Structural characteristics and mechanisms of fluorapatite mechanochemical synthesis

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SUMMARY
This paper analyzes mechanisms of fluorapatite mechanochemical synthesis and its structural characteristics. Several studies of Jokanovic et al. published in appropriate journals and the book “Nanomedicine, the biggest challenge of the 21st century” are the base for this article. Characteristics of obtained materials show numerous biological advantages associated with the specific structural design of material during the process of synthesis. X-ray diffraction (XRD) and infrared spectroscopy with Fourier transform (FTIR) were used for studying the processes of fluorapatite synthesis.

Keywords: fluorapatite; mechanochemical synthesis; X-ray diffraction; infrared spectroscopy; low-temperature treatment

INTRODUCTION
Fluorapatite (FA), chemical formula Ca5(PO4)3F, or Ca10(PO4)6F2, is the most stable, least soluble, and the hardest calcium orthophos mineral (Mohs hardness scale 5). Such characteristics of fluorapatite are associated to the specific position of F- ions in the center of the Ca2 triangle and its crystal structure. The synthesis techniques are similar to those of hydroxyapatite, but it should be noted that synthesis of fluorapatite involves the presence of F- ions, which are transmitted into synthesis through CaF2, NaF or NH4F. Compared to hydroxyapatite (HA), which is Ca-deficient, there are no data to suggest Ca-deficiency of fluorapatite. The chemical formula of fluorapatite is Ca10(PO4)6(F-,OH)2 as the most frequent modification of OH-ions by F-ions is not complete. Among all human calcified tissues, the greatest concentration of fluorapatite is found in bones, and the lowest in enamel. However, even where there is the largest concentration of fluorapatite, the amount of fluoride is usually reduced related to stoichiometric quantities. Due to its low solubility (degradation rate), it is rarely used as a bone substitute.

Due to mechanical stability, its solubility is reduced and proliferation of bone tissue is improved. Hydroxyapatite / fluorapatite (FHA / FA) has been used as clinical restorative material in the recent years [1, 2]. In addition, FHA and HA / FA, are used in biomedicine as carriers of drugs and catalysts or absorbents [3, 4].

Compared to HA [1], FHA / FA has better thermal and chemical stability [5, 6]. When a certain number of OH groups in the HA matrix is replaced by F ions, thermal and chemical stability of FHA / FA ceramics increases significantly. Theoretically, the ratio F : OH ≥ 1 within the chain OH (in the FHA structure) would be sufficient to arrange HA crystals, stabilizing their structure due to alternating schedule of F ions among OH ions.

In practice, materials that contain F ions are widely used for dental restorations as they prevent tooth decay and reduce bacterial activity in an acidic environment. In addition, F ions themselves favour mineralization and crystallization of calcium phosphate during bone formation [7]. Furthermore, in vitro studies FHA / FA have indicated its slow dissolution, better deposition layer as with hydroxyapatite, better adsorption of the protein [6-8], and similar or better cell attachment compared to pure HA [7, 9] as well as improved activity of alkaline phosphatase [6].

It has also been shown that the presence of fluoride affects the increase in quantity and quality of bone in body [5]. Fluoride ion is used to treat osteoporosis because bone mass increases with the application of F ions [9]. F ions also stimulate the activity of osteoblasts, both in vitro and in vivo. In addition, the mineral phase of enamel consists of HA (95 - 97%) with from 0.04 to 0.07 wt. % Fluoride. A dose of about 1.5-4 mg of fluoride per day significantly reduces the risk of tooth decay [5]. In addition to FHA and FHA phase, materials like CaF2 are also important in dentistry, because they can be used as reservoir of labile fluoride in caries prevention [10-14].

Some studies have shown that dual delivery system of (F and Ca2+ ions) is necessary to allow homogeneous nucleation and formation of very small crystals of CaF2 in the mouth. These amounts are very efficient in increasing the deposition and retention of labile F ions in the mouth, while at the same time remineralization effect increases.
without consequent increasing of F-content [15-23]. According to the research of Jokanovic et al. [24] it was described for the first time not only a specific method of synthesis of fluorapatite, but also a synthesis of combined system encapsulated in surface-active substance polyethylene vinyl acetate / versatate, which is a potential source of labile CaF2 phase. This is very important in order to maintain a balance of F ions content and to improve chemical and mechanical stability of the tooth.

For the synthesis of FHA / FA using precipitation, different methods are used like sol-gel, hydrolysis, hydrothermal method and solid phase reactions. They include appropriate ion exchange between the reactants that are used in the synthesis of FA [23-26]. Most chemical methods require very precise control of parameters of the synthesis process, product composition control and control of its characteristics, which is not so easy to achieve. Therefore, those methods are not suitable for the synthesis of FHA / FA on an industrial scale [27].

On the other hand, mechanochemical process is simple method that takes place in the solid state, allows synthesis of materials through the extremely efficient process of mixing different ion types due to shear forces, which using reduction of particle size and their alternating layers positioning improve thermodynamics and kinetic reactions between different solid substance precursors. In addition, compared to other above-mentioned processes, this method is more suitable regarding economic and technical sides because it enables mass production of nanocrystalline powders and high flexibility of process parameters [13].

The aim of this study was to present the method of synthesis of Nano powders fluorohydroxyapatite / fluorapatite using the method of mechanical alloying. Milling parameters such as speed of rotation, diameter, number of spheres, and weight ratio of the dust-spheres were constant, while the influence of milling time on phase composition was carefully defined. The kinetics and mechanism to obtain FHA / FA and other transitional phases were examined using XRD and FTIR spectroscopy.

