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Synthesis and mechanical behaviour of chlorapatite and chlorapatite/β-TCP composites

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Abstract

Chlorine substituted hydroxyapatite (HAP) and biphasic mixtures (HAP + β-TCP) were prepared through an aqueous precipitation method. Characterization studies using XRD, thermograms, elemental analysis and FT-IR spectra have confirmed the incorporation of added chlorine into the apatite structure forming a solid solution. Substitution of chlorine in the calcium deficient apatites tends to form biphasic mixtures of HAP and β-TCP and the proportions in the formed mixtures were dependent on the deficiency of calcium in the precursors used. The thermal stability of the chlorine substituted apatites was evident up to 1200 °C from the present results. The cell parameters for chlorine substituted apatite powders tend to follow significant expansion with respect to those of stoichiometric HAP, being always smaller than those of the stoichiometric chlorapatite sample. The mechanical properties of the solid solution of chlorapatites have shown promising features when compared to the pure stoichiometric chlorapatite sample.

Keywords: Apatite; Chlorapatite; Mechanical properties

1. Introduction

Synthetic hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, HAP] materials are proved potential substitutes for bone in both total replacement and augmentation surgeries due to their structural and crystallographic similarities with the biological apatites and also to their ability to exhibit bioactivity upon implantation process.[1,2] Current interest is turning towards the modification of synthetic apatites by introducing chemical species found in natural bone.[3,4] The incorporation of such species into the apatite structure influences the behaviour of the materials after implantation, namely their chemical and physical properties as well as their bone bonding capability.[5] Under this perspective, a number of research results have been reported so far on the incorporation of trace elements into synthetic apatites, which include cations like magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+) and anions like fluorine (F^-) and carbonates.[6–10]

No significant emphasis has, however, been laid on the substitution of the chloride ion in the apatite, which exists as a trace element in the mineral phase of bone and teeth. Some research results have proved that chlorine can be incorporated into the HAP lattice replacing the hydroxyl group.[11–13] The significance of chloride ions resides in their ability to develop an acidic environment on the surface of bone that activates osteoclasts in the bone resorption process.[14,15] Thus their incorporation in apatites may be vital in the development of low pH to solubilize the alkaline salts of bone mineral and to digest the organic matrix by the action of the acid hydrolases which osteoclasts secrete. However, pure chlorapatite rather than chlorine-substituted HAP, could not be a good biomaterial because the total replacement of hydroxyl group by chlorine will enhance the local environment acidity, leading to a fast solubilization of alkaline salts. Moreover the content of chlorine in natural bone[16] is about ≈0.13 wt.%, whereas its composition in pure chlorapatite is of 6.8 wt.%.

Another significant perspective in the modern research is the development of biphasic mixtures that comprise HAP and β-TCP components in varied proportions as a potential bone substitute.[17–19] The different dissolution behaviours of these two components (HAP—non-resorbable and β-TCP—resorbable)

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Table 1
Molar concentrations of the precursors Ca, P and Mg used in the synthesis

Sample code	Molar concentrations of the precursors			Ca/P ratio	Wt.% of incorporated chlorine
	Ca	P	Cl		
HAP	1.0	0.6		1.67	–
Clap	1.0	0.6	0.20	1.67	6.42
Clap-1	1.0	0.6	0.025	1.67	0.72
Clap-2	0.972	0.6	0.025	1.62	0.69
Clap-3	0.948	0.6	0.025	1.58	0.64

have tended to make the HAP/β-TCP composites more suited to promote new bone formation at the implant site in comparison with individual HAP or β-TCP. Generally the preparation procedure for the biphasic mixtures is the formation of calcium deficient apatite and subsequent calcination beyond 700 °C to form a mixture of components containing HAP and β-TCP with the resultant proportions dependent on the calcium deficiency of the precursors.[4,20,21]

The aim of our present investigation is to prepare chlorine substituted HAP and biphasic mixtures (HAP + β-TCP) which promise to be better materials in the resorption process upon implantation when compared with pure HAP and biphasic mixtures without any substituents. Some previous studies on the preparation of chlorapatite have been performed through hydrothermal treatments at temperatures in the range of 200–800 °C.[22] In a recent study the authors have reported that chlorine can be substituted for OH group in the apatite lattice through wet chemical synthesis and the extent of chlorine incorporation depends on the concentration of the precursors used.[23] In the present study, attention was focused on the preparation of HAP and biphasic mixtures with a chlorine content that closely mimics the bone composition. The methodology of calcining the calcium deficient apatites above 700 °C to form biphasic mixtures was adapted in the present study to form chlorine substituted biphasic ceramics. The synthesized powders were characterized using thermal analysis, X-ray diffraction and FT-IR spectra. The mechanical properties such as flexural strength and hardness were also evaluated to determine the effects of incorporated chlorine on the mechanical behaviour of the substituted apatites.

