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THERMAL ANALYSIS OF PURE AND MULTISUBSTITUTED HYDROXYAPATITE PASTES

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ABSTRACT. The thermal stability over time of the pure and multisubstituted hydroxyapatite (HAP) pastes, doped with magnesium, silicon, strontium and zinc, synthesized using aqueous precipitation method were investigated by thermal analyses (TG-DTA). Results show high thermal stability of pure and multidoped hydroxyapatite pastes, up to 1000 ^{o}C and even after ageing for 1 year, making these pastes promising nano materials for medical applications.

Keywords: *hydroxyapatite, doped hydroxyapatites, paste, thermal analysis*

INTRODUCTION

The hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ (HAP), composition is similar to bone, has good biocompatibility and bioactivity therefore is increasingly used in medicine, especially in repairing bone defects as bone grafts, coating material for metallic implants, dental implants, and drug delivery systems [1-3]. Nanocrystalline HAP paste is suitable bone substitute in dental and orthopedic surgery for filling bone defects in minimally invasive surgery. HAP pastes have various applications: as tooth pastes for remineralising and repairing of teeth enamel, for the fabrication of 3D printed bioactive ceramic scaffolds [2, 4].

The biological properties of HAP based materials can be improved by the incorporation of divalent essential metal ions. The effect of silicon [5, 6], magnesium [7, 8], strontium [9, 10], manganese [11] and zinc [11-13] as doping elements on characteristics of hydroxyapatite with potential biomedical applications has been studied extensively [1, 2, 11].

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Multidoped hydroxyapatites with improved properties are more suitable for biomedical application, thus many recent studies have focused on simultaneous doping of hydroxyapatite with copper, zinc and carbonate ions [14]; manganese and strontium [15], strontium and copper [16] and magnesium, zinc and silicon [17, 18]. Hydroxyapatite co-doped with strontium and magnesium, strontium and zinc, magnesium and zinc [19] and simultaneously doped with three essential elements Sr, Mg and Mn [20] and Sr, Mg and Zn [21] were also reported.

Continuing our interest in the field of bioactive materials [22-26] we present here some results concerning thermal stability of three HAP pastes simultaneously doped with essential elements magnesium, strontium, silicon and zinc, with previously described compositions [27]. Water content of pastes was determined by thermal analysis. The thermal stability of the pastes was monitored for one year, namely thermal analyses were performed after 4 months and one year from their preparation.

RESULTS AND DISCUSSION

Thermal stability over time, of four hydroxyapatite pastes, with previously reported composition [27] were investigated, namely pure hydroxyapatite (HAP, 1) and doped HAP pastes, containing Mg 1.5 wt%, Zn 0.2 wt% and Si 0.2 wt% (2); Mg 1.5 wt%, Zn 0.2 wt%, Si 0.2 wt% and Sr 5 wt% (3) and Mg 1.5 wt%, Zn 0.2 wt%, Si 0.2 wt% and Sr 10 wt% (4). The pure and doped pastes kept under storage conditions for 4 months, respectively 1 year, at room temperature in well-closed conditions, were heated in air with the rate of 10 °C/min from the room temperature up to 1000 °C. Thermogravimetric data are presented in Table 1 and in Figures 1 and 2.

Table 1. Thermogravimetric data of pure and doped HAP pastes, after 4 months

Paste	Temperature (°C)	Weight loss (%)
1.	30-160	65.96
HAP	160-1000	1.19
	30-1000	**67.15**
2.	30-162	71.08
HAP 1.5%Mg, 0.2%Si, 0.2%Zn	162-1000	1.68
	30-1000	**72.76**
3.	30-163	64.11
HAP 1.5%Mg, 0.2%Si, 0.2%Zn, 5%Sr	163-1000	1.67
	30-1000	**65.78**
4.	30-150	53.22
HAP 1.5%Mg, 0.2%Si, 0.2%Zn, 10%Sr	150-1000	1.93
	30-1000	**55.15**

