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Effect of sodium addition on the preparation of hydroxyapatites and biphasic ceramics

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Abstract

HAP and biphasic ceramics of two different HAP and β-TCP proportions with substituted sodium were prepared through an aqueous precipitation method. The prepared powders were characterized by XRD, thermal analysis, FT-IR and elemental analysis. Sodium was found to incorporate into the apatite structure without showing any significant change in the phase behaviour of the resultant apatites. The substitution of sodium in the calcium deficient apatites tends to form a biphasic mixture of HAP and β-TCP, while the effect of calcination beyond 700 °C and the resultant mixtures were dependent on the initial Ca/P ratios of the precursors. The calculated lattice parameter values for sodium substituted apatites have shown a marginal increase in *c*-axis values thereby leading to the enlargement of the hexagonal cell volume with respect to the pure HAP prepared under the same experimental conditions. Powders obtained from the present results were stable up to 1200 °C.

Keywords: HAP; β-TCP; Sodium; Biphasic mixtures; Calcium def-apatites

1. Introduction

Hydroxyapatite [HAP, $Ca_{10}(PO_4)_6(OH)_2$] and β-tricalcium-phosphate [β-TCP, β-$Ca_3(PO_4)_2$] are widely recognized as potential bioceramics for both dental and orthopaedic applications due to their close chemical similarity with the inorganic component of vertebrate bone and tooth mineral [1,2]. Currently, biphasic calcium phosphate ceramics (BCP) comprising a mixture of HAP and β-TCP are considered better when compared with either single phase HAP or β-TCP components, because of their unique dissolution characteristics promoting new bone formation at the implant site [3,4]. Nowadays interest is turning towards modified synthetic apatites involving the substitution of chemical species found in natural bone. The incorporation of such species is considered to have tremendous influence on the physical, chemical and physiological properties of the solid and consequently on the mineralization, demineralization and remineralization process of the calcified tissues [5,6].

It is well known that sodium (Na) has been detected as an abundant trace element next to the presence of calcium and phosphorous in natural bone and tooth mineral. The essential characteristics of Na in biological apatites is its potential role in cell adhesion and also in the bone metabolism and resorption process [7,8]. Some previous studies have dealt with the processing of sodium and carbonate co-substituted hydroxyapatites through several processing techniques such as hydrolysis of monetite ($CaHPO_4$) in Na_2CO_3 solutions, the double decomposition method and also through solid state reaction [9–11]. These studies have proved that sodium can be substituted in the hydroxyapatite lattice at the calcium sites. It has been reported that substitution of calcium ions by sodium creates supplementary vacancies (in calcium sites) [12]. Although these above-mentioned studies have given some understanding on the incorporation of Na into the apatite lattice, many of them have focussed on low temperature processing as well as on the formation of single phase HAP. To date, no significant attention has been paid to the preparation of biphasic mixtures of different HAP and β-TCP proportions with substituted sodium in its structure, which will be certainly a better material than single phase sodium substituted hydroxyapatite in terms of the biological behaviour on implantation.

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Hence, the aim of the present study is to attempt to synthesize thermally stable sodium substituted hydroxyapatite and biphasic mixtures through an aqueous precipitation method. Generally, the synthesis of biphasic ceramics via wet precipitation is accomplished by forming calcium deficient apatites (Ca/P < 1.67, def-apatites) and subsequent calcination at above 700 °C to yield phase mixtures [13,14]. This type of synthesis route was adapted during the present study by introducing sodium ions in the calcium deficient apatites. $NaNO_3$ as a precursor for sodium was used in the synthesis of substituted apatites following a systematic experimental approach. Techniques such as XRD, thermal analysis, FT-IR and elemental analysis were utilized to characterize the resultant powders.

