Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 131 (2017) 140–145

Energy Procedia

www.elsevier.com/locate/procedia

5th International Symposium on Innovative Nuclear Energy Systems, INES-5, 31 October – 2 November, 2016, Ookayama Campus, Tokyo Institute of Technology, JAPAN

Preparation and properties of hydroxyapatite nano-spheres for immobilization of Sr isotopes

Branko Matovic [a,]*, Marija Prekajski Djordjevic [a], Jelena Maletaskic [a], Katsumi Yoshida[b], Toyohiko Yano[b]

[a]University Belgrade, Center of Excellence-CEXTREME LAB, Institute of Nuclear Sciences Vinca, 11001 Belgrade, Serbia

[b]Laboratory for Advanced Nuclear Energy, Institute of Innovative Research, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8550 Japan

Abstract

In this work immobilization of Sr long-lived fission product (LLFP) was evaluated using stable isotope instead of radioactive isotope. Nano-emulsion technique was applied for synthesis calcium - strontium hydroxyapatite as the inert matrix for transmutation of LLFP at room temperature. X-ray powder diffraction analysis accompanied reviled that synthesized powders were single-phase hydroxyapatite and they displaying solid solutions over the full range of relative concentrations. Field emission scanning electron microscopy analysis reveals that the synthesized hydroxyapatite particles were spherical in shape and that their sizes were in the nanometer range. At higher temperature shape is changed due to the sintering process. Nano-emulsion strategy procedure provides a simple pathway for immobilization of Sr isotopes as a single-phase Sr hydroxyapatite at room temperature.

Peer-review under responsibility of the organizing committee of the 5th International Symposium on Innovative Nuclear Energy Systems.

Keywords: ^{90}Sr isotope, immobilization, Ouzo effect, solid solutions, apatite stucture

---

* Corresponding author.
E-mail address: mato@vinca.rs

1876-6102 © 2017 The Authors. Published by Elsevier Ltd.
Peer-review under responsibility of the organizing committee of the 5th International Symposium on Innovative Nuclear Energy Systems.
10.1016/j.egypro.2017.09.419

1. Introduction

Mineral hydroxyapatite (denoted as HAp) is known as a phase with extensive compositional variation. The structure and chemistry of HAp allow for numerous substitutions, including a multitude of metal cations, i.e., K, Na, Mn, Ni, Cu, Co, Zn, Sr, Ba, Pb, Cd, Sb, Y, U.., which substitute Ca in structure. Although these substitutions are usually in trace concentrations, the presence of HAp in geological environments (igneous rocks, metamorphic rocks, and low temperature sedimentary and hydrothermal environments) can strongly influence their trace element signature and evolution [1,2]. Especially are important elements which have radioisotopes and can be utilized as geochronometers. Therefore, dating of apatite has become an important tool for studying rocks in which it is found.

Apatite materials have a number of useful applications including bone tissues [3], fertilizer [4], ionic conductors [5], fission track dating of geological record, and nuclear waste applications [6]. Apatite was suggested for storage of a number of nuclear wastes including I, Cs, Sr, rare earth elements, and actinides (e.g., U, Th). Thus, HAp has a great potential for storage of a number of radioactive nuclear waste elements because of its long-term durability and irradiation stability.

Nuclear power plants generate spent nuclear fuels containing large amount of fission products, among them more dangerous are unstable isotopes known as radioactive waste. Thus the disposal of radioactive waste becomes a critical issue. One of the more important products of nuclear fission is ^{90}Sr which presents a health problem due to substitutes for Ca in bone, preventing expulsion from the body. On the other side, one of the most common substituent in HAp is strontium and there is a continuous solid solution between Ca- and Sr end-members in synthetic hydroxyapatite, although the Sr end-member is still not found in nature [7,8]. Hence optimizing the nuclear waste performance could be managed through different apatite compositions, i.e., Ca-Sr solid solution.

The great variety of methods for powder synthesis had been published in the literature. One of the most promising methods to produce a single phase and highly pure powders with a precise stoichiometry is the liquid-liquid nucleation process, known as Ouzo effect [9].

According to the literature data Sr-doped Ca- hydroxyapatite powders have not been obtained by this method so far [10]. The effect of dopant concentration on stability of apatite solid solution was examined in order to consider the possibility of using ceria as a host material for storage of radioactive ^{90}Sr isotope.

2. Experimental work

The end-members Ca and Sr HAp (denoted as CHAp and SHAp, respectively) as well as their solid solutions with varying compositions of same chemical elements were synthesized using analytical grade $Ca(NO_3)_2{\cdot}4H_2O$, $Sr(NO_3)_2{\cdot}4H_2O$ (Riedel-de Haën, 99% purity), $(NH_4)_2HPO_4$ (Riedel-de Haën, 99% purity) and analytical grade acetone. An acetone solution of $Ca(NO_3)_2{\cdot}4H_2O$ was mixed with an aqueous solution of $(NH_4)_2HPO_4$ at a molar ratio of (Ca^{2+}; $Ca^{2+}+Sr^{2+}$; Sr^{2+}) : PO_4^{3-} = 1.67 : 1 using a magnetic stirrer. The aqueous solution was adjusted to pH 11 with sodium hydroxide (1 M) prior to mixing. The mixed solutions were stirred for 5 min at temperature below the boiling point of acetone of 56.3 °C. In experiments, no surfactant was used. The resultant nanoprecipitates in the solutions were immediately filtered using a vacuum filtration set to avoid particle agglomeration and then washed three times using deionized water. Obtained slurry was dried at 70 °C during the night.

The phase purity and crystallinity of obtained HAp powders were examined using X-ray diffraction (Riguku Ultima IV, Japan). The X-ray beam was nickel-filtered Cu$K\alpha_1$ radiation (λ = 0.1540 nm, operating at 40 kV and 40 mA). XRD data were collected from 5 to 80° (2θ) at a scanning rate of 5°/min. Phase analysis accompanied with Rietveld refinement was done by using the PDXL2 software (version 2.0.3.0), with reference to the patterns of the International Centre for Diffraction Database (ICDD), version 2012. Calculation of the average crystallite size (D) was performed on the basis of the full width at half maximum intensity (FWHM) of the *hkl* (211) reflection by using Scherrer's formula [11]:

$$D_{hkl} = 0.9\lambda / \beta \cdot \cos\theta \qquad (1)$$

where λ is the wave lengths of the X-rays, θ is diffraction angle, β is corrected half-width for instrumental broadening $\beta = (\beta m - \beta s)$, βm observed half-width and βs is half-width of the standard CeO_2 sample.