2. Experimental

2.1. Powder preparation

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. Reagent grade Calcium nitrate tetrahydrate [($Ca(NO_3)_2{\cdot}4H_2O$, Vaz-Pereira, Portugal] diammonium hydrogen phosphate [$(NH_4)_2HPO_4$, Vaz-Pereira, Portugal] and ammonium chloride [(NH_4Cl), Merck] were used as starting chemicals precursors, respectively, for calcium, phosphorous and chlorine.

For the preparation of chlorine substituted apatites, a $(NH_4)_2HPO_4$ solution was slowly added to the solution containing $Ca(NO_3)_2{\cdot}4H_2O$ under stirring at a rate of 1000 rpm. To this solution mixture a predetermined concentration of NH_4Cl was added slowly (molar concentrations of precursors are 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 a constant stirring at 1000 rpm. Additionally, stoichiometric HAP and pure chlorapatite were prepared under the same conditions for the comparison of results. The precipitated suspension was removed from the reactor and allowed to settle for 24 h for the maturation of the precipitate. After 24 h, the precipitates were separated using a 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. Characterization techniques

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) to analyze the thermal behaviour during heating. 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 both as prepared and calcined powders were carried out using a high resolution Rigaku Geigerflex D/Mac, C Series diffractometer with copper Kα radiation ($\lambda = 1.5406$ nm) produced at 30 kV and 25 mA scanning the diffraction angles (2θ) between 20° and 50° 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. Silicon was used as internal standard. The volume V of the unit cell was determined for each HAP formulation. Quantitative determination of the phase compositions of biphasic mixtures were made using X'Pert High Score 1.0*f*, PANalytical BV using the International Center for Diffraction Data (2004) database. Crystallographic identification of the phases of synthesized apatites was accomplished by comparing the experimental XRD patterns to standards compiled by the International Center for Diffraction Data (ICDD), which were card # 09-0432 for HAP, # 09-0169 for β-TCP and # 33-0271 for chlorapatite.

Elemental analysis for the presence of chlorine at 1200 °C was 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. Infrared spectra for both as prepared and calcined powders 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.

2.3. Mechanical tests

The as prepared powders were calcined at 1100 °C and then milled in a high speed porcelain mill, resulting in powders with mean particle size around 1.5 μm for all powders (measured in a particle size analyser COULTER LS230, UK, with Fraunhofer optical model). A stock suspension of each powder was prepared with 55 vol.% solids loading and stabilised using 1.5 wt.% Targon 1128 (BK Ladenburg, Germany), according to a procedure previously described.[24] In order to obtain good compaction during pressing, 3 wt.% of a binder (Mowilith DM 2 HB, Clariant, Spain) and 1.5 wt.% of a plasticizer (PEG200, Aldrich, Germany), based on the dry mass of solids, were added to suspensions, and the mixtures left to homogenize for 1 h in a rolling system. The as-prepared suspensions were then granulated by freeze granulation (PowerPro freeze granulator LS-2, Sweden) and the granules dried in a freeze dry system (Labconco, LYPH Lock 4.5) for 72 h. After complete drying, the granules were pressed to form rectangular bars with dimensions 4 mm × 5 mm × 50 mm by uniaxial pressing (80 MPa). After debinding at 550 °C for 2 h, the bars were sintered at 1200 °C, for 2 h at a heating rate of 5 °C/min.Flexural strength was measured in series of 20 specimens using a three-point bending device and Shimadzu equipment (Shimadzu Autograph AG-IS—10 kN, Kyoto, Japan), at a strain rate of 0.5 mm/min. For all the samples, the load–displacement curves presented an elastic region ending with brittle fracture.Vickers hardness tests were carried out using a Zwick/Roell hardness tester (Zwick/Roell ZHU, Ulm, Germany). Polished samples were indented with a Vickers diamond pyramidal indenter having a square base and 136° pyramidal angles. The load was 5 kg and 20 indentations were made and the averaged hardness values were taken for the analysis.Microstructure observations made at the etched surfaces of the sintered bars (immersion in 15% H_3PO_4 solution for 15 s) were done by scanning electronic microscopy (SEM HITACHI, S-4100, Tokyo, Japan, 25 kV acceleration voltage, beam current 10 μA). The density of the sintered samples was determined by Archimedes method by immersion in mercury.