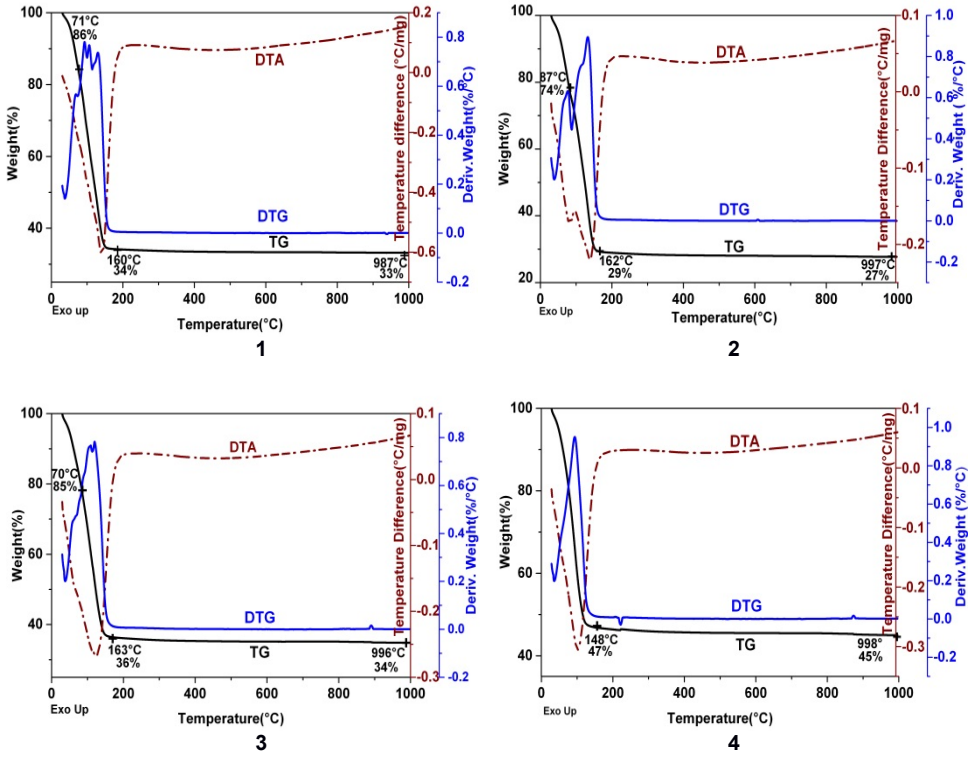

Figure 1. Thermal curves of the four pastes: 1) pure HAP (sample 1); 2) HAP 1.5%Mg, 0.2%Si, 0.2%Zn (sample 2); 3) HAP 1.5%Mg, 0.2%Si, 0.2%Zn, 5%Sr (sample 3); 4) HAP 1.5%Mg, 0.2%Si, 0.2%Zn, 10%Sr (sample 4), after 4 months.

Thermal analysis shows that the thermal curves (TG, DTA) of the pure and the doped HAP pastes have the same shape in the range of 30-1000 °C. After 4 months no significant differences were observed in thermal behavior. The only differences refer to the moisture content of the sample. Thermogravimetric monitoring of weight loss shows that weight of all samples decreases continuously with increasing temperature. The highest weight loss occurs in the range 30-200 °C and can be attributed to very high water content of pastes, since the water molecules surround the hydroxyapatite particles. The corresponding DTA data indicate an endothermic transformation for all samples at around 160 °C (Fig. 1 and 3).

