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# Magnetic properties study on Fe-doped calcium phosphate

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## Abstract

Calcium phosphates are very important for applications in medicine due to their properties such as biocompatibility and bioactivity. In order to enhance these properties, substitution of calcium with other ions has been proposed. Partial substitution of calcium by different ions has been made in order to improve the properties of the calcium phosphates and also to allow new applications of apatite in medicine. In this work, hydroxyapatite [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>—HAP] was prepared by high-energy dry milling (20 h) and mixed with iron oxide (5 wt.%). The mixture was calcinated at 900 °C for 5 h with a heating rate of 3 °C min<sup>-1</sup> in an attempt to introduce iron oxide into the HAP structure. The sintered sample was characterized using x-ray diffraction (XRD) and magnetization. The <sup>57</sup>Fe-Mössbauer spectra of the calcium phosphate oxides were also measured, revealing the presence of iron in three different phases: Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub> and hydroxyapatite.

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(Some figures in this article are in colour only in the electronic version.)

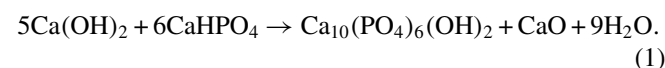
## 1. Introduction

The presence of iron in the hydroxyapatite structure seems to be important because it is a vital element in the circulatory system and essential for the functioning of numerous proteins in cells [1]. Materials for use in medicine must not have a significant influence on the metabolism. Several materials and composites are used in the production of prostheses, for example, metallic alloys, metallic materials covered with hydroxyapatite films, alumina and polyethylene [2]. Biomaterials containing iron oxide have a very important role to play in medicine. As an example, ferrimagnetic bioglass ceramics (FBC) was introduced for hyperthermic treatment of bone cancer [3–6] and HAP, obtained by the sol–gel method, with different iron concentration, and after treatment at different temperatures, has been used for hyperthermia treatment of bone tumors [7]. The main purpose of the work is to prepare HAP ceramics with iron oxide and study the

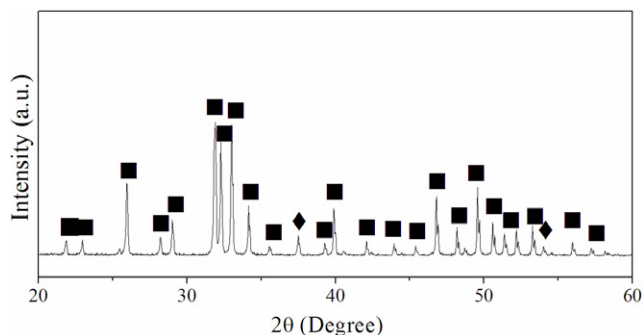
effect of the iron oxide in the <sup>57</sup>Fe-Mössbauer spectra on the ceramic in the hydroxyapatite ceramic. X-ray diffraction and magnetization analyses of the magnetic momentum versus magnetic field ( $H$ ) were also performed to characterize such ceramics.

## 2. Experimental

HAP crystalline powders were prepared by high-energy dry milling for 20 h. Equation (1) represents the expected chemical reaction (see figure 1):



The raw materials, CaHPO<sub>4</sub> and Ca(OH)<sub>2</sub>, with stoichiometric proportionality for 10 g of total powder, were placed in a stainless steel vessel inside a Fritsch Pulverisette 6-planetary mill system. The ratio between the powder and the ball mass



**Figure 1.** XRD pattern of the HAP sample milling at 20 h. HAP (■) and CaO (◆) (see footnote 4).

was near 1/6. The milling was performed at 370 rpm for 20 h. To avoid excessive heating the milling was performed in 30 min milling steps with 10 min pauses.

Iron oxide ( $\text{Fe}_2\text{O}_3$ ) with 5%wt was added to the HAP powder. Hereafter, the sample is named HAPFe5 where the number is the iron concentration. The mixture was calcinated at  $900^\circ\text{C}$  for 5 h with a heating rate of  $3^\circ\text{C min}^{-1}$ .

