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Synthesis and thermal stability of potassium substituted hydroxyapatites and hydroxyapatite/β-tricalciumphosphate mixtures

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Abstract

Hydroxyapatite (HAP) and biphasic ceramics of two different HAP and β-tricalcium phosphate (β-TCP) proportions with substituted potassium were prepared through the aqueous precipitation method. The prepared powders were characterized using XRD, FT-IR and elemental analysis. The results have shown that potassium added during the synthesis was found present in the apatite structure even after calcination at 1300 °C without showing any significant change in the phase behaviour of resultant apatites. The substitution of potassium in the calcium deficient apatites was accompanied by the formation of biphasic mixture of HAP and β-TCP ceramics, upon calcination beyond 700 °C and the resultant mixtures were dependent on the initial Ca/P ratios of the precursors. The calculated cell constant values for potassium substituted apatites have shown contraction in *a*-axis and irregular changes in the *c*-axis relative to those of pure HAP prepared under the same experimental conditions.

Keywords: Potassium; HAP; β-TCP; Biphasic mixtures; Calcium-deficient apatite

1. Introduction

During the past two decades both synthetic hydroxyapatite [HAP, $Ca_{10}(PO_4)_6(OH)_2$] and biphasic (BCP) mixtures of controlled HAP and β-tricalcium phosphate [β-$Ca_3(PO_4)_2$, β-TCP] ratios have received significant attention for application in bone augmentation and replacement programs [1–3]. It is notorious that biological apatites are non-stoichiometric with structural imperfections caused by the embedded ions (Na^+, Mg^{2+}, K^+, Sr^{2+}, F^-, Cl^- and $CO_3{}^{2-}$) in trace levels [4,5]. Several studies proved that the presence of these elements in trace levels play essential roles in the biological process upon implantation [6,7]. Hence, the substitution of these elements in the apatite structure has been the subject of special interest in recent years. Till date a number of studies have been reported on the synthesis of HAP with substituted Mg, Sr, F and carbonate in its structure [8–11]. However, a least number of studies have been carried out on the synthesis of potassium substituted HAP [12]. The significance of potassium in the bone composition is its tremendous influence on the biomineralization process [13]. Some studies have also proved the versatile nature of potassium in the regulation of biochemical process and its important role in the apatite mineral nucleation process [14,15]. Literature reports revealed that potassium can be substituted in the apatite lattice without significant changes in the structural parameters [12,16]. Nevertheless, in the studies reported so far, attention was given only on the preparation of potassium substituted hydroxyapatites. Till now, there is no literature evidence focusing on the processing of biphasic mixtures of HAP and β-TCP components with substituted potassium that will be certainly a better material when compared with the individual HAP or β-TCP components. Hence, the aim of the present study is an attempt to form potassium substituted HAP and biphasic mixtures through 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 [17,18]. This type of synthesis route was adapted during the present study by introducing potassium ions in the calcium deficient apatites. KNO_3 as a precursor for potassium was used in the synthesis of

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substituted apatites following a systematic experimental approach. Techniques such as XRD, 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 postassium nitrate (KNO_3) were used as starting chemicals precursors for calcium, phosphorous and potassium, respectively. For the preparation of potassium substitution in the apatites, an appropriate amount of $Ca(NO_3)_2{\cdot}4H_2O$ was dissolved in water by vigorously stirring at a rate of 1000 rpm. $(NH_4)_2HPO_4$ solution was slowly added to the $Ca(NO_3)_2{\cdot}4H_2O$ solution to achieve predetermined Ca/P molar ratios of 1.67, 1.62 and 1.58. Different amounts of KNO_3 solution were added individually to attain the (Ca + K)/P molar ratios of 1.67 + 0.05 (coded as Khap-1), 1.62 + 0.05 (coded as Khap-2) and 1.58 + 0.09 (coded as Khap-3), respectively. 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 pH (pH 9) and stirring (1000 rpm) conditions. The precipitated suspension was discharged from the reactor and allowed to settle down for 24 h for the maturation of precipitate. A pure stoichiometric HAP (Ca/P molar ratio = 1.67) was also prepared under the same conditions to compare the results. After 24 h, the precipitates were separated through vacuum filtration technique 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 prepared powders were heat treated at different temperatures ranging from 700 °C 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 the predetermined temperature followed by a dwelling time of 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 Cu Kα radiation ($\lambda = 0.15406$ Å) produced at 30 kV and 25 mA scanned the diffraction angles (2θ) between 20° and 50° with a step size of $0.02^\circ\ 2\theta\ s^{-1}$. 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. For this purpose, the reflection planes (0 0 2), (2 1 1), (1 1 2), (3 0 0), (2 2 2) and (2 1 3) for HAP was used for calculation. The volume V of the hexagonal unit cell was determined for each HAP formulation.

