



# Key parameters for spark plasma sintering of wet-precipitated iodate-substituted hydroxyapatite



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## ARTICLE INFO

### Article history:

Received 4 September 2015

Received in revised form 19 February 2016

Accepted 22 February 2016

Available online 28 February 2016

### Keywords:

Iodine

Apatite

Iodate

Sintering

Nuclear waste

## ABSTRACT

A possible strategy for the management of radioactive iodine-129 is to incorporate it under the form of iodate in hydroxyapatite matrices (HA-CaI) intended to be stored in deep geological repositories. To meet disposal requirements, powder materials that were here obtained by a wet-precipitation route required shaping. In this work, we demonstrate that sintering of HA-CaI could be achieved by spark plasma sintering (SPS) at low temperature ( $T < 300^\circ\text{C}$ ) without iodine volatilization. Such densification was only possible if a non apatitic hydrated calcium phosphate layer was present at the surface of grains, the content of which directly depended on synthesis conditions. The higher the proportion of hydrated layer, the better uniaxial cold compaction and densification during sintering. For an optimised HA-CaI powder, a relative density of 88% could be reached using a pressure of 100 MPa, a dwell temperature of  $250^\circ\text{C}$  and a heating rate of  $30^\circ\text{C min}^{-1}$ .

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## 1. Introduction

In France, a common strategy to manage long-lived nuclear wastes relies on their immobilization in borosilicate-based glasses followed by their disposal in a deep geological repository [1]. However, some radioactive isotopes coming from spent nuclear fuel reprocessing like iodine-129 cannot be immobilized into such matrices due to volatilization issues [2]. Iodine-129 is classified as a long-lived intermediate level waste (ILW-LL) with one of the longest half-lives (15.7 million years) among fission products. In order to ensure its retention over geological time scales, investigations have been carried out to immobilize it into specific robust ceramic matrices [3–6].

Apatite-derivative minerals of general formula  $\text{Me}_{10}(\text{XO}_4)_6\text{Z}_2$  are promising candidates for such applications because of their resistance to aqueous corrosion in neutral media and their capacity to incorporate a wide range of ions. In the open literature, two specific compositions are mentioned for

their suitability for iodine conditioning: an iodide-bearing apatite ( $\text{Pb}_{10}(\text{VO}_4)_{6-x}(\text{PO}_4)_x\text{I}_2$ ) [4,7–14] and an iodate-substituted hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{IO}_3)_x(\text{OH})_{2-x}$ ) [15–17].

In the case of iodide-bearing apatites, the crystalline lattice can incorporate a high iodine content (8.4 wt%) [4] and shows a good chemical durability (down to  $2.4 \cdot 10^{-3} \text{ g m}^{-2} \text{ d}^{-1}$  for the forward rate on the basis of iodine release in pure water at  $90^\circ\text{C}$ ) [4]. Their synthesis and consolidation can be achieved in one step at low temperature by spark plasma sintering [9,10,13,18] or by microwave sintering [11]. Nevertheless, the use of toxic reactants ( $\text{Pb}_3(\text{VO}_4)_2(1-x)(\text{PO}_4)_{2x}$  and  $\text{PbI}_2$ ) can hinder their development at an industrial scale.

More recently, studies have been devoted to an iodate-substituted apatite (HA-CaI) which allows the drawback of using toxic reactants to be avoided [16,17]. This material can incorporate iodine under the form of iodate using low temperature synthesis routes. Particularly, these studies have demonstrated that the iodine content could reach around 7 wt% [15,17], which is comparable to what has been obtained for iodide-bearing apatites. The synthesis of HA-CaI can be achieved by cementation [17] or by wet-precipitation [15]. However, whatever the synthesis route, a high exchange surface has been obtained, these two protocols result-

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ing in a highly porous cement or a powder, respectively. Given that the amount of iodine released by contact with groundwater will be proportional to the exposed surface, a minimization of this surface is thus required to improve the whole confinement of iodine-129. However, in contrast to iodide-bearing apatites, to our knowledge, no dense monolith has been shaped from iodate-substituted hydroxyapatites yet, meaning that no dense material without open porosity has ever been obtained.

In the case of hydroxyapatite powders, consolidation is generally achieved by sintering at high temperature ( $T > 1000^\circ\text{C}$ ) with long dwell times ( $t > 1\text{ h}$ ) [19–26]. In such conditions, partial dehydration of hydroxyapatite into oxyhydroxyapatite can occur [25,26]. Furthermore, calcium-deficient hydroxyapatites are decomposed into stoichiometric hydroxyapatite and  $\beta$  TCP ( $\text{Ca}_3(\text{PO}_4)_2$ ) for a temperature range of  $700\text{--}1000^\circ\text{C}$  [27,28]. Due to the lower thermal stability of iodate-substituted hydroxyapatites compared to pure hydroxyapatite [15], with the volatilization of iodine starting around  $500\text{--}550^\circ\text{C}$  [15,17], pressureless sintering techniques are inefficient for these phases. However, recently, Grossin and co-workers have shown the possibility to consolidate nanocrystalline hydroxyapatite powders at very low temperature ( $T < 300^\circ\text{C}$ ) by Spark Plasma Sintering (SPS) (relative density  $\sim 92\%$ ) [29]. In this work, apatite sinterability was linked to the presence of a metastable hydrated calcium phosphate layer (hereafter referred to as HL) at the surface of apatite crystals [29,30]. However, the suitability of such a procedure to other types of apatites is not known and has never been studied.

The current work deals with the first attempt to produce a monolith from iodate-substituted hydroxyapatite powders synthesized by wet-precipitation with a maximized densification rate and without iodine volatilization by means of SPS. First, the influence of synthesis parameters on the properties of iodate-substituted hydroxyapatite powders (stoichiometry, thermal stability, specific surface area, ...) will be presented. Then, the sinterability and the influence of some sintering parameters on the relative density and microstructure of the resulting materials will be discussed.