### 2.1. X-ray diffraction (XRD)

The XRD pattern data were obtained at room temperature using powder samples in an X'Pert MPD Philips diffractometer (with  $K_\alpha$  radiation,  $\lambda = 1.54056 \text{ \AA}$ ) at 40 kV and 30 mA. Intensity data were collected by the step counting method (step  $0.02^\circ$  and a time per step of 1 s) between  $20^\circ$  and  $60^\circ$  ( $2\theta$ ). The output data obtained from Rietveld refinement [8] is used to calculate  $R_{\text{wp}}$ , which is the more significant statistical factor of all of the quantitative criteria and better reflects the progress of the refinement because it involves the method of square minima, between calculated and observed intensities. In agreement with Young and Wiles [9], the results of  $R_{\text{wp}}$  are considered reliable in the strip of 2–10%, while the obtained typical values vary between 10–20%.

### 2.2. Mössbauer spectroscopy

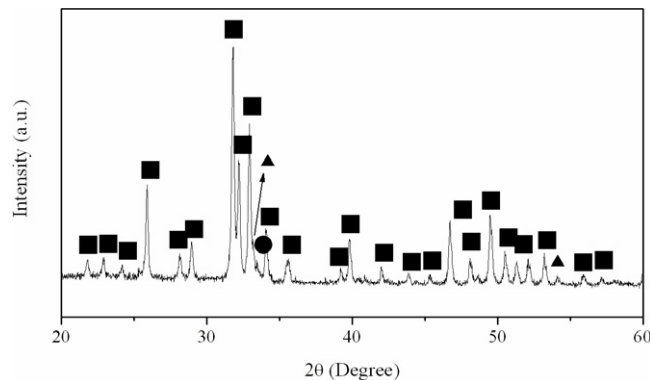
The Mössbauer spectrum was measured at room temperature in transmission geometry and in constant acceleration mode with a  $^{57}\text{Co}$  source in the Rh matrix. The spectrum was analysed using the Normos software package, where a discrete set of subspectra constructed from Lorentzian functions was fitted to the experimental data using a least-square fitting routine. Mössbauer velocity and isomer shift are relative to  $\alpha\text{-Fe}$ .

### 2.3. VSM

The magnetization ( $M-H$ ) was measured using an Oxford Instruments vibrating sample magnetometer (VSM) between 50 and 300 K, on a field-cooled sample under an applied field of 100 Oe.

## 3. Results and discussion

Figure 1 presents the XRD pattern of the HAP obtained for milling at 20 h, showing beyond HAP, the CaO



**Figure 2.** XRD pattern of the HAPFe5 calcinated sample at  $900^\circ\text{C}$ . HAP (■),  $\text{Ca}_2\text{Fe}_2\text{O}_5$  (●) and  $\text{Fe}_2\text{O}_3$  (▲) (see footnote 4).

**Table 1.** Quantitative criterion obtained in the rietveld refinement for the sample.

Samples	$R_{\text{wp}}$	% Mass			
		HAP	CaO	$\text{Ca}_2\text{Fe}_2\text{O}_5$	$\text{Fe}_2\text{O}_3$
HAPFe0.5	13.6	96.93	1.62	1.45	–
HAPFe1	14.6	95.37	1.95	2.68	–
HAPFe2.5	14.8	94.67	0.94	4.39	–
HAPFe5	14.6	90.97	–	6.77	2.26