Quantitative determinations of the phase compositions of biphasic mixtures were made using X'Pert High Score 1.0 *f*, PANalytical B.V., using International Centre for Diffraction Data (2004) database. Crystallographic identification of the phases of synthesized apatites was accomplished by comparing the experimental XRD patterns to standards complied by the International Centre for Diffraction Data (ICDD), namely the following card numbers: #09-0432 for HAP and #09-0169 for β-TCP. 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). For this purpose each powder was mixed with KBr in the proportion of 1/150 (by weight) for 15 min and pressed into a pellet using a hand press. Elemental analyses for the presence of Ca, K 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 to each chemical element could be determined as ±1 of the last digit of the measured values.

3. Results

3.1. As prepared powders

The XRD patterns for the as prepared powders are presented in Fig. 1. All the powders have indicated the formation of apatite phase differing only in peak width and absolute intensity of the diffraction patterns. All the potassium substituted powders except HAP, which can be termed as non-stoichiometric are viewed with the broad diffraction patterns indicative of poor crystallinity in comparison with the stoichiometric HAP powder. The addition of potassium did not found to affect the diffraction pattern of as prepared powders. It should be noted that X-ray diffraction analysis of as-precipitated apatite powders resulted in diffraction patterns that could resemble HAP even though the Ca/P ratio was greater or less than the stoichiometric molar ratio of 1.67 for HAP [19,20].

FT-IR spectra displayed in Fig. 2 also confirm the formation of apatite phase for all the powders with the observed fundamental vibrational modes of PO_4 group at 475 cm^{-1}, 574 cm^{-1}, 609 cm^{-1}, 966 cm^{-1} and 1020–1120 cm^{-1}. The bands witnessed at 630 cm^{-1} and 3570 cm^{-1} could be

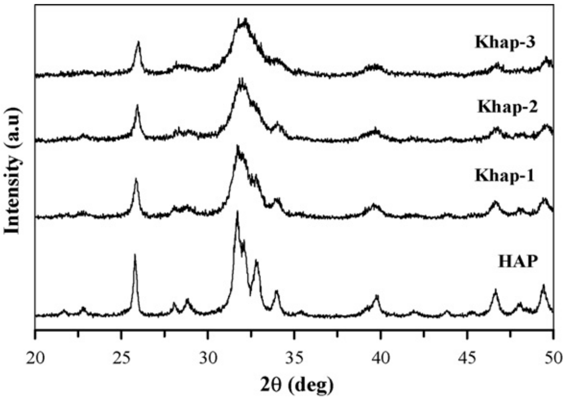

Fig. 1. XRD patterns for as prepared powders.

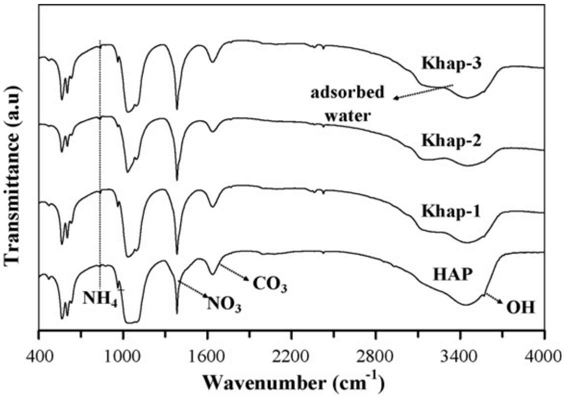

Fig. 2. FT-IR spectra for as prepared powders.

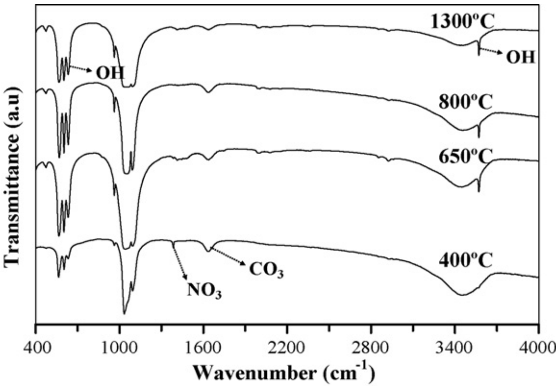

Fig. 4. FT-IR spectra for Khap-1 heat treated at different temperatures.

