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# $CaSn(OH)_6$ hydroxides, $CaSnO_3$ oxides and $CaSnF_6$ fluorides: Synthesis and structural filiation. Cationic environment impact on $Pr^{3+}$ doped compounds luminescence

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## ABSTRACT

$CaSn(OH)_6$, $CaSnO_3$ and $CaSnF_6$ compounds were elaborated from a “one-batch” synthesis route: the coprecipitation of the pure double hydroxide leads to pure double oxide or fluoride after annealing treatments under air or HF as anhydrous gas, respectively. Structural and morphological features of the three matrices were carefully investigated by X Ray Diffraction analysis and Scanning Electron Microscopy, respectively. In addition, the luminescent properties of the Pr-doped compounds were performed and compared. The nanometric size of the double hydroxide inhibits the luminescence. The interpretation of the emission spectra obtained for Pr-doped $CaSnO_3$ and $CaSnF_6$ compounds is based on the covalence/ionic balance of the M–O or M–F bonds.

## 1. Introduction

Because of their wide range of applications, perovskite-type alkaline earth metal stannates of formula $MSnO_3$ have been deeply investigated. Surprisingly, the luminescent properties of rare earth doped perovskite related structure are not largely reported yet [1–9]. However, promising results describe the photoluminescence of praseodymium doped perovskite as novel materials for multifunctional devices as the absorption lines of this rare earth overlaps the emission of commercial blue diode [10–19].

The $CaSn(OH)_6$, $CaSnO_3$ and $CaSnF_6$ exhibit obvious structural filiation. Indeed, these compounds have a structural network built on corner-sharing octahedra constituting the covalent skeleton. $CaSn(OH)_6$ and $CaSnF_6$ can be described as “double - $ReO_3$” structure in which $Ca^{2+}$ and $Sn^{4+}$ are strictly alternately distributed to form the octahedral chains. The octahedral sites of the double hydroxide are anisotropic, with low point group symmetry. Historically, $CaSn(OH)_6$ crystal was described as an orthorhombic perovskite structure with a $P\ n\ -3$ space group, where the $Ca(OH)_6$ and $Sn(OH)_6$ octahedra share corners. More important, this framework can facilitate the mobility of the charge carriers, and then enhance the photocatalytic activity of $CaSn(OH)_6$ under light irradiation [20]. Nonetheless, the twist of the octahedral sites can also occur in such a way that a cubic unit-cell is maintained with $P\,n\,-3m$ space group [21], as for the Ca-Sn hydroxides (burtite) prepared in our work. The double fluoride is constituted of non-twisted isotropic octahedral sites that lead to a cubic unit-cell with $F\ m\ -3\ m$ space group. Regarding $CaSnO_3$, the octahedral skeleton is built on $[SnO_6]$ tilted octahedra ($P\ b\ n\ m$ space group), the $Ca^{2+}$ ions occupying the interstitial icosahedral sites. A scheme emphasizing the structural similarities and differences between the three studied compounds is reported (Fig. 1.).

Even if a common skeleton is clearly visible and although cationic local environment is quite similar in the three matrices, the anionic group or ligands deeply change the nature of the chemical bonding. Because of their low phonon energy, their high transparency in the infrared and their stability under an exciting beam, fluoride hosts are of great interest for laser, up-converting or up-conversion materials [22–27]. Nevertheless, the increase of the chemical bonding ionicity is generally associated to an UV/blue shift of the spectral distribution, which can reduce drastically the efficiency of the absorption process regarding the matching with excitation sources.

Synthesis flow charts of $CaSn(OH)_6$ were recently described in literature [28,29]. $CaSnO_3$ perovskite compounds are typically synthetized at high temperature (over 1200 °C) from traditional solid state reaction between CaO and $SnO_2$ oxide [30–32] Nevertheless, a two-step method was already employed for $CaSnO_3$ sample preparation

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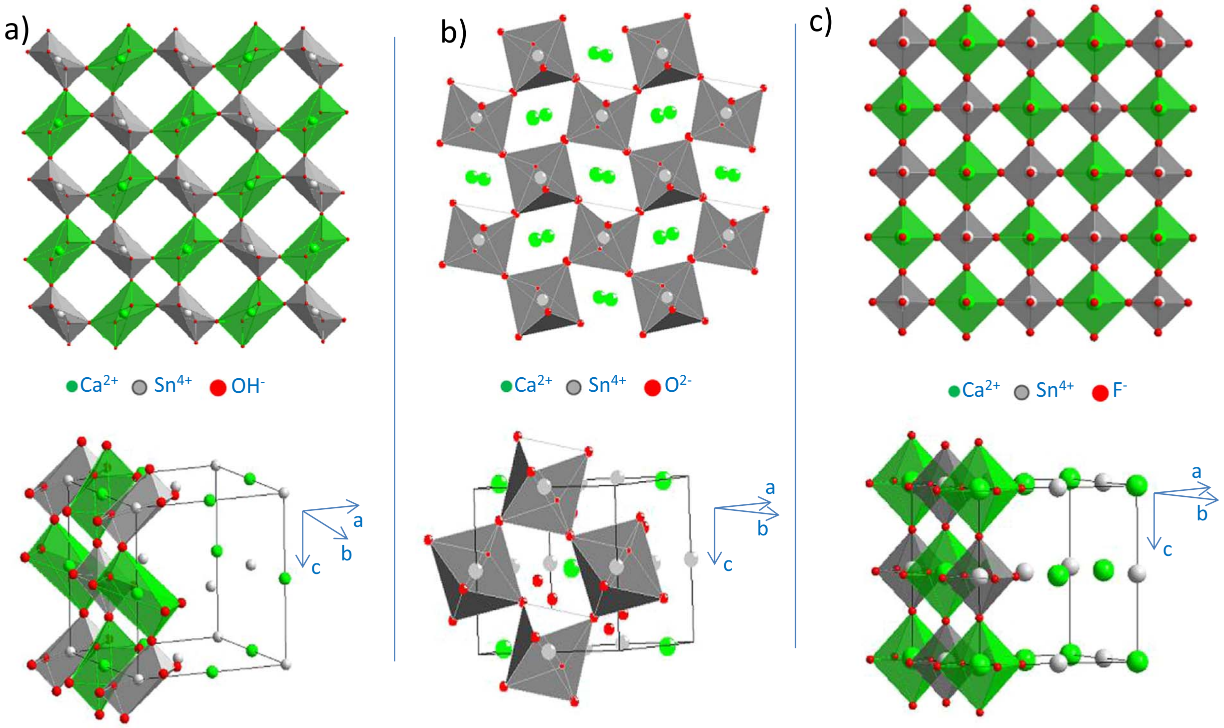