3. Results and discussion

3.1. Synthesized 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 powders except HAP display broad diffraction patterns indicative of poor crystallinity. The substitution of chlorine did not appear to affect the diffraction pattern of the as prepared powders. It should be noted that X-ray diffraction analysis of the as-precipitated apatite powders resulted in diffraction patterns similar to that of HAP even though the Ca/P ratio was greater or less than the stoichiometric molar ratio of 1.67 for HAP.[25,26] 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, 574, 609, 966 and 1020–1120 cm^{-1}. The bands at 630 and 3570 cm^{-1} for all the powders except for the sample Clap, could be attributed to the presence of OH group in the HAP phase. The absence of the peaks respective of OH groups from the sample Clap indicates that the substituted chlorine has totally replaced the OH group of apatite phase. The other chlorine substituted samples such as Clap-1, Clap-2 and Clap-3, with partial replacement of the OH group with substituted chlorine show the presence of OH groups. However, it is difficult to explain the role of substituted chlorine in the as prepared powders due to their low degree of crystallinity. For a more precise characterization, a heat treatment is therefore required. The presence of the adsorbed water in the as prepared powders could also be detected from FT-IR spectra in the region around 3300–3600 cm^{-1}. The presence of carbonate (CO_3) groups at 1660 cm^{-1}, which might

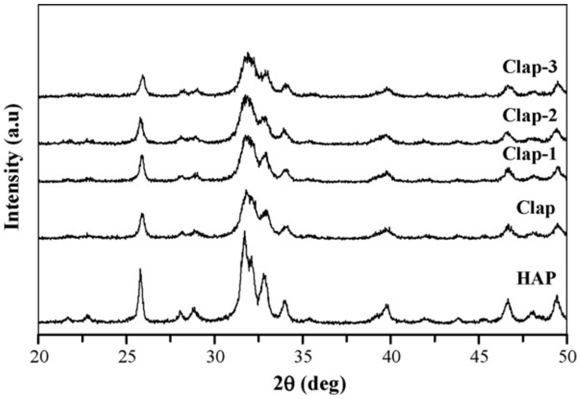

Fig. 1. X-ray diffraction patterns for the as prepared powders.

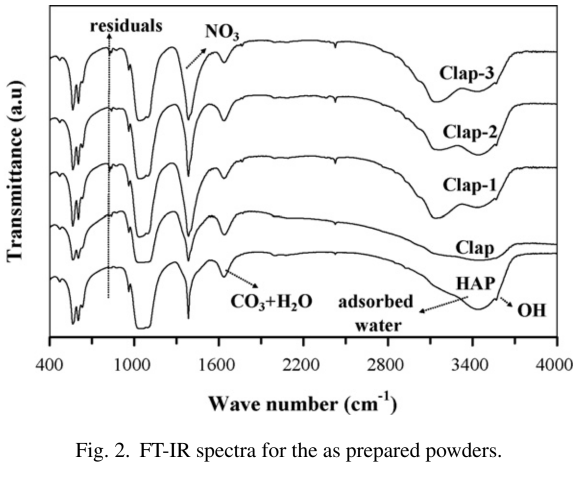

Fig. 2. FT-IR spectra for the as prepared powders.

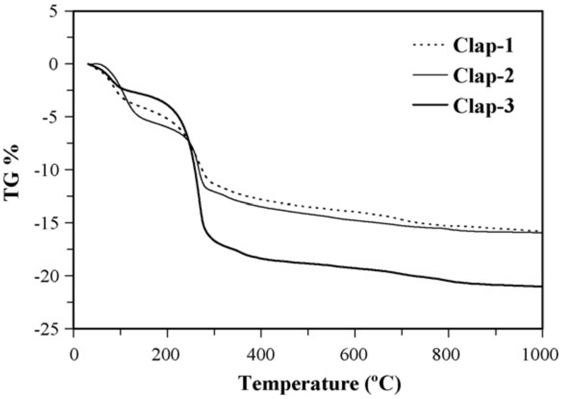

Fig. 3. Thermogravimetric (TG) analysis for different chlorine substituted apatites.

be due to the adsorbed species remaining from the aqueous precipitation was detected in all the synthesized powders. Residual nitrates (NO_3) in the as dried powders are also found in the FT-IR patterns in the region around 1320–1480 cm^{-1}. The presence of residual NH_4^+ ions at 875 cm^{-1} and nitrates, apparent in all the as prepared powders, tends to coincide with the observations made in a previous study.[27]