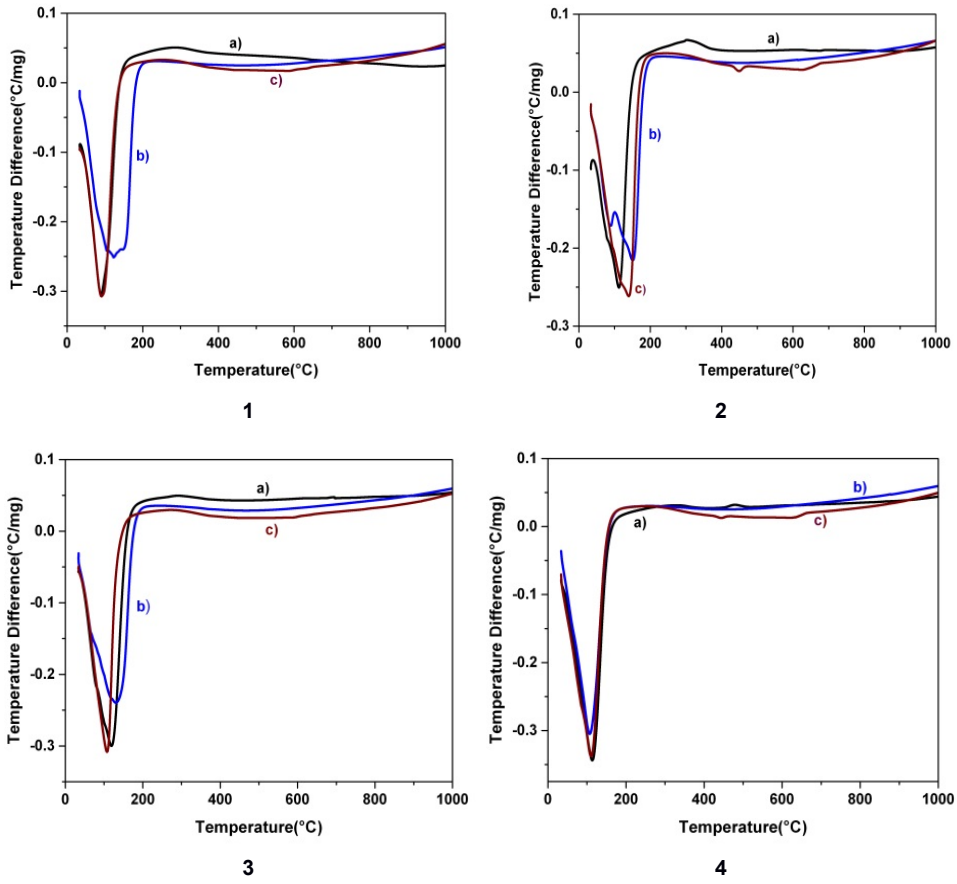

Figure 2. Comparative DTA curves for fresh (a), 4 months (b) and 1 year (c) old samples: 1) pure HAP (sample 1); 2) HAP 1.5%Mg, 0.2%Si, 0.2%Zn (sample 2); 3) HAP 1.5 % Mg, 0.2%Si, 0.2%Zn, 5%Sr (sample 3); 4) HAP 1.5% Mg, 0.2%Si, 0.2%Zn, 10%Sr (sample 4).

The weight loss in the range 30-200 °C was 53.5-71.3%; it indicates the removal of moisture and physically adsorbed water, followed in the temperature range of 200-1000 °C by small gradual weight loss, 1-2%, which can be associated with the removal of chemically adsorbed water on the surface of HAPs particles, in agreement with the literature data [27, 28].

Above 200 °C the thermogravimetric curves became parallel to each other and up to 1000 °C (Figure 1 and 3) with x-axis. Pure and doped HAP pastes are very stable up to 1000 °C, as found for at least one year aged samples.