**Fig. 1.** a) Structural description of a) $CaSn(OH)_6$; b) $CaSnO_3$; c) $CaSnF_6$ crystals.

including the synthesis at room temperature of the precursor $CaSn(OH)_6$ and then its conversion into $CaSnO_3$ by calcination [29,33–35]. $CaSnF_6$ compounds were typically made by solid state synthesis in a sealed tube [36]. By consequence, it represents a high challenge to find new synthesis routes of doped $CaSnF_6$ phases, cost-effective and with industrial feasibilities.

The first part describes the synthesis and the structural characterizations of the $CaSn(OH)_6$, $CaSnF_6$ and $CaSnO_3$ compounds. Especially, the description of a specific synthesis process based on the fluorination of $CaSn(OH)_6$ precursor is detailed. In a second part, the balance of the ionic-covalent bonds surrounding the luminescent ions is compared. We propose here to follow the evolution of the luminescent properties of $Pr^{3+}$ doped compounds as a function of the chemical bonding nature. Crystal field effect will be highlighted through the *4f–4f* absorption and emission lines of trivalent praseodymium. These three compounds issued from a single synthesis batch and which present a strong structural filiation constitute school-case examples for studying the impact of the iono-covalence of the bonds around the luminescent ion, on the optical properties. This constitutes a first step to control and drive the emission properties to a targeted range.

## 2. Materials and methods

### 2.1. Synthesis

A co-precipitation process in aqueous solution allows obtaining the polycrystalline hydroxide compounds with $CaSn(OH)_6$ or Pr-doped $CaSn(OH)_6$ target formulae. $CaCl_2$ and $SnCl_4.5H_2O$ with eventually $Pr(NO_3)_3$, are firstly introduced into stoichiometric concentration into 25 mL of water. NaOH aqueous solution is added to the cationic solution in order to adjust the final pH to 10, 11.5 or 13. Once the precipitation has occurred, a maturation time of the precipitate under magnetic stirring is made during 2 h; the precipitate is filtered and washed with demineralized water. The solid residue is then crushed into an agate mortar. The as-prepared powders are then placed into a tubular furnace and treated at 1200 °C – 12 h under air, or between 100 and 250 °C – 2 h under HF gas atmosphere in order to obtain the mixed oxides and mixed fluorides, respectively. It can be noted that HF gas requires necessary warming: an inductive heater allows the heating avoiding HF and resistance contacts and the HF outgas is neutralized through KOH traps in order to be free of toxic exhaust gas production.

The $CaSnO_3$ and $CaSnF_6$ matrices and the corresponding 2 mol% Pr-doped oxide or fluoride ($CaSn_{0.98}Pr_{0.02}O_3$ and $CaSn_{0.98}Pr_{0.02}F_6$) are crushed before characterization.

### 2.2. X-ray diffraction analysis

Powder X Ray Diffraction (XRD) patterns were collected on a Philips X′Pert MPD diffractometer operating in Bragg-Brentano geometry with a Cu $K_{\alpha1,2}$ radiation ($10 < 2\theta < 130°$, step 0.02° and counting time of 30 s). Some of the diffraction patterns were refined using the full-pattern matching method (Le Bail) with the conventional reliability factors (Fullprof program package). Unit-cell parameters, zero-shift and peak profile parameters were refined.

### 2.3. ICP titration

ICP/OES (Inductively Coupled Plasma / Optical Emission Spectrometry) was conducted on Varian ICP/OES 720 ES apparatus.

### 2.4. SEM images

The Scanning Electron Microscopy (SEM) analyses were performed with a JEOL Field Emissive Gun – Scanning Electron Microscope (FEG-SEM) in order to characterize the crystallite (shape, size and special rearrangement) with a spatial resolution of about 1 nm.

### 2.5. Mossbauer investigation

$^{119}$Sn Mossbauer measurements were carried out using a constant-acceleration Halder-type spectrometer operating in transmission geometry with a room temperature $^{119m}$Sn source (370 MBq, $CaSnO_3$ matrix). Thin absorbers containing about 10 mg cm$^{-2}$ of Sn ($^{119}$Sn natural abundance 8.59%) were placed into a liquid helium bath