Acta Materialia 135 (2017) 35–43

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Interconfigurational and intraconfigurational transitions of Yb^{2+} and Yb^{3+} ions in hydroxyapatite: A cathodoluminescence study

Luz A. Zavala [a], Paloma Fernández [b], Ekaterina Novitskaya [c], Jorge N. Díaz [a], Manuel Herrera [a, *], Olivia A. Graeve [c, **, 1]

[a] Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Km 107 Carretera Tijuana-Ensenada, C.P. 22800, Ensenada, Baja California, Mexico
[b] Departamento de Física de Materiales, Universidad Complutense de Madrid, Facultad de Física 2° planta, C.P. 28040, Madrid, Spain
[c] Department of Mechanical and Aerospace Engineering, University of California, San Diego, 9500 Gilman Drive - MC 0411, La Jolla, CA 92093-0411, USA

ARTICLE INFO

Article history:
Received 21 October 2016
Received in revised form
28 May 2017
Accepted 2 June 2017
Available online 2 June 2017

Keywords:
Hydroxyapatite
Ytterbium
Cathodoluminescence
Interconfigurational transitions
Intraconfigurational transitions

ABSTRACT

We present a cathodoluminescence (CL) study of the interconfigurational transitions of Yb^{2+} and intraconfigurational transitions of Yb^{3+} dopant ions in hydroxyapatite (HAp) powders. Our results demonstrate that strong electric fields present in the HAp lattice induce manifold levels in the electronic configuration of the ytterbium ions, due to splitting of the $4f^{13}5d^1$ orbitals. CL spectra of Yb^{2+} display a series of sharp peaks centered at 3.27, 2.98, 2.85, 2.53, 2.27, 2.09 and 1.63 eV, corresponding to transitions between multiple levels produced by a trigonal distortion of the regular octahedral crystal field of the Yb^{2+} $4f^{13}5d^1$ configuration. CL spectra of Yb^{3+} display four emissions centered at 1.17, 1.21, 1.24 and 1.27 eV, generated by intraconfigurational transitions between the $^2F_{5/2}$ and $^2F_{7/2}$ states of Yb^{3+} ions. Two types of samples were synthesized at different pH values, resulting in variations of the valence of the ytterbium ions, such that the ratios of Yb^{2+}/Yb^{3+} were 0.31 and 0.55 in calcined powders synthesized at pH values of 6 and 4, respectively, as determined from X-ray photoelectron spectroscopy. Infrared CL images of the two samples show an inhomogeneous spatial distribution of the Yb^{3+} dopant in the powders. Thermal treatment of the samples, at 873 K in an oxygen atmosphere, result in quenching of the Yb^{2+} luminescence due to oxidation of the Yb^{2+} into Yb^{3+}.

1. Introduction

Rare-earth doped hydroxyapatite (HAp:RE; $Ca_{10-x}RE_x(PO_4)_6(OH)_2$) is of interest due to its luminescent properties which, when combined with its compatibility to human bone, makes it an ideal material for a variety of biomedical applications. HAp:RE has been used as image contrast agent [1], antibacterial agent [2], and drug delivery carrier [3,4], among others. Luminescence in this material is a consequence of the substitution of rare-earth ions into the Ca^{2+} sites of the HAp lattice. This substitution can be selective and dependent on the rare-earth ion valence state. Recently, we have demonstrated that it is possible to adjust the relative concentration of Eu^{2+} and Eu^{3+} ions in HAp [5,6] by inducing the formation of a calcium-deficient HAp (Ca-D HAp) phase. We explain this effect in terms of the limitations of the Ca-D HAp lattice to compensate for the excess charge that is generated when substituting Eu^{3+} in Ca^{2+} sites.