attributed for the presence of OH group of HAP phase. However, it is difficult to explain the role of substituted potassium in the as prepared powders since the observed phases exhibit a low crystallinity. Therefore, heat treatments will be required to enhance crystallinity for a more precise characterization. In fact, the FT-IR patterns also tend to coincide with the results from XRD by the way that the peak resolution of OH and PO_4 bands are viewed with less intensity when compared with the stoichiometric HAP. The presence of the adsorbed water could also be detected from FT-IR spectra in the region around 3300–3600 cm^{-1}. Other information from the FT-IR spectra of the powders is the presence of carbonate (CO_3) groups at 1660 cm^{-1}, which might be due to the adsorbed species remaining from the aqueous precipitation [21]. The presence of nitrates (NO_3) in the as dried powders is obvious, being witnessed in the FT-IR patterns at the region around 1320–1480 cm^{-1}. The presence of nitrates (1320–1480 cm^{-1}) and residual NH_4^+ ions (875 cm^{-1}) in the as synthesized powders tend to agree with the observations made in a previous study [22].

3.2. Effect on heat treatment

The FT-IR patterns for the HAP, Khap-1 and Khap-3 heat treated at different temperatures are presented in Figs. 3–5, respectively. The gradual loss of nitrates and carbonates is evidenced by the decrease in the resolution of corresponding peaks in the region around 1320–1480 cm^{-1} and 1660 cm^{-1} that are clearly depicted from the FT-IR spectra obtained at 400 °C, 650 °C and also at 800 °C. In the FT-IR patterns of Khap-2 (not presented) and Khap-3 (Fig. 5) that possess calcium deficiency (Ca/P < 1.67), the presence of hydrogenophosphate ions (HPO_4^{2-}) is apparent at 400 °C which was not detected for Khap-1 (Fig. 4) and also for pure HAP (Fig. 3) powder. The FT-IR patterns obtained at 650 °C indicate the presence of bands corresponding to pyrophosphates ($P_2O_7^{4-}$) at 720 cm^{-1} for both the powders Khap-2 and Khap-3 (Fig. 5). Hence, the groups HPO_4^{2-} and $P_2O_7^{4-}$ detected for Khap-2 and Khap-3 show that these powders have different features in comparison to those of HAP and Khap-1 and tend to behave similarly to calcium deficient apatites without any substituted elements that have been described elsewhere [23,24].

3.3. Evolution of phases

The X-ray diffraction patterns for the powders Khap-1, Khap-2 and Khap-3 over a wide calcination temperatures range (700–1300 °C) are illustrated in Figs. 6–8, respectively. The diffraction patterns obtained at 700 °C confirm the presence of poorly crystalline apatite phase with no other extra peaks for all the powders. However, calcination at 800 °C have effected the formation of β-TCP phase for the powders Khap-2 and Khap-3, which could be attributed to the transformation of deficient apatite to biphasic mixtures of HAP and β-TCP as evident from

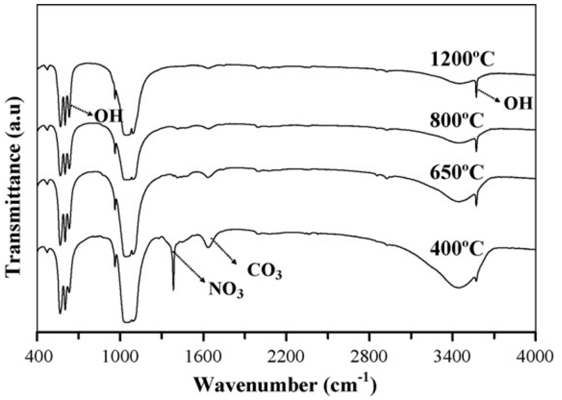

Fig. 3. FT-IR spectra for pure HAP heat treated at different temperatures.

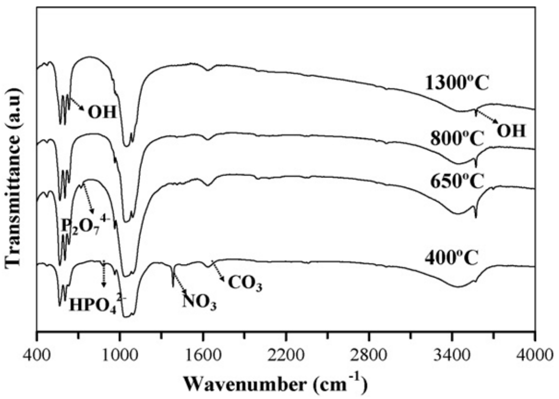

Fig. 5. FT-IR spectra for Khap-3 heat treated at different temperatures.