phase<sup>4</sup>. Figure 2 presents the XRD pattern of the HAP with iron oxide (5%wt) calcinated at  $900^\circ\text{C}$ . Brownmillerite or srebrodolskite ( $\text{Ca}_2\text{Fe}_2\text{O}_5$ ) [10] was identified. This structure ( $\text{Ca}_2\text{Fe}_2\text{O}_5$ ) can be seen as a perovskite deficient in oxygen, whereas brownmillerite ( $\text{A}_2\text{B}_2\text{O}_5$ ) is a type of oxygen-deficient perovskite structure that is composed of a perovskite-like three-dimensional framework of corner-sharing  $\text{BO}_6$  octahedra alternating with slabs containing rows of corner-sharing  $\text{BO}_4$  tetrahedra formed by oxygen deficiency during the formation of the structure [11–13]. The  $\text{Fe}_2\text{O}_3$  (see footnote 4) phase was detected in the XRD of the sample (figure 2), but the CaO phase was not (table 1). The brownmillerite phase was formed by the reaction of iron oxide with CaO formed through the dissociation of the  $\text{Ca}(\text{OH})_2$  during the preparation of HAP (equations (1) and (2)). It can be observed from the XRD that the  $\text{Ca}_2\text{Fe}_2\text{O}_5$  phase shows a calcium–iron interaction. Investigations of magnetic resonance are also of special interest, since  $\text{Ca}_2\text{Fe}_2\text{O}_5$  is a many-sublattice system with a nontrivial magnetic layer structure [14]. No substitution of calcium by iron ions was observed in the HAP structure. Another phase identified in the samples heat-treated at  $900^\circ\text{C}$  was  $\text{Fe}_2\text{O}_3$ :

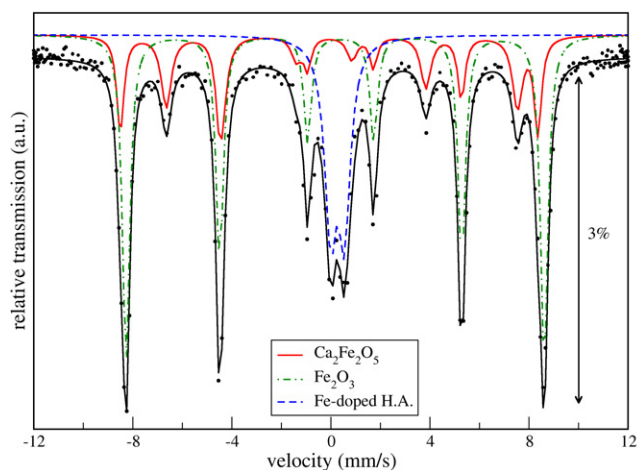


Figure 3 shows the Mössbauer spectrum for the sample. Mössbauer [15–20] studies have shown that  $\text{Ca}_2\text{Fe}_2\text{O}_5$  is an antiferromagnet ( $T_N = 725 \text{ K}$ ) with the antiferromagnetic vector directed along the  $c$ -axis [21, 22]. Fitting the spectrum allows the identification of four different Fe-bearing sites (see table 2 for fit results), three sextets and one doublet. The hyperfine parameters (table 2) of the most intense

<sup>4</sup> JCPDS-Pattern 24-0033 (HAP-REF), 74-1860 ( $\text{Ca}_2\text{Fe}_2\text{O}_5$ ), 82-1691 (CaO) and 79-0007 ( $\text{Fe}_2\text{O}_3$ ).

**Table 2.** Hyperfine parameters obtained from fitting the Mössbauer spectrum.

	Área (%)		ISO (mm s <sup>-1</sup> )	QUA (mm s <sup>-1</sup> )	BFH (T)
Fe <sub>2</sub> O <sub>3</sub>	49		0.39	-0.22	52.3
Ca <sub>2</sub> Fe <sub>2</sub> O <sub>5</sub>	29	Tetra	0.19	0.71	44.0
		Octa	0.27	-0.46	52.3
HAP	22		0.37	-0.56	

**Figure 3.** Mössbauer spectrum of sample HAPFe5. (Dots) experimental data; (black line) Fit; (—) subspectrum associated with Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>; (---) Fe<sub>2</sub>O<sub>3</sub>; (- -) Fe-doped HAP.