3.2. Thermal behaviour

The TG-DTA analysis for the samples Clap-1, Clap-2 and Clap-3 are presented in Figs. 3 and 4. During the course of heating of the precipitated apatites, mainly three stages of mass loss could be differentiated: (i) from 30 to 200 °C: all the samples have indicated similar weight losses of about 7%, thus accounting for the lattice bound water loss with no significant structural changes in this temperature range. (ii) 200–700 °C: in this region the samples Clap-1, Clap-2 and Clap-3 experienced different weight losses of 6, 8 and 13%, respectively. Although the loss of residuals, chemisorbed water and carbonates are favored in this temperature range (Fig. 5), the main difference in weight loss could be attributed to the varied concentrations of the precursors used during preparation. Since the same concentration of chlorine and phosphorous was used in all the samples, the observed differences in weight loss could be solely due to the different levels of added calcium.

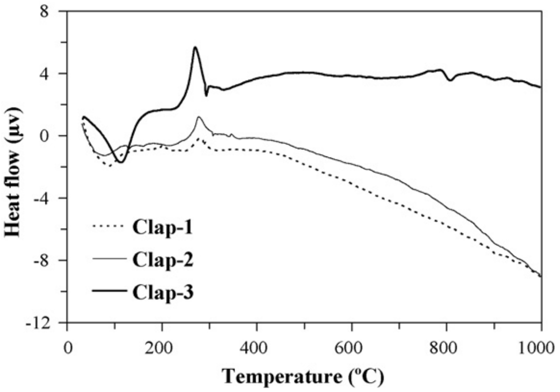

Fig. 4. Differential thermograms (DTA) for different chlorine substituted apatites.

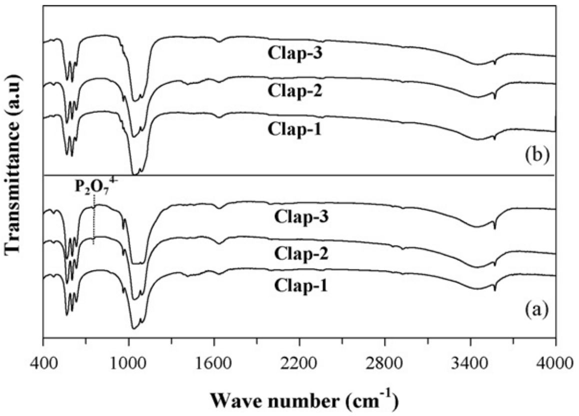

Fig. 5. FT-IR spectra for the powders Clap-1, Clap-2 and Clap-3 calcined at (a) 650 °C and (b) 800 °C.

The exothermic peaks observed in the DTA curve at 280–310 °C, especially for the powders Clap-2 and Clap-3, indicate that some structural reorganization occurred in this particular temperature range. These exothermic effects can be attributed to the condensation of hydrogenophosphate ions (HPO_4^{2-}) due to calcium deficiency ($Ca/P < 1.67$) to form pyrophosphates ($P_2O_7^{4-}$) as given in Eq. (1).

$$2Ca^{2+} + 2HPO_4 \rightarrow Ca_2P_2O_7 + H_2O \tag{1}$$

(iii) 700–800 °C: in this temperature range the already formed $Ca_2P_2O_7$ converts to β-tricalcium phosphate (β-$Ca_3(PO_4)_2$)[28–30] following a reaction according to Eq. (2), leading to a noticeable weight loss of about 1.5% for the sample Clap-3 in the narrow temperature range around 780–800 °C.

$$Ca_2P_2O_7 + 2OH^- \rightarrow Ca_3(PO_4)_2 + H_2O \tag{2}$$

This, in conjunction with the endothermic effect appearing in the DTA curves within the same temperature range confirms the formation of β-TCP. However this endothermic effect at 780–800 °C is not apparent for the sample Clap-2 with less calcium deficiency ($Ca/P = 1.62$), when compared to the sample Clap-3 ($Ca/P = 1.58$). This is according to the lower degree of transformation into β-TCP that is expected to occur under these conditions. The FT-IR spectra shown in Fig. 5 also confirm the presence of $P_2O_7^{4-}$ ions at 730 cm^{-1} for the powders Clap-2 and Clap-3 at 650 °C that were not found in the sample Clap-1. The peak corresponding to $P_2O_7^{4-}$ disappeared after calcination at 800 °C, indicating that the transformation was complete after this heat treatment.

In summary for the thermal analysis, the added chlorine into the precipitated apatites did not have a great impact during the heat treatment. The non-significant changes observed in the thermograms made it possible to infer that substituted chlorine tended to form a solid solution of chlorapatites.