## 2. Experimental

### 2.1. Powder synthesis

Iodate-substituted hydroxyapatite (HA-CaI) powders were synthesized by wet-precipitation according to a previously published procedure [15]. All powders were obtained from reagent grade materials, namely  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (VWR, France, 99.9% purity),  $(\text{NH}_4)_2\text{HPO}_4$  (VWR, France, 99.4% purity),  $\text{NH}_4\text{IO}_3$  (Alfa Aesar, Germany, 99% purity), with a molar ratio Ca/P/I of 10/6/2. A “cationic” solution was obtained from dissolution in 100 mL of deionized water of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and an “anionic” solution was prepared by dissolution of  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{NH}_4\text{IO}_3$  in 100 mL of deionized water. After dissolution, pH of both solutions was adjusted to 10.0 by addition of concentrated ammonia (Alfa Aesar, Germany). The anionic solution was slowly added to the cationic one during 1 h under magnetic stirring and under inert atmosphere (to avoid any introduction of carbonates in the final material). The suspension was then aged under stirring. During the synthesis, the temperature was measured directly inside the reaction medium and pH was regularly adjusted in order to keep its value close to the initial one. At the end of the ageing step, the precipitate was filtered, washed, and dried.

The synthesis parameters listed below were varied to monitor their influence on the properties of the final material:

- synthesis temperature: room temperature or  $90^\circ\text{C}$ ,

- reactant concentrations:  $[\text{IO}_3^-]_{\text{in anionic solution}} = 1.13 \cdot 10^{-2}$  or  $3.79 \cdot 10^{-2}\text{ M}$ ,
- drying conditions: freeze drying ( $T = -60^\circ\text{C}$ ) during two days, or thermal treatment at  $250^\circ\text{C}$  during 24 h,
- ageing time: 0 or 5 h.

### 2.2. Spark plasma sintering

Spark plasma sintering experiments were performed on a FCT system HPD125 apparatus using graphite dies (Mersen 2333 grade, external diameter of 90 mm, inner diameter of 30.7 mm and height of 50 mm) and pistons (35 mm high and 30 mm diameter). The temperature was monitored by a K-type thermocouple set in the die wall at 2 mm from the sample and half height of the die. A 1:1 pulse pattern was used, meaning that 1 pulse of current of 20 ms was followed by 1 step of 20 ms without current.

For each experiment, 4.95 g of powder were consolidated. The powder was first cold compacted under 100 MPa in the SPS furnace. During the temperature cycle, mechanical pressure was fixed at 100 MPa for all experiments, as a consequence of preliminary trials (see Supplementary materials, S1). This pressure was applied at room temperature before the beginning of the temperature cycle and was maintained until temperature went down to  $50^\circ\text{C}$ . All the sintering cycle was carried out under a 1 atm Ar pressure: first, air was expelled from the SPS furnace by applying a dynamic primary vacuum and then, argon was introduced to get a 1 atm (the overall procedure lasted less than 10 min) during the cold compaction.

### 2.3. Sample characterizations

Dried powders were characterized by X-ray diffraction at room temperature with a Panalytical MPD Pro fitted with a copper anode using the Cu  $K\alpha$  radiation ( $K\alpha_1 = 1.54056\text{ \AA}$ ) generated at 40 mA and 40 kV. Practically, the  $2\theta$  range between  $10$  and  $70^\circ$  was used, and this range was scanned with a  $0.017^\circ$  step. Diffractograms were analyzed using the EVA version 10.0 rev. 1 program (DIFFRACplus, Bruker). The Ca/P molar ratio was calculated after calcination of the powder at  $1000^\circ\text{C}$  following the quantitative X-ray diffraction analysis method described by Raynaud et al. [27]. Crystallite mean sizes (length along the  $c$ -axis and width) were estimated using Scherrer's formula, from the analysis of the (002) and (200) peak widths at half maximum respectively.

For further characterizations, Fourier transform infrared (FTIR) and Raman spectroscopies were performed. In order to point out iodine oxidation state, Raman spectra were acquired on a Horiba Jobin LabRam Aramis spectrometer in the  $100\text{--}1600\text{ cm}^{-1}$  range, using a 532 nm wavelength laser. In order to check for the presence of a hydrated layer (HL) and to quantify it, FTIR spectra were obtained on a FTIR Vertex 70 (Bruker) spectrometer in the  $400\text{--}4000\text{ cm}^{-1}$  range (resolution of  $4\text{ cm}^{-1}$ ). Before FTIR characterization, pellets composed of 300 mg of dried KBr and 3 mg of dried powder were prepared. Spectral deconvolutions with Lorentzian curves were carried out in the  $500\text{--}700\text{ cm}^{-1}$  wave number range, this region being associated to characteristic absorptions of the apatitic structure and the hydrated layer. The position of each contributing band was set based on previously reported wave numbers [31–34]. The presence of a non-apatitic calcium phosphate hydrated layer at the surface of the crystals leads to the presence of shoulders at  $525$  and  $617\text{ cm}^{-1}$  attributed respectively to non-apatitic hydrogen phosphate and orthophosphate ions belonging to this hydrated layer. A hydrated layer index (noted as HLI) was calculated from the ratio between the non-apatitic hydrogen phosphate/orthophosphate band intensities ( $\nu(\text{HPO}_4^{2-})$  at  $525\text{ cm}^{-1}$  and  $\nu(\text{PO}_4^{3-})$  at  $617\text{ cm}^{-1}$ ) and the sum of apatitic hydrogen phosphate/orthophosphate band intensities in the  $500\text{--}700\text{ cm}^{-1}$  range

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