The luminescent properties of ytterbium ions have significant importance because of their use in applications such as diode-pumped lasers [7,8], scintillators [9,10], solar cells [11,12], and phosphors with up-conversion properties [13–15]. The luminescence of Yb^{3+} is generated by inner $^2F_{5/2}$ — $^2F_{7/2}$ transitions, or intraconfigurational transitions, while the luminescence of Yb^{2+} is between the $4f^{13}5d^1$ — $4f^{14}$ states or interconfigurational transitions. However, the presence of strong electric fields in the lattice of some ionic crystal hosts produces Stark splitting of the Yb^{2+} $5d$ states [16–18], generating numerous non-degenerate manifold levels that participate in the electronic transitions of this ion. At present, no reports of ytterbium luminescence from apatite compounds are available, neither is evidence of the generation of

* Corresponding author.
** Corresponding author.
E-mail addresses: zaldivar@cnyn.unam.mx (M. Herrera), ograeve@ucsd.edu (O.A. Graeve).
[1] http://graeve.ucsd.edu.

http://dx.doi.org/10.1016/j.actamat.2017.06.003
1359-6454/

Table 1
Atomic composition of the undoped and doped powders determined by energy dispersive spectroscopy.

Sample	Elemental composition (at.%)				$\frac{Yb}{(Ca+Yb)}$	$\frac{(Ca+Yb)}{P}$
	Ca	O	P	Yb		
HAp-Ref (calcined)	22.45	64.10	13.50	0.00	0.00	1.66
HAp:Yb6 (as-synthesized)	19.40	66.60	12.83	1.17	0.06	1.60
HAp:Yb6 (calcined)	19.57	66.42	12.85	1.16	0.06	1.61
HAp:Yb4 (as-synthesized)	18.06	68.09	12.67	1.18	0.06	1.52
HAp:Yb4 (calcined)	18.20	68.21	12.43	1.16	0.06	1.56

manifold levels by Stark effect in the HAp lattice.

In this study, we have induced a selective incorporation of Yb^{2+} and Yb^{3+} in the HAp host and report interconfigurational transitions of Yb^{2+} between manifold levels generated by the splitting of *d* orbitals due to the strong electric fields present in the HAp lattice, as well as intraconfigurational transitions of Yb^{3+}. We have used the cathodoluminescence technique to identify these electronic transitions. Additionally, we report evidence of the generation of manifold levels corresponding to the splitting of the $^2F_{5/2}$ and $^2F_{7/2}$ states. Our results have significant implications for the use of ytterbium ions in a variety of hosts since we have demonstrated that the luminescence response can be tuned based on the presence of mixed valence ions, as well as the possibility of exposing these ions to strong electric fields in the HAp host.

