess of charge is compensated by the migration of Ca on the Sn site (Ca_{1-2x}Ln_{2x})(Sn_{1-x}Ca_x)O₃ [1]. In this study, we verify that this mechanism of incorporation can be applied on three REE (Ln = La, Pr and Nd) in the structure of CaTiO₃ and we also investigate their durability.

CaTiO₃ powder was synthesized by the solid-state method, then mixed with trivalent REE oxide and sintered at 1500°C during 24h. Samples of different compositions (ranging from 5 to 25 wt% of REE) were then characterized by XRD, EMPA, SEM, XAS and Raman spectroscopy. The structure of those doped perovskites is orthorhombic and the suggested substitution mechanism is the same as for REE-doped CaSnO₃ (Ca_{1-2x}Ln_{2x})(Ti_{1-x}Ca_x)O₃.

Alteration experiments were conducted at 80°C and pH 1 on powdered samples of our REE-doped perovskites during several months. In order to evaluate the impact of another doping mechanism, the durability of Ca_{1-3x/2}Ln_xTiO₃ perovskite was studied in the same conditions. The leachates were analyzed by ICP-OES to determine the concentration of released Ca and REE. The dissolution of those doped perovskites revealed a dependence on the incorporation rates and on the nature of the trivalent REE. The dissolution rate increase with larger ionic radii and the incorporation rates of REE. The residual powders were analyzed by Raman spectroscopy and SEM, an alteration product was identified as anatase, a titanium oxide phase on the reacted surface in agreement with Zhang *et al.* (2005) [2]. Finally, the dissolution behavior of doped perovskites are different depending of the substitution mechanisms.

[1] Goethals *et al.* (2018), *Physics and Chemistry of Mineral* 46, 143-155.

[2] Zhang *et al.* (2005), *Journal of Materials research* 20, 2462-2473.