2. Experimental

2.1. Preparation method

The synthesis was carried out in a fully automated apparatus with a specific device to control the stirring of suspensions, addition rate and temperature control system. Calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$), diammonium hydrogen phosphate $(NH_4)_2HPO_4$ and sodium nitrate ($NaNO_3$) were used as starting chemicals for calcium, phosphorous and sodium. For the preparation of Na substituted apatites, $(NH_4)_2HPO_4$ solution was added at a rate of 50 ml/min to the solution mixture containing nitrates of Ca and Na stirred at a rate of 1000 rpm (solution concentrations of precursors detailed in Table 1). The pH of the mixed solution was maintained at 9 by the addition of concentrated ammonium hydroxide (NH_4OH) solution. After the completion of addition, the reaction was performed at 90 °C for 2 h under constant stirring condition of 1000 rpm. The precipitated suspension was discharged from the reactor and allowed to settle for 24 h for the maturation of the precipitate. A pure stoichiometric HAP (Ca/P molar ratio = 1.67) was prepared simultaneously under the same conditions to compare the results. After 24 h, the precipitates were separated through vacuum filtration and were dried at 80 °C overnight. The dried cakes were ground to fine powders, sieved through a mesh size of 200 μm and used for characterization studies.

2.2. Sample characterization

The as dried powders were subjected to thermal analysis with a heating rate of 5 °C/min between 30 and 1000 °C in air atmosphere (Labsys Setaram TG-DTA/DSC, France). The prepared powders were heat treated at different temperatures ranging from 700 to 1300 °C to study the phase changes. The heat treatment/calcination was carried out in a Thermolab furnace (Pt30%Rh/Pt6%Rh-thermocouple) with a heating rate of 5 °C/min to achieve a predetermined temperature range and a dwelling time for 2 h and again cooled to room temperature at the rate of 5 °C/min. X-ray diffraction studies on the calcined powders were carried out using a high resolution Rigaku Geigerflex D/Mac, C Series diffractometer with Copper Kα radiation (λ = 1.5406 nm) produced at 30 kV and 25 mA with diffraction angles (2θ) between 20° and 60° and with a step size of 0.02° $2\theta\ s^{-1}$. Lattice constants were determined by least square refinements from the well-determined positions of the most intense reflections, which are processed by MDI Jade 6.1 software. The average crystallite size (D) of the calcined samples was calculated using the Scherrer equation [15].

Densities of the powders were determined by helium gas multi-pycnometry with an Accupyc Quantachrome apparatus (Florida, USA). The density value for each powder was determined as the average of five measures. Infrared spectra of the as-prepared powders and powders calcined at different temperatures were obtained using an Infrared Fourier Spectrometer (FT-IR, model Mattson Galaxy S-7000, USA). Elemental analyses for the presence of Ca, Na and P were made using X-ray fluorescence spectroscopy (Philips PW2400 X-Ray Fluorescence Spectrometer). The vacuum of the chamber was lower than 2 Pa. The error associated with each chemical element could be determined as ±1 of the last digit of the measured values. The calcined powders were uniaxially pressed using a steel die at 125 MPa to form rectangular bars of size 4 mm × 5 mm × 50 mm and the pressed bodies were sintered at 1200 °C. The morphology of the sintered samples was observed by scanning electron microscope (SEM-4100-1, Hitachi, Japan).

3. Results and discussion

3.1. Synthesized powders

The XRD patterns for the as synthesized powders are presented in Fig. 1. All the powder patterns indicate the hydroxyapatite phase except for the differences in peak width and absolute intensity. The stoichiometric HAP powder has indicated better crystallinity when compared to the Na substituted apatites. The substitution of Na in the powder Nhap-1 (Ca/P = 1.67) shows sharp diffraction patterns when

Table 1
Molar concentrations of the precursors used in the preparation of Na substituted apatites

Sample code	Molar concentrations of the precursors			Ca/P molar ratio	(Ca + Na)/P molar ratio
	Ca	P	Na		
HAP	1.0	0.6	–	1.67	–
Nhap-1	1.0	0.6	0.032	1.67	1.72
Nhap-2	0.972	0.6	0.032	1.62	1.67
Nhap-3	0.944	0.6	0.058	1.58	1.67