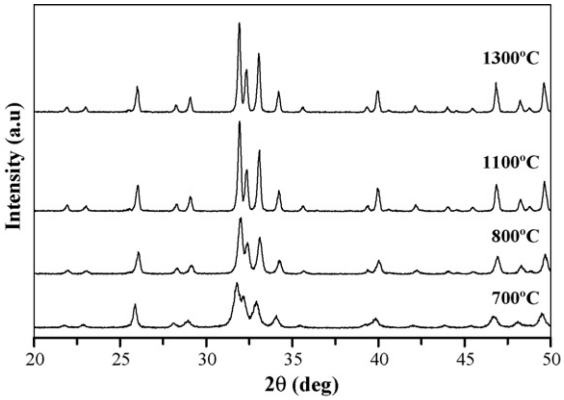

Fig. 6. XRD patterns for Khap-1 calcined at different temperatures.

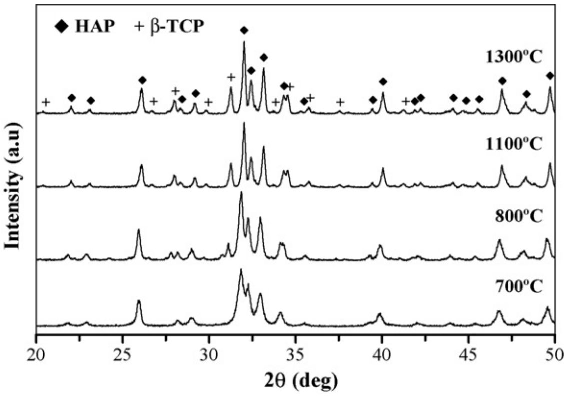

Fig. 8. XRD patterns for Khap-3 calcined at different temperatures.

Figs. 7 and 8. The calculated β-TCP content for the powder Khap-3 that possesses higher degree of calcium deficiency was 35% when compared to only 19% of β-TCP detected for the powder Khap-2. Pure HAP phase was detected for the powder Khap-1 even in the presence of added potassium in the sample. The detected HAP and β-TCP phases for all the potassium substituted apatite powders showed exact matches with the ICDD diffraction standards, card numbers 09-432 and 09-169 for HAP and β-TCP, respectively. Further heat treatment revealed thermal stability for all the potassium substituted powders till 1300 °C, whereas the pure HAP powder (Fig. 9) started decomposing to α-TCP phase at 1300 °C. The FT-IR spectra for Khap-1 and Khap-3 recorded at 1300 °C indicate the presence of HAP phase for all the powders. Bands respective of PO_4 tetrahedra are visible at 485 cm^{-1} (O–P–O bending υ_2), 576 cm^{-1} (O–P–O antisymmetric bending υ_4), 605 cm^{-1} (O–P–O bending υ_4), 980 cm^{-1} (P–O stretching υ_1) and 1095 cm^{-1} (P–O stretching υ_3). The vibrational modes respective of hydroxyl groups were also apparent at 630 cm^{-1} and 3570 cm^{-1} from the FT-IR spectra.

3.4. Chemical analysis and structural parameters

Table 1 shows the chemical analysis for the calcined powders. All the potassium substituted apatite powders indicate the presence of this element in the composition and both Ca/P and (Ca + K)/P molar ratios tend to coincide with the ratios that were planned upon synthesis. The calculated lattice parameters presented in Table 2 reveal that the hexagonal apatite phase was retained in spite of the presence of potassium in substituted apatite powders. However, there are apparent contractions in the variations of the cell parameters *a* and *c*, the first steadily decreases with increasing added amounts of potassium, while the changes observed in the second appear more irregular. The powder Khap-3 which possesses higher amount of potassium in its composition shows higher contraction in *a*-axis in comparison to the other powders.

