

Structural investigation of Nd incorporation in CaSnO₃ perovskite

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The perovskite structure type ABO₃, which is adopted by a large variety of materials of geological and technological interest, has been extensively investigated in the past decades. Among the interesting compounds the CaSnO₃ perovskite has received increasing attention either for its use as analogue for the mantle material (Redfern & al. 2011) or for its wide range of potential applications such as dielectric bodies, gas sensors and anode materials for Li-ion batteries (Cheng & Lu 2008). When doped with a trivalent rare earth element (REE³⁺), the CaSnO₃ perovskite exhibits promising luminescence properties (Lu & al. 2005; Orsi Gordo & al. 2015). However, the exact distribution of the REE³⁺ between the two potential substitution sites is yet not completely understood. Although it could yield better insights on these luminescence properties. This study thus focuses on the determination of the Nd³⁺ distribution in the CaSnO₃ perovskite.

Ceramics have been sintered at high temperature (1550°C) for a wide range of composition (1-x)CaSnO₃-xNd₂O₃ (with 0 ≤ x ≤ 0.7). X-ray diffractometers have been measured in the 2θ range 10°-110°. Rietveld refinements of the structures have been performed using Fullprof. Raman spectra have been measured using a 477 nm laser in order to reduce the presence of a fluorescence signal. It is shown that CaSnO₃ can incorporate a large amount (up to x ≈ 0.5) of Nd, at the difference with CaZrO₃ that can only accommodate up to x ≈ 0.35 in the system (1-x)CaZrO₃-xNd₂O₃ (Larguem, 2006). For x ≤ 0.5, the unit cell parameters were obtained using the Treor software, and the space groups were determined in an orthorhombic system using Checkcell. It is observed that the unit cell parameters increase linearly with the amount of incorporated Nd. Below x = 0.3, the X-ray patterns are indexed in the orthorhombic Pbnm space group. Over this value, the appearance of new reflections leads to a lowering of the symmetry to the Pmnm space group. This result suggests a phase transition induced by the Nd incorporation. On the whole range of compositions, Raman vibration modes are strongly affected by the Nd incorporation. An important broadening of almost all the vibrational bands and a shift of some of them are observed. Substitution of divalent and tetravalent cations on A and B sites have produced similar effects on Raman spectra of the solid solution systems (Sr_xCa_{1-x})ZrO₃, Ca(Zr_ySn_{1-y})O₃ (Tarrida & al. 2009). Combining Rietveld refinement on the different samples and Raman spectra analysis, the modifications of the CaSnO₃ structure in presence of Nd³⁺ are consistent with a majority of Nd³⁺ substituting Ca²⁺ in the A site. A slight proportion of Nd³⁺ however substitutes Sn⁴⁺ in the B site.

The data obtained in this study complement the existing literature on the substitution of trivalent cations in the perovskite structure especially by evidencing a phase transition, although a linear evolution of the unit cell parameters is observed.

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