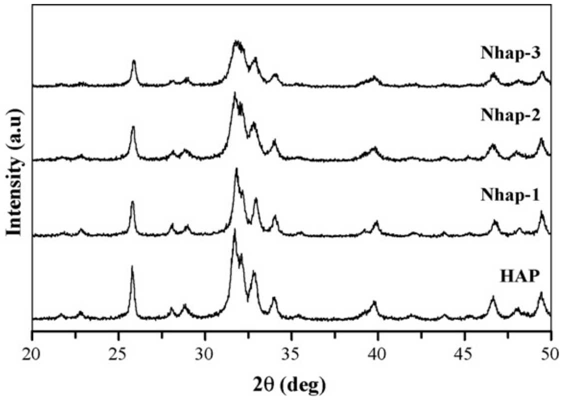

Fig. 1. XRD patterns for as-prepared powders.

compared to the other two powders Nhap-2 and Nhap-3 that are calcium deficient in increasing order even in the presence of Na. In fact, this results tend to agree with those reported in some previous works showing that X-ray diffraction analysis of an as-precipitated apatite powder can result in diffraction patterns resembling that of HAP even though the Ca/P ratio is greater or less than the stoichiometric molar ratio of 1.67 [16]. Similar observations were made also for apatites with elements substituted in trace levels [17].

FT-IR spectra for the as dried powders presented in Fig. 2 have indicated the vibrational modes of PO_4 groups at 475, 574, 609, 966 and 1020–1120 cm^{-1} and OH groups (630 and 3570 cm^{-1}) of the apatite phase for all the powders. FT-IR patterns also tend to coincide with the results from XRD by the way that the intensity of peak resolution of OH and PO_4 bands becomes lower with increase in Na concentration. The presence of adsorbed water and carbonates could also be detected from FT-IR spectra respectively in the region around 3300–3600 and 1660 cm^{-1}. It has been reported that Na incorporation into apatite is facilitated by the presence of carbonates in the as-prepared powders [18]. It is also interesting to note that as-prepared stoichiometric HAP also indicates the presence of trace levels of carbonate. Hence, the presence of carbonates in all the as-prepared powders is solely due to the adsorption of species remaining from the aqueous precipitation [19]. The presence of nitrates (NO_3) in the as dried powders is also obvious from the infrared spectra in the region around 1320–1480 and a band at 875 cm^{-1} [20].

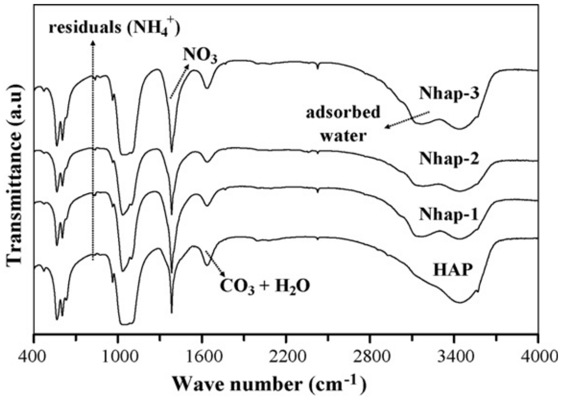

Fig. 2. FT-IR spectra for as-prepared powders.

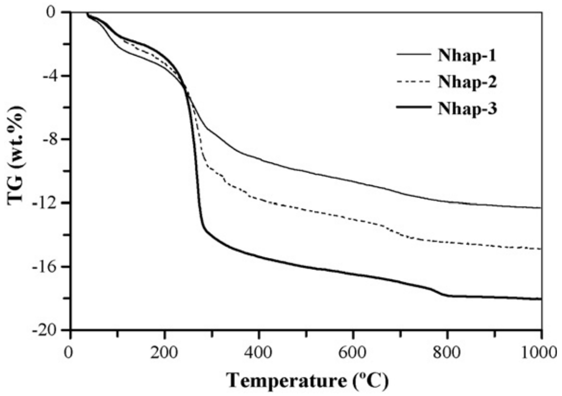

Fig. 3. TG plots for the different sodium substituted apatitic powders.