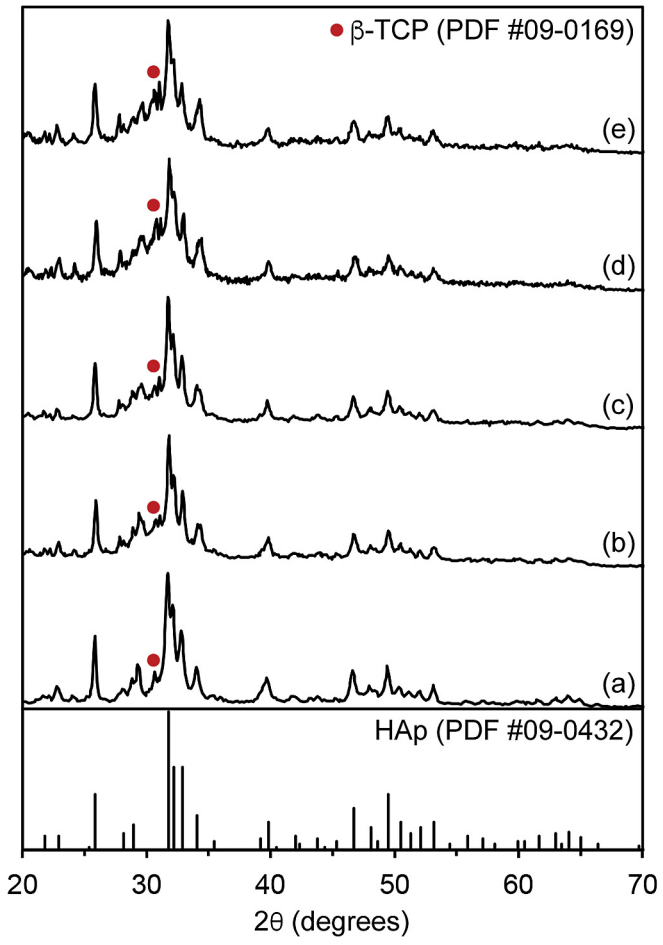

Fig. 1. X-ray diffraction patterns of (a) calcined HAp-Ref, (b) as-synthesized HAp:Yb6, (c) calcined HAp:Yb6, (d) as-synthesized HAp:Yb4, and (e) calcined HAp:Yb4 powders.

2. Experimental methodology

Three types of samples were prepared, an undoped reference sample (HAp-Ref) and two ytterbium doped calcium-deficient HAp samples, by solution combustion synthesis [19–24] according to our previous study [5]. For the HAp-Ref sample, the reagents used were calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$, 99%, Alfa Aesar, Ward Hill, MA], ammonium hydrogen phosphate [$(NH_4)_2HPO_4$, 98%, Alfa Aesar, Ward Hill, MA], and carbohydrazide [$CO(NHNH_2)_2$ 97%, Alfa Aesar, Ward Hill, MA]. The ytterbium doped HAp samples, HAp:Yb6 and HAp:Yb4 (the latter number referring to the pH of the solutions during synthesis), were prepared using ytterbium nitrate pentahydrate [$Yb(NO_3)_3 \cdot 5H_2O$, 99.9% Alfa Aesar, Ward Hill, MA] as the dopant source according to the following procedure: (1) 6.695 g of $Ca(NO_3)_2 \cdot 4H_2O$ and 0.628 g of $Yb(NO_3)_3 \cdot 5H_2O$ were dissolved in 28 mL of deionized water to form a 1.00 M Ca + Yb solution, (2)

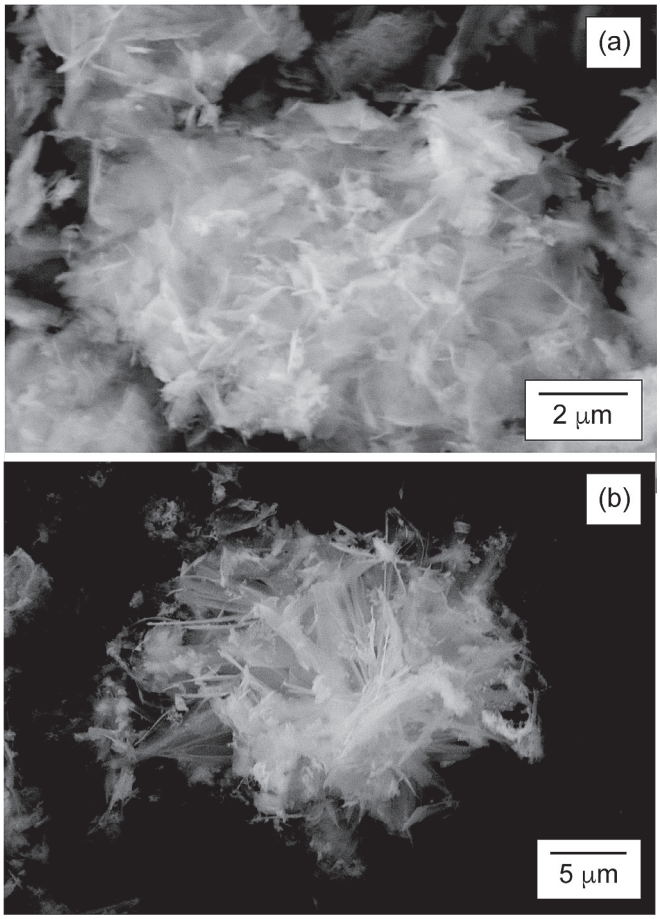

Fig. 2. Scanning electron micrographs of the calcined (a) HAp:Yb6 and (b) HAp:Yb4 powders.