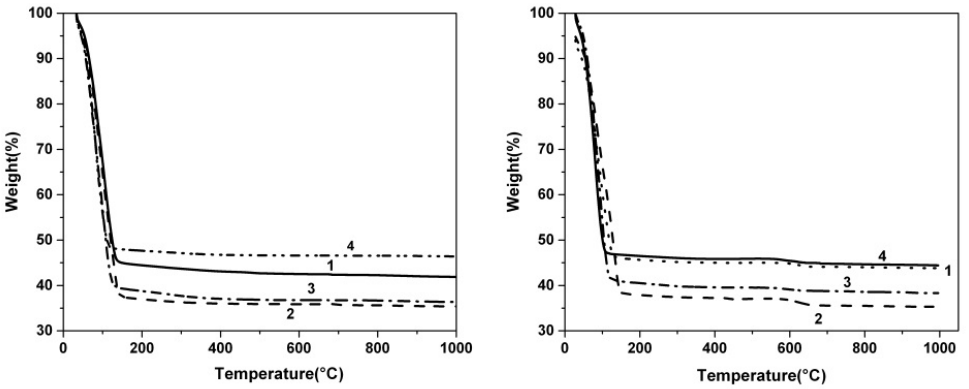

Figure 3. TG curves for fresh pastes (a) and 1 year aged (b) pastes: 1) pure HAP (sample 1); 2) HAP 1.5% Mg, 0.2%Si, 0.2%Zn (sample 2); 3) HAP 1.5%Mg, 0.2%Si, 0.2%Zn, 5%Sr (sample 3); 4) HAP 1.5%Mg, 0.2%Si, 0.2%Zn, 10%Sr (sample 4).

The pure and doped hydroxyapatite pastes may contain small content of carbonate, whose decomposition cause insignificant mass loss. The moisture content of these pastes is high but comparable with those found for commercial available pure HAP paste [27].

CONCLUSIONS

The results of thermal analysis confirm high thermal stability of pure and multidoped hydroxyapatite pastes, up to 1000 °C, even after ageing for 1 year from their preparation. The thermal behavior of pure and doped hydroxyapatite pastes in time shows that this depends mainly on the loss of physically adsorbed and chemically bounded water. The high stability of these ceramic pastes without significant modifications in the structure of pastes makes them appropriately for further use in biomedical applications, as drug delivery systems of antimicrobials and for coating of metallic implants.

EXPERIMENTAL SECTION

Materials and methods

The following compounds were used as starting materials: $Ca(NO_3)_2 \cdot 4H_2O$, $(NH_4)_2HPO_4$, $Mg(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Sr(NO_3)_2$ and tetraethyl orthosilicate $(C_2H_5O)_4Si$, (TEOS). Pure HAP and three doped

hydroxyapatites with the same content of Mg, Zn, Si and different contents in Sr were obtained by a wet precipitation method, previously reported [6, 10, 13, 26]. All chemicals were reagent grade procured from Merck and Sigma-Aldrich, solutions were prepared with double distilled water, deionized in Elgastat purification system.

Synthesis of pure HAP and doped HAP

A pure HAP paste was prepared by wet precipitation method, previously described [6, 10, 13, 26]; using equal volumes of aqueous 0.25 M Ca^{2+} solutions and 0.15 M PO_4^{3-} solutions. The pH of the reaction mixture was fixed at 11.5 using 25% ammonia solution (Ca/P atomic ratio 1.67). The reaction mixture was stirred 24 h at 22 °C, and 24 h at 70 °C. The precipitated solid phase was filtered, washed with distilled water until pH 7. The wet precipitate, considered paste was used as it is.

The doped hydroxyapatites were obtained similarly, with the following modification: the Ca^{2+} containing solution contains also the doping cations (0.25 M in Ca^{2+}+Mg^{2+}+Zn^{2+}+Sr^{2+}) in calculated amount for the proposed composition of the doped HAP. The anions containing solution (0.15 M in PO_4^{3-}+SiO_4^{4-}) was obtained from $(NH_4)_2HPO_4$, and tetraethyl orthosilicate, TEOS. The pH was fixed at 11.5 by adding a 25% ammonia solution. Equal volumes of the two solutions were mixed at 22 °C keeping the mole ratio (Ca+Mg+Zn+Sr)/(P+Si) at the value of 1.67. The obtained pastes were processed in the same way as the pure HAP.

Characterization methods

Thermal behavior of pure HAP and doped HAP pastes was determined by thermogravimetric analysis (TGA), for the temperature range from 30-1000 °C, using Universal SDTQ600 TA Instruments. Samples were heated in alumina crucibles at a constant heating rate of 10 °C/min, in flowing air, using simultaneous TG/DTG-DTA/DSC techniques.

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