3.2. Calcined powders

The thermal analyses of the different sodium substituted apatites are represented in Fig. 3. The relatively high calcium deficient powder Nhap-3 (Ca/P = 1.58) shows a severe weight loss of 18% due to its non-stability in comparison to the other two powders. All the Na substituted apatitic powders show a similar weight loss of about 5% in the region of 30–250 °C that is attributed to the removal of physically adsorbed water. In the range of 250–800 °C, difference in weight loss could be noticed for the powders for Nhap-1, Nhap-2 and Nhap-3 which show losses of about 4.5, 7 and 13%, respectively, depending on their stoichiometry. It should be noted that the increased calcium deficiency for the powder Nhap-3 leads to high weight loss when compared to the other two powders. The weight loss observed in this particular region (250–800 °C) from the thermal analysis can be accounted for the loss of residual NH_4^+ ions, nitrates and carbonates [21,22]. However, the differences in weight loss in this particular temperature range could be due to the different level of Ca and Na precursors used in the system. Although (Ca + Na)/P molar ratios of the powders Nhap-2 and Nhap-3 were equal to 1.67, both these powders tend to behave in a similar fashion to def-apatite as described elsewhere [23,24]. FT-IR spectra

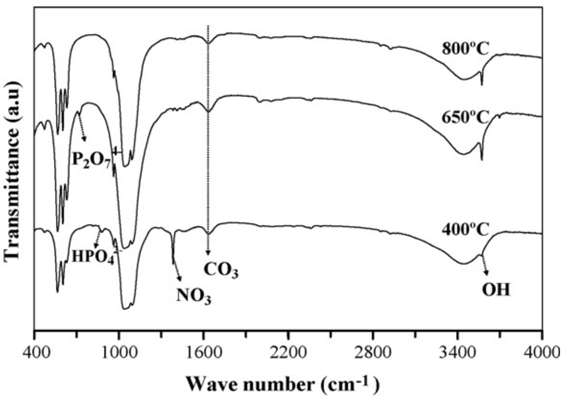

Fig. 4. FT-IR spectra for Nhap-3 heat treated at different temperatures.

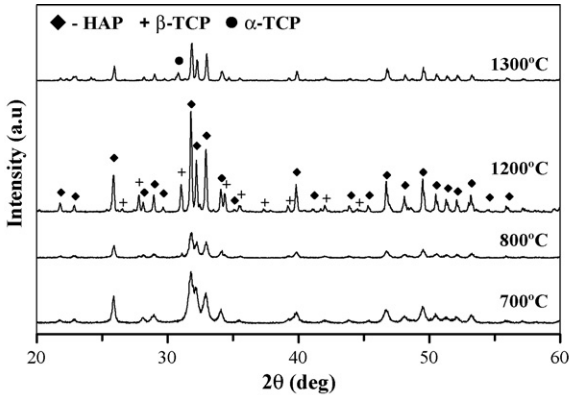

Fig. 5. XRD patterns for Nhap-2 calcined at different temperatures.

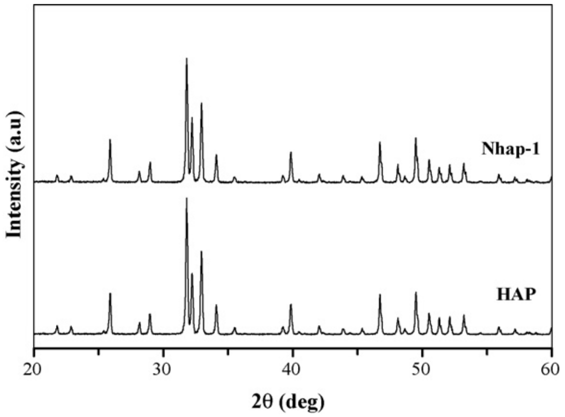

Fig. 7. XRD patterns for the HAP and Nhap-1 heat treated at 1200 °C.