Table 1
Elemental analysis for the calcined powders [HAP, 1200 °C; Khap-1, Khap-2 and Khap-3, 1300 °C]

Sample	wt.% of elements measured after calcinations			Ca/P ratio		(Ca + K)/P ratio	
	Ca	P	K	Expected	Measured	Expected	Measured
HAP	39.89	18.5	–	1.67	1.668	–	–
Khap-1	39.76	18.42	1.31	1.67	1.67	1.72	1.726
Khap-2	38.96	18.56	1.27	1.62	1.622	1.67	1.676
Khap-3	38.24	18.71	2.14	1.58	1.579	1.67	1.671

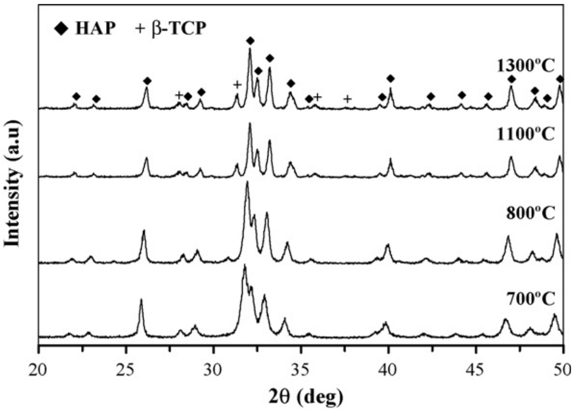

Fig. 7. XRD patterns for Khap-2 calcined at different temperatures.

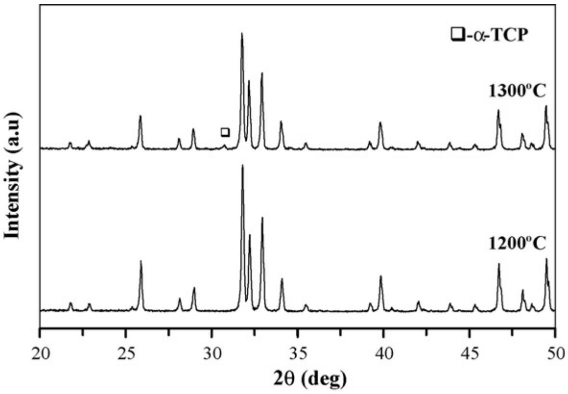

Fig. 9. XRD patterns for pure HAP calcined at different temperatures.

Table 2
Calculated lattice parameters for the calcined powders [HAP, 1200 °C, Khap-1, Khap-2 and Khap-3, 1300 °C] #HAP-JCPDS PDF 09-0432: $a = 9.418$ Å; $c = 6.884$ Å; $V = 528.80$ Å^3 (the errors for the unit cell constants were detected only in the last digit, which are given in parentheses)

Sample	Lattice parameters *a* and *c* and differences Δ*a* and Δ*c* (Å)				Unit cell volumes (*V*) and differences (Δ*V*) (Å^3)	
	a	Δ*a*	*c*	Δ*c*	*V*	Δ*V*
HAP	9.4137(3)		6.8489(4)		525.62(4)	
Khap-1	9.3982(2)	−0.0155	6.8483(2)	−0.0006	523.84(3)	−1.78
Khap-2	9.3973(4)	−0.0164	6.8451(3)	−0.0038	523.50(7)	−2.12
Khap-3	9.3858(3)	−0.0279	6.8477(3)	−0.0012	522.41(5)	−3.21

4. Discussion

The formation of potassium substituted HAP (Khap-1) and two different proportions of biphasic mixtures (Khap-2 and Khap-3) were found to be effective from the present method of synthesis. It is clear from the elemental analysis and X-ray pattern results that Khap-1 has detected single phase HAP even though the calculated (Ca + K)/P molar ratio after calcination was found to be 1.72. In case of Khap-2 and Khap-3 the calculated (Ca + K)/P molar ratio for the powders after calcination has indicated the value of ~1.67. However, the powder Khap-3 that possess increased calcium deficiency (Ca/P = 1.58) have yielded higher proportion of β-TCP in the composition of biphasic mixtures when compared to Khap-2 (Ca/P = 1.62). Hence, it is apparent from the present results that addition of potassium during the synthesis of calcium apatites did not cause significant changes in the phase behaviour and the resultant hydroxyapatites or biphasic mixtures are solely dependent on the Ca/P ratios of the precursors used during the synthesis. The FT-IR spectra for Khap-2 (not presented) and Khap-3 (Fig. 5) showing the presence of HPO_4^{2-} ions at 400 °C and $P_2O_7^{4-}$ ions at 650 °C and the formation of biphasic mixtures at 800 °C that has been confirmed by XRD analysis tend to follow the similar condensation mechanism for calcium deficient apatites as proposed by Mortier et al [24] that are presented in Eqs. (1) and (2).