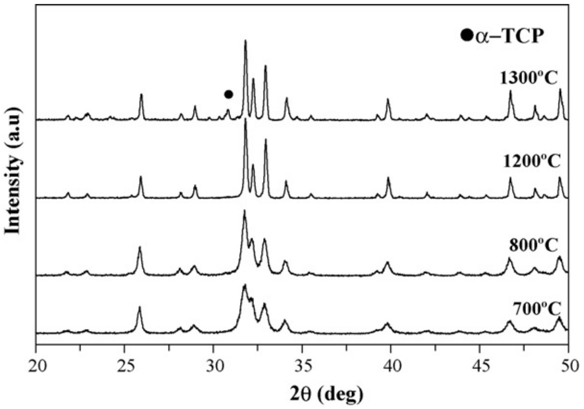

Fig. 6. X-ray diffraction patterns for the powder Clap-1 calcined at varied temperatures.

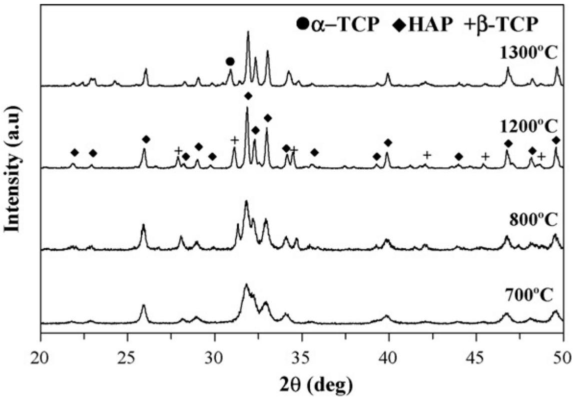

Fig. 7. X-ray diffraction patterns for the powder Clap-2 calcined at varied temperatures.

3.3. Calcined powders

3.3.1. XRD analysis

The evolution of crystalline phases with the heat treatment temperature for the different chlorine substituted apatites within the 2θ range from 20° to 50° is shown in the XRD patterns of Figs. 6–8. At the lower heat treatment temperature (700 °C), poor crystalline apatite phase, characterized by broad diffraction bands, can be observed for all the samples. The transformation into biphasic mixtures is apparent from the XRD patterns for the powders Clap-2 and Clap-3 calcined at 800 °C presented in Figs. 7 and 8. The increase in the calcium deficiency of the powder Clap-3 (Ca/P = 1.58) resulted in the formation of a higher proportion of β-TCP (32%) in the biphasic mixture in comparison to the 19% of β-TCP determined for the sample Clap-2 (Ca/P = 1.62). The XRD analysis of the powders heat treated at higher temperatures indicated thermal stability of the phase mixtures till 1200 °C. The XRD patterns for pure HAP and Clap calcined at 1200 °C displayed in Fig. 9 also confirmed their thermal stability till 1200 °C. This thermal stability is not commonly observed in biphasic mixtures without any substituted elements. As a matter of fact, β-TCP readily transforms into α-tricalcium phosphate (α-TCP) at 1120 °C.[31,32] This unusual behaviour suggests that the chlorine incorporated in the apatite lattice tends to stabilize the phase mixtures.

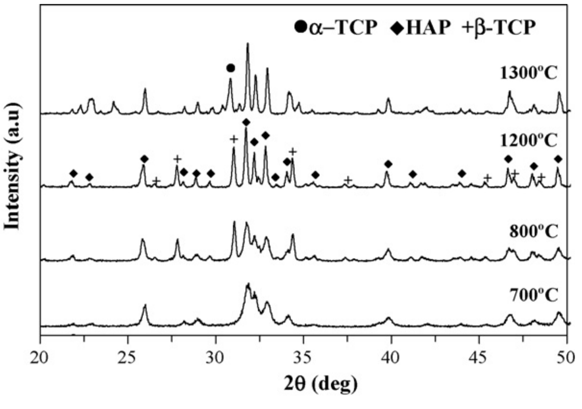

Fig. 8. X-ray diffraction patterns for the powder Clap-3 calcined at varied temperatures.

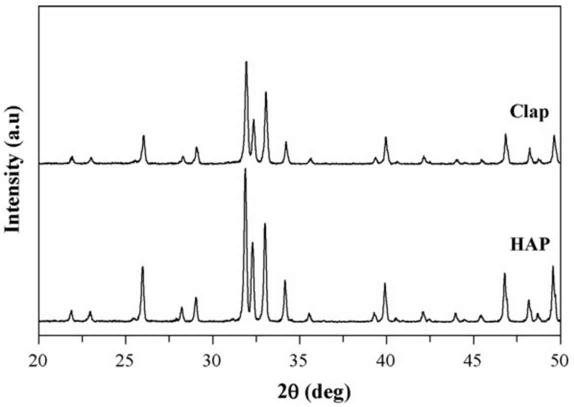

Fig. 9. X-ray diffraction patterns for HAP and Clap calcined at 1200 °C.