for the selected sample Nhap-3 calcined at different temperatures are presented in Fig. 4. The loss of NH_4^+ ions, nitrates and carbonates is apparent from the patterns as indicated by the decrease in intensity of the corresponding peaks on heating. Additionally, the presence of hydrogenophosphate groups (HPO_4^{2-}) is detected at 400 °C from the peak at around 875 cm^{-1}, while at 650 °C the peak for pyrophosphate groups ($P_2O_7^{4-}$) was witnessed at 730 cm^{-1}. It seems that the stoichiometric ratio of pure HAP (Ca/P = 1.67) was not retained with the addition of Na. The presence of HPO_4^{2-} ions and $P_2O_7^{4-}$ ions within the temperature range of 350–720 °C tends to agree with the condensation mechanism proposed by Mortier et al. [25]. The decomposition of pyrophosphates ($P_2O_7^{4-}$) to biphasic mixtures is obvious by the observed sharp weight losses of about 1% in the temperature range around 750–800 °C and also from the absence of corresponding peaks for $P_2O_7^{4-}$ at 800 °C.

3.3. Formation of biphasic mixtures

The X-ray diffraction patterns for all the powders Nhap-2 and Nhap-3 calcined at different temperatures are presented in Figs. 5 and 6. Calcination of the powders at 700 °C indicates the improvement in crystallinity by the increase in the resolution of peaks when compared to the as-prepared powders. It is well seen from the patterns that only the HAP phase is detected in all the Na substituted powders. At 800 °C, both Nhap-2 and Nhap-3 indicate the formation of β-TCP in addition to HAP thus confirming the formation of biphasic mixtures as discussed in the above section. The peaks pertaining to both HAP and β-TCP exactly match those of ICDD PDF # 09-432 and ICDD PDF # 09-169, respectively. The calculated percentage compositions of β-TCP in the biphasic mixture are 27 and 36% of β-TCP for Nhap-2 and Nhap-3 respectively with respect to HAP phase. The increase of β-TCP in the Nhap-3 powder is due to an higher Ca deficiency. For Nhap-1 (Fig. 7), only single phase HAP has been detected and the diffraction patterns were similar to stoichiometric HAP, except for the differences in the calculated crystallite sizes, which show a decreasing trend with increasing Na content, as reported in Table 2. The formation of apatite phase is also evident from the FT-IR spectra (Fig. 8) for the calcined powders at 1200 °C. Bands respective of PO_4 tetrahedra are visible at 475 cm^{-1} (O–P–O bending ν_2), 576 cm^{-1} (O–P–O antisymmetric bending ν_4), 605 cm^{-1} (O–P–O bending ν_4), 975 cm^{-1} (P–O stretching ν_1) and 1086 cm^{-1} (P–O stretching ν_3). The presence of OH group of apatite phase can be detected from the FT-IR patterns for all the powders from the observed stretching vibrational mode at 3570 cm^{-1} and the bending mode at 630 cm^{-1}. However, the bands corresponding to both OH groups and PO_4 tetrahedra for all Na substituted apatites are less intense when compared to the pure HAP owing to their poor crystalline features.

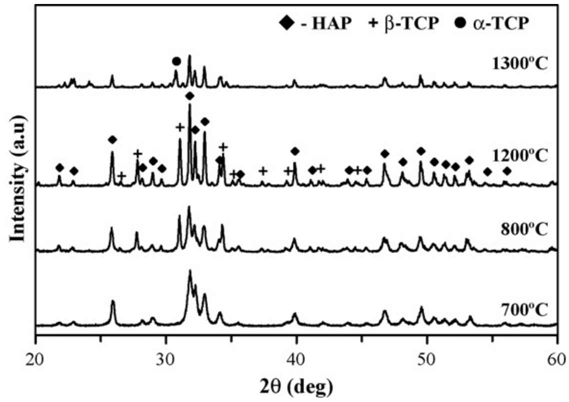

Fig. 6. XRD patterns for Nhap-3 calcined at different temperatures.