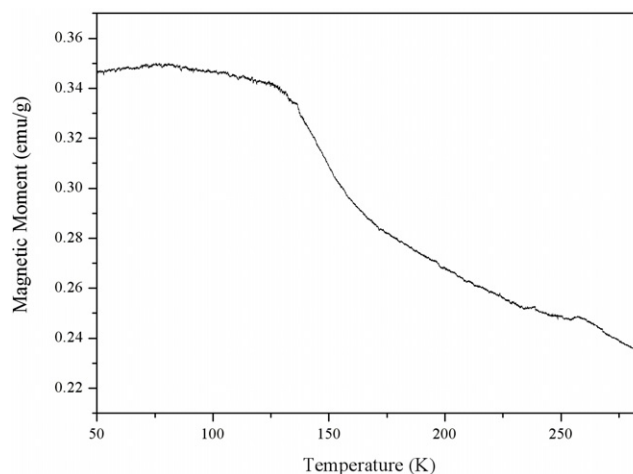
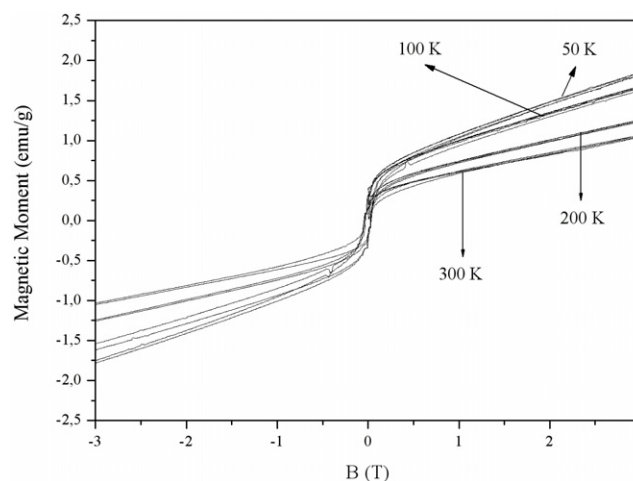
sextet subspectrum in figure 3, with about 49% of the total spectrum, are consistent with those of Fe<sup>3+</sup> in Fe<sub>2</sub>O<sub>3</sub> [23]. The subspectrum in figure 3 is comprised of two Fe-bearing sites consistent with the octahedral and tetrahedral symmetries (in a 50:50 ratio) of Fe<sup>3+</sup> sites in Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> [24]. The central doublet is associated with Fe-doped HAP [25].

Figure 4 shows the magnetization as a function of temperature. There is a decrease in magnetization with an increase in temperature, characteristic of brownmillerite. The Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> structure is a weak antiferromagnet directed along the *c*-axis [26]. This observation shows that the magnetocrystalline anisotropy in the *a*-*c* plane is small.

Figure 5 shows the *M*-*H* hysteresis loop taken from 50 K up to 300 K done by the VSM analysis (variation in magnetization, *M*, versus bias field, *H*) as a function of the temperature. There is a decrease in the magnetization (*M*) with an increase in temperature. This effect can be explained by the vibrational energy (thermal vibrations) of atoms increasing with temperature, making it more difficult to align magnetic dipoles [27].

#### 4. Conclusions

The Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> (brownmillerite) phase was obtained in the 5% iron added to HAP (figure 2). The formation of the brownmillerite showed that we have not a substitution of calcium by iron ions in the HAP structure. The brownmillerite phase was formed by the reaction of iron oxide with CaO formed through the dissociation of Ca(OH)<sub>2</sub> during the preparation of HAP. The Mössbauer spectrum shows

**Figure 4.** Temperature dependence of the magnetization for HAPFe5.**Figure 5.** Magnetic field (*H*) dependence of the magnetization for HAPFe5.

the presence of Fe in Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub> and HAP, with three sextets and one doublet. The VSM analysis shows that the Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> structure is a weak antiferromagnet directed along the *c*-axis. Between 50 and 300 K there is a decrease in magnetization with temperature, characteristic of the brownmillerite [26]. This observation shows that the magnetocrystalline anisotropy in the *a*-*c* plane is small.

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