$$\begin{aligned} &\mathrm{Ca}_{10-z}(\mathrm{HPO}_4)_{2z}(\mathrm{PO}_4)_{6-2z}(\mathrm{OH})_2 \\ &\quad \rightarrow \mathrm{Ca}_{10-z}(\mathrm{P}_2\mathrm{O}_7)_{z-s}(\mathrm{PO}_4)_{6-2z+2s}(\mathrm{OH})_{2(1-s)} \\ &\qquad + (z+s)\mathrm{H}_2\mathrm{O} \end{aligned} \tag{1}$$

$$\begin{aligned} &\mathrm{Ca}_{10-z}(\mathrm{P}_2\mathrm{O}_7)_{z-s}(\mathrm{PO}_4)_{6-2z+2s}(\mathrm{OH})_{2(1-s)} + (z+s)\mathrm{H}_2\mathrm{O} \\ &\quad \rightarrow (1-z)\mathrm{Ca}_{10}(\mathrm{PO}_4)_6(\mathrm{OH})_2 + \mathrm{Ca}_3(\mathrm{PO}_4)_2 \\ &\qquad + (z-s)\mathrm{H}_2\mathrm{O} \end{aligned} \tag{2}$$

Although the present results do not evidence changes in the phase behaviour of HAP and biphasic mixtures, the differences observed in the calculated lattice parameters for the potassium substituted powders when compared to those of stoichiometric HAP are doubtlessly obvious. Some previous studies have explained the role of substitution of biocompatible cations in the apatite structure. Among the biocompatible elements, the most commonly studied ones were magnesium, zinc and strontium [10,25,26]. All these bivalent [Mg^{2+} (0.66 Å), Zn^{2+} (0.74 Å) and Sr^{2+} (1.12 Å)] ions were considered to replace Ca^{2+} (0.99 Å) sites in the apatite structure leading to contraction or expansion of the lattice parameters depending upon their size mismatch with that of Ca^{2+} ions. It is worthy to note that substitutions of these bivalent ions for Ca^{2+} can cause no charge imbalance in apatite lattice. The substituted monovalent ions like Na^+ and K^+ for Ca^{2+} in the apatite structure cause a charge imbalance that can be neutralized by creating supplementary vacancies [27] or by the occurrence of simultaneous substitutions of cations and anions like in case of substitution of Ca^{2+} by Na^+ and of PO_4^{3-} by CO_3^{2-} without any vacancy creation or loss of charge balance [28]. A recent study has also proved that the substituted monovalent ions Na^+ ions could stabilize the apatite till 1300 °C without significant phase decomposition [29].

The present work shows that a similar stabilization effect occurred for the potassium substituted apatite structure. However, the calculated lattice parameters obtained from the present results showed significant contraction in the cell parameter *a* leading to the contraction in unit cell volume with respect to that of stoichiometric HAP. The powder Khap-3 that posses higher content of potassium showed greater contraction with respect to that of Khap-1 and Khap-2. The reason could be explained in a following manner. It is a well established fact that the hexagonal architecture of hydroxyapatite can accommodate a wide variety of ions in its structure [30]. According to Feki et al. [16], a decrease in the cell parameter *a* with the incorporation of monovalent K^+ can be explained by two antagonist effects: (i) the substitution of the larger K^+ (1.33 Å) can induce the extension of *a* parameter; (ii) the substitution of a bivalent cation by a monovalent one can decrease the channel diameter of *a* parameter. The contraction of lattice parameters observed in present work suggests that the second effect is the prevalent one.

Additionally, the influence of potassium on the apatite structure can be assured from the outstanding thermal stability of the potassium substituted hydroxyapatites and biphasic mixtures till 1300 °C without any phase decomposition. This is obvious because the thermal stability of stoichiometric stability HAP prepared by the present method of synthesis was kept only till 1200 °C (Fig. 9) and calcination at 1300 °C promoted its partial decomposition into α-TCP.

5. Conclusions

The present study was successful in the preparation of potassium substituted hydroxyapatites and biphasic mixtures. The substituted potassium HAP did not show significant changes in the phase behaviour of resultant apatites but just small discrepancies in the calculated lattice parameters. However, the substitution of potassium into apatite lattice improved its thermal stability till 1300 °C when compared to that pure stoichiometric HAP. This improved thermal stability of hydroxyapatites and biphasic mixtures with substituted potassium obtained from the present study can be of immense importance in the development for medical applications like: (i) as porous or granulated materials useful in bone surgery, (ii) as additives to organic polymers improving their biofunctionality and (iii) as coatings, plasma sprayed or prepared by laser ablation, necessarily need heat treatments at elevated temperatures.

Acknowledgements

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