Table 2
Calculated lattice parameters and crystallite size for all the powders calcined at 1200 °C

Sample	Cell parameters for HAP (Å)			Crystallite size (Å)
	a-Axis	*c*-Axis	Volume	
HAP	9.4137 (4)	6.8489 (2)	1571.35 (3)	789
Nhap-1	9.4118 (3)	6.8796 (3)	1577.75 (4)	707
Nhap-2	9.4106 (4)	6.8802 (4)	1577.49 (5)	548
Nhap-3	9.4126 (3)	6.8747 (3)	1576.90 (5)	473

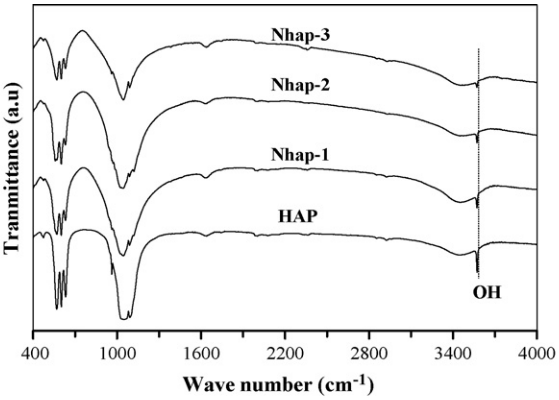

Fig. 8. FT-IR patterns for the sodium substituted apatitic powders calcined at 1200 °C.

Table 3
Elemental analysis and density of sodium substituted apatites measured at 1200 °C

Sample	wt.% of elements measured after calcination			Density (g/cm^3)
	Ca	P	Na	
HAP	39.89	18.50	–	2.998
Nhap-1	39.59	18.37	0.72	2.966
Nhap-2	38.07	18.22	0.69	2.861
Nhap-3	36.67	17.97	1.11	2.851

3.4. Role of sodium

The elemental analysis presented in Table 3 confirms the presence of Na in the calcined powders. Some previous studies have reported the synthesis of sodium substituted apatites through solid state reaction and have shown that Na can stabilize the apatite phase while heat treated at higher temperatures. A study by Schaeken [26] who heated mixtures of $CaHPO_4$, $CaCO_3$ and Na_2CO_3 at temperatures between 700 and 1000 °C and found that sodium was incorporated into the crystal structure of β-TCP and apatite. According to Schaeken [26], Na_2O could be assumed to react with β-TCP and then form sodium containing β-TCP. In the present case no peak corresponding to the presence of Na_2O can be detected in the XRD patterns in the region around 700–1000 °C, which is due to the nature of the precursors as well as the different adapted procedure from the previous one explained above. Another study by Suchanek et al. [27] has reported the sintering of HAP with selected additives containing Na source and has given different results. A recent study by Lin et al. [28] has also shown that Na^+ ions can stabilize the β-TCP phase till 1300 °C depending upon the concentration of the additive $Na_4P_2O_7 \cdot 10H_2O$ that was used. In the present study, the powder Nhap-1 gave pure HAP phase without additional phase even after calcination at 1200 °C. The powders Nhap-2 and Nhap-3 formed biphasic mixtures and exhibit thermal stability till 1200 °C. The allotropic transformation to α-TCP seemed to occur between the temperature range 1200–1300 °C. It is well established that the transformation of pure β-TCP to α-TCP is favored around the region at 1120 °C [29,30]. Hence, it could be stated from the present results that the incorporated Na influenced the thermal stability of apatites and delayed the allotropic transformation until 1200 °C. Hence, the statement that “ionic system of apatite welcomes a variety of substitutions both cationic and anionic