3.3.2. Influence of chlorine

Evidence for the incorporation of chlorine in the apatite structure during synthesis were given from the XRD analysis and confirmed by elemental analysis obtained at 1200 °C. It should be noted that the detected chlorine is nearly equal to its content in natural bone. No significant changes were found in the XRD patterns due to chlorine incorporation. The main changes derived from the extent of calcium deficiency in the samples Clap-2 and Clap-3 that yielded biphasic mixtures of HAP and β-TCP. Significant evidence for the incorporation of chlorine in the apatite structure is also given by the calculated lattice parameters of the samples calcined at 1200 °C. From the values reported in Table 2, one can infer that the hexagonal apatite structure was retained for all the chlorine substituted samples with no major structural distortion. As the apatite architecture is ready to accept a wide variety of substitutions both anionic and cationic,[33] the negatively charged Cl^- ions added during the synthesis tend to replace the OH^- ions of HAP. It is meaningful to mention that the cell parameters are expected to be significantly affected if total replacement of Cl^- ions (1.81 Å) by OH^- ions (1.68 Å) would take place as it is well seen for the sample Clap. A significant expansion of all the parameters of *a*-axis, *c*-axis and of the unit cell volume (V) has been observed for Clap with respect to that of HAP. The samples Clap-1, Clap-2 and

Table 2
Calculated lattice parameters for the different chlorine substituted apatites (the values given in parenthesis denote the ±errors measured for the last digit)

Sample	Calculated lattice parameters (*a* and *c*) and unit cell volume (*V*)		
	a (Å)	*c* (Å)	*V* ($Å^3$)
HAP	9.4087 (3)	6.8489 (4)	525.06 (3)
Clap	9.4397 (4)	6.8843 (4)	531.26 (4)
Clap-1	9.4106 (4)	6.8534 (3)	525.62 (4)
Clap-2	9.4117 (3)	6.8635 (2)	526.52 (3)
Clap-3	9.4207 (2)	6.8713 (3)	527.97 (2)

Chlorapatite JCPDS PDF # 33-071 ($a = 9.641$, $c = 6.771$, $V = 1629.40$). Hydroxyapatite JCPDS PDF # 09-432 ($a = 9.418$, $c = 6.884$, $V = 1580.84$).

Clap-3 in which partial replacement of OH^- ions by substituted Cl^- ions occurred, have shown comparably lower expansion in the lattice parameter values in comparison to HAP and contraction with respect to the values of sample Clap. It could be also inferred from the present results that substituted chlorine tends to form solid solution of chlorine substituted apatites.

3.3.3. FT-IR spectra

FT-IR spectra of three different chlorine substituted apatites heat treated at 1200 °C are presented in Fig. 10. The fundamental vibrational modes of $PO_4{}^{3-}$ tetrahedra of apatite phase are witnessed for all the powders in the region around at 960 cm^{-1} (ν_2), 1015 and 1085 cm^{-1} (ν_3), 565 and 590 cm^{-1} (ν_4) and 470 cm^{-1} (ν_1) for all the powders.[3,34] The presence of OH group (stretching mode at 3570 cm^{-1} and bending mode at 630 cm^{-1}) of apatite phase can be detected from the FT-IR patterns for all the powders except for Clap sample. It is interesting to mention that no specific bands for chlorine could be detected in the FT-IR spectra of Clap sample but the evidence of its incorporation in the apatite structure is confirmed by the total replacement of OH^- ions by Cl^- for sample Clap. For this sample, the bands corresponding to OH group have been detected neither at 3570 cm^{-1} nor at 630 cm^{-1}. However, the bands corresponding to OH group for the samples Clap-1, Clap-2 and Clap-3 are viewed with less intensity in comparison to those of OH groups of stoichiometric HAP. This confirms that partial replacement occurred in these compositions. Hence the infra red spectra coincides with the results obtained from X-ray patterns with no observed significant changes or distortions in the position of functional groups, thus accounting for the formation of solid solution of chlorine substituted apatite.