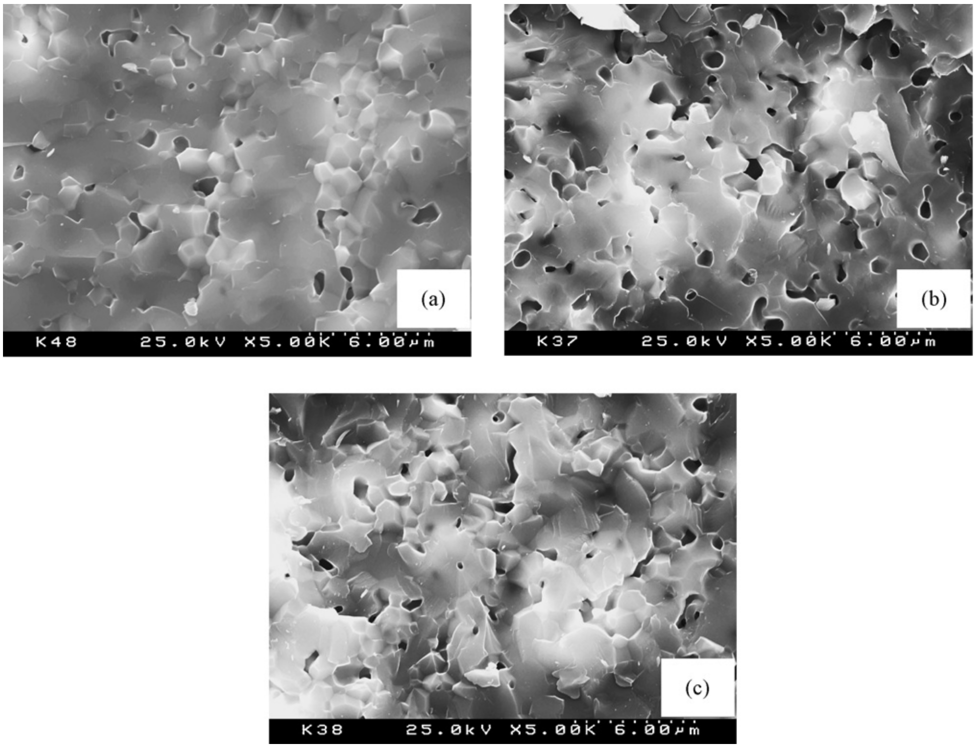

Fig. 9. SEM morphology of the fractured surface of the different sodium substituted apatites sintered at 1200 °C: (a) Nhap-1, (b) Nhap-2 and (c) Nhap-3.

in its structure without any significant modification in its hexagonal system'' [31] is confirmed from the present results. However, the calculated lattice parameter values (Table 2) for all the sodium substituted apatites calcined at 1200 °C have also confirmed the formation of hexagonal apatite phase. However, a slight increase in the *c*-axis values leading to the expansion in cell volume have been detected for all the sodium substituted apatites with respect to that of pure HAP phase, which might be due to the role of Na in the apatite structure.

3.5. Microstructure analysis of sintered samples

Scanning electron micrographs of fracture surfaces of different samples sintered at 1200 °C are presented in Fig. 9. Micrographs of the samples Nhap-2 and Nhap-3 are slightly porous when compared to the relatively dense Nhap-1, in agreement with density values of 2.966, 2.861 and 2.851 g/cm^3 measured for Nhap-1, Nhap-2 and Nhap-3, respectively. However, porosity will contribute to a rapid resorption when biphasic mixtures with considerable amounts of β-TCP are implanted, causing remodeling around the implant site.

4. Conclusions

Sodium substituted hydroxyapatites and biphasic mixtures (HAP and β-TCP) were successfully synthesized by the aqueous precipitation method. The experimental results from elemental analysis and X-ray diffraction have shown that sodium incorporates into the apatite structure. A slight increase in the *c*-axis parameters leading to the increase in cell volume has been observed for all the sodium substituted apatites when compared to pure HAP. The incorporation of sodium into the apatite lattice increased the thermal stability of apatites till 1200 °C. Finally, the thermally stable Na substituted biphasic mixtures with two different HAP and β-TCP proportions achieved from the present method could be a potential bioceramic for medical applications since the resorbable β-TCP and stable HAP phase can promote rapid bone remodeling at the defective site on implantation.

Acknowledgements

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