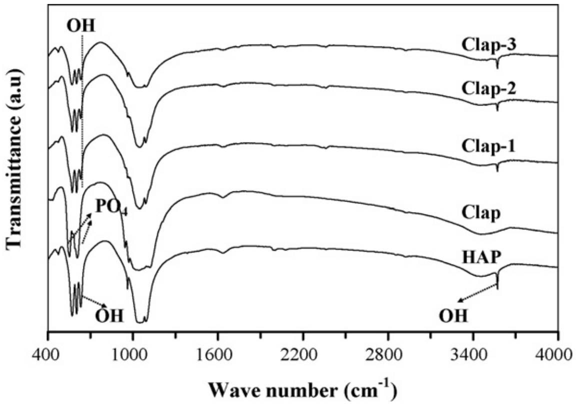

Fig. 10. FT-IR spectra for HAP and different chlorine substituted apatite powders calcined at 1200 °C.

Table 3
Mechanical test data obtained for the sintered bars after sintering at 1200 °C

Sample code	Mechanical data		
	Flexural strength (MPa)	Vickers hardness (HV5)	Density (g/cm^3)
HAP	57.68 ± 15.36	297.45 ± 9.53	2.83 ± 0.05
Clap	39.21 ± 13.04	170.11 ± 6.70	2.23 ± 0.03
Clap-1	57.76 ± 10.89	237.99 ± 7.41	2.75 ± 0.02
Clap-2	54.15 ± 12.43	191.31 ± 7.58	2.50 ± 0.05
Clap-3	45.02 ± 3.52	120.47 ± 4.66	2.47 ± 0.08

3.3.4. Formation mechanism

The formation of solid solution of chlorine substituted apatites from the present study can be represented in the form of chemical equations as given below. For Clap sample the chemical expression can be represented as in Eq. (3).

$$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 2NH_4Cl + 6NH_4OH \rightarrow Ca_{10}(PO_4)_6Cl_2 + 20NH_4NO_3 + 6H_2O \qquad (3)$$

For the sample Clap-1 where partial replacement occurred, the chemical reaction can be represented by Eq. (4) as

$$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + xNH_4Cl + (8 - x)NH_4OH \rightarrow Ca_{10}(PO_4)_6[(OH)_{2-x}(Cl)_x] + 20NH_4NO_3 + H_2O \qquad (4)$$

For Clap-2 and Clap-3 samples, in which chlorine was found incorporated into the apatite structure with the simultaneous formation of biphasic mixtures, the transformations can be represented by the modified forms of Mortier[27] expression, Eqs. (5) and (6) as

$$Ca_{10-z}(HPO_4)_{2z}(PO_4)_{6-2z}[(OH)(Cl)]_2 \rightarrow Ca_{10-z}(P_2O_7)_{z-s}(PO_4)_{6-2z+2s}[(OH)(Cl)]_{2(1-s)} + (z + s)H_2O \qquad (5)$$

$$Ca_{10-z}(P_2O_7)_{z-s}(PO_4)_{6-2z+2s}[(OH)(Cl)]_{2(1-s)} + (z + s)H_2O \rightarrow (1 - z)Ca_{10}(PO_4)_6[(OH)(Cl)]_2 + Ca_3(PO_4)_2 + (z - s)H_2O \qquad (6)$$

3.3.5. Microstructural features and mechanical properties

The scanning electron micrographs of the etched surfaces of all the sintered samples are presented in Fig. 11. The microstructures of HAP (Fig. 11a) and Clap-1 (Fig. 11c) exhibit dense microstructures, which are expected to improve the mechanical properties, as observed (Table 3). The microstructures of Clap-2 (Fig. 11d) and Clap-3 (Fig. 11e) samples after sintering at 1200 °C show less dense microstructures in comparison to

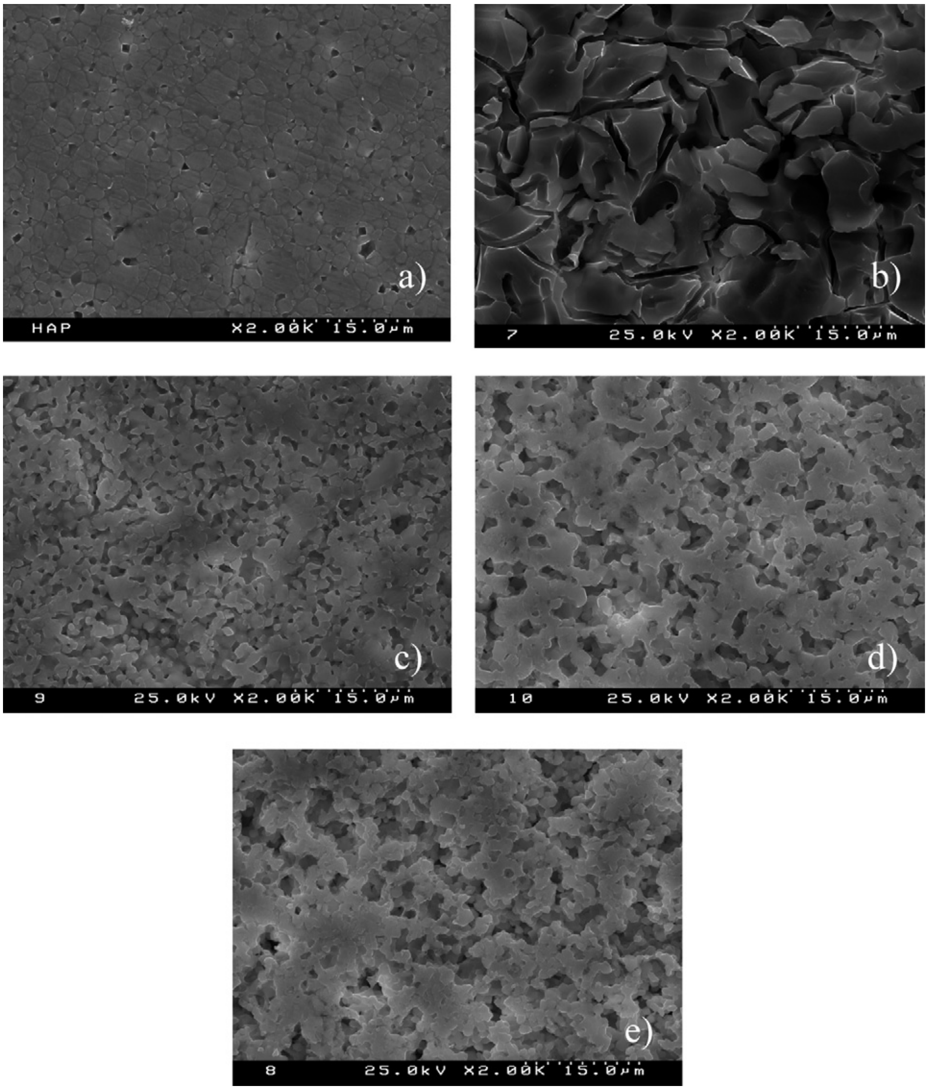

Fig. 11. Scanning electron micrographs for the etched surface of sintered HAP and chlorapatites sintered at 1200 °C (a) HAP, (b) Clap, (c) Clap-1, (d) Clap-2 and (e) Clap-3.

those of HAP and Clap-1. This explains the poorer mechanical properties measured for the samples Clap-2 and Clap-3. On the other hand, the stoichiometric pure Clap (Fig. 11b) sample is significantly porous due to its poor sintering behaviour, thus leading to very low mechanical performance.

From the data on the mechanical properties of all the sintered apatite samples presented in Table 3 it is apparent that the samples HAP and Clap-1 exhibit improved values of flexural strength, hardness and density in comparison to the other samples. The mechanical properties decreased in the following order: Clap-1 (Ca/P = 1.67) > Clap-2 (Ca/P = 1.62) > Clap-3 (Ca/P = 1.58). This is exactly the same order of increasing calcium deficiency in the compositions. Surprisingly, the lowest values of mechanical properties were measured for stoichiometric chlorapatite (Clap). This suggests that the total replacement of OH by the substituted Cl in the apatite lattice can destabilize the apatite structure, unlike substituted F, which proved to have a positive influence on the stability of the apatite structure. The present results also show that the incorporation of a very low concentration of Cl, as in the case of sample Clap-1, has a negligible effect on the mechanical properties of the apatite, since the measured values for Clap-1 and stoichiometric HAP are more or less similar.

4. Conclusions

The following conclusions can be drawn from the present results:

(1) Synthesis of solid solutions of chlorine substituted hydroxyapatites and biphasic mixtures were achieved through aqueous precipitation.
(2) The substitution of chlorine in the calcium deficient apatites resulted in the formation of chlorine substituted biphasic mixtures upon calcination above 800 °C, in which the proportions of β-TCP increased with increasing the degree of calcium deficiency.

(3) The substituted apatites revealed thermal stability till 1200 °C, while calcination at 1300 °C led to the formation of α-TCP.
(4) The calculated unit cell parameters tend to agree with the influence of substituted chlorine in the apatite structure.
(5) FT-IR spectra has provided a good understanding about the influence of chlorine on the apatite structure and proved the presence of functional groups (PO_4 tetrahedra and OH groups) characteristic of apatite phase, in good agreement with the results from X-ray patterns and thermal analysis.
(6) The microstructural features of the samples support the results measured for the mechanical properties.

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