**MECHANISMS OF FLUORAPATITE SYNTHESIS**

The mechanisms of fluorapatite synthesis are shown in the case of the most commonly used precursors such as calcium hydroxide Ca(OH)2, phosphorus pentoxide P2O5, and calcium fluoride CaF2 (synthesis 1) and calcium hydroxide Ca(OH)2, phosphorus pentoxide P2O5 and ammonium fluoride NH4F with the addition of surface-active substance vinyl acetate / versate (EVA / AVV) (synthesis 2). Both mechanisms are carried out through the series of processing steps that can be analyzed using IR spectroscopy and X-ray diffraction [24]. It was noted that each phase is followed by certain degree of transformation of starting reactants in fluorhydroxyapatite with smaller segments of OH groups and larger segments of F ions instead of OH groups, until complete transformation of fluorapatite is finished. Generally, the reaction is carried out with an incomplete stoichiometry where x is the value that defines deviation from complete symmetry and can be found in the interval $x_1 < x < x_k$.

$$\text{Ca}_{10(PO_4)_{1-y}(CO_3)_y} \text{(PO}_4\text{)}_2 \text{(OH)}_{2x_1} \text{(F)}_{2x_1} + (2-2x_1) \text{HF} \rightarrow \text{Ca}_{10(PO_4)_{1-y}(CO_3)_y} \text{(PO}_4\text{)}_2 \text{(OH)}_{2x_2} \text{F}_{x_2} + (2-x_2) \text{HF} + \text{H}_2\text{O};$$

where $x_1$ maximum value is 1 and $x_2$ minimum value is 0.

So, the summary reaction in the reaction with total stoichiometry would be:

$$9 \text{Ca(OH)}_{2-y} \text{(CO}_3\text{)}_y + 3\text{P}_2\text{O}_5 + \text{CaF}_2 \rightarrow 9 \text{Ca}(\text{PO}_4)_{1-y} \text{(CO}_3\text{)}_y \text{(PO}_4\text{)}_2 \text{(F)}_{x_2} + 9\text{H}_2\text{O} ; x=1$$

Based on X-ray diffraction, it was found that after only 1h of mechanochemical treatment, amorphization had occurred.

Due to extremely high concentration of mechanical strain on a very small contact surface (the contact that is realized in mutual globe collision or in globe collision with the surface of the inner lining) conditions are generated for the emergence of high shear stresses in a relatively small contact surface. Thus, the size of tension strain depends primarily on the diameter of spheres used in mechanochemical treatment (the size of the contact portion of a sphere indentation deformation in a crash) and the speed collision. Simultaneously, strain transfer leads to mechanical activation of the system and highly resilient flow that follows intense chemical and phase changes in the material (reaction shift, mixing ionic types, creating new phase, etc.). These changes can be such that material during the relaxation time partly suffers reversible deformation (highly resilient flow) or can be entirely irreversible when creep mechanism dominates.

The tension of critical deformation depends on the system exposure time to deformation (the number of sphere blows), in other words the number of pressure cycles, so that with time, the tension which provokes critical deformation demolition/formation of fissures and new areas, has less and less value, leading to larger amorphousness of the system. The process of mechanical activation in which water appears as a reaction product, is additionally accelerated by facilitating the transport of adequate ion types to places that correspond to the minimum of free energy of the system.

In this case, because of the exceptional hydrophilicity of P2O5, immediately upon its adding to other reactive substances, the process creates phosphorus acid (P2O5 + 3H2O → 2H3PO4), which then reacts with Ca(OH)2 (CO3) (carbonate calcium hydroxide) and creates Ca(HPO4) (carbonate calcium hydrogen phosphate).

After 4h of milling, the distinctive HPO42- start to vanish intensively and 5h after completely disappears, while the band on 963 cm⁻¹, appears (carbonate calcium hydroxyfluorapatite) (Figure 1). Simultaneously, during the whole process, CaF2 dissociates and F ions that enter into reactonare created with calcium deficient hydroxide fluorapatite until the formation of its final chemical form. Finally, on previously mechanically treated samples during the period of 6 and 9 hours, and their afterwards thermic treatment on 1100°C, the bands belonging to CO32- disappear on 1420 and 1455 cm⁻¹. In samples mechanically treated for 6 hours one band ap-
pears on 630 cm\(^{-1}\) indicating that exchange between fluor and hydroxide group was not completed. The band on 726 cm\(^{-1}\) that belong to F ions, is constantly present during the whole process demonstrating that F coordination is not significantly changed through the process of F transfer from CaF\(_2\) into calcium hydroxide fluorapatite.

The rate of deprotonation of HPO\(_4^{2-}\) and ion exchange of OH and F regulate the rate of formation of fluorapatite in all stages of the process. The process of dissociation of calcium fluorite occurs through the process of chemical etching of its particles, within the defects of the system (open surfaces, corrosion pits, dislocations, dislocation loops, vacancies), and tears Ca\(^{2+}\) ions away from these places, leaving exposed F ions which are carried by water molecules and then transported to places that correspond to a given fluctuating concentration gradient / concentration gradient of the local surface.

This indicates that it is realistic to assume that reactions in larger and smaller initial particles of the system take place in different ways and at different time intervals reach equilibrium conditions for the final reaction of fluorapatite formation. The reaction on the surface of large particles probably runs immediately after the beginning of the mechanochemical treatment, while the cores that are still associated to given initial reactants remained in the depth of the particles. The morphology of the particles, which even in the remote stages of the treatment (4-6 hours) remains the same, testifies that the reactions in every particle / particle group advance individually. The reaction in smaller particles proceeds quickly, and in medium and large particles it progresses with full intensity along the newly created paths (new surface areas, the border of the crystallites / block mosaics, etc.), until the reaction of conversion of the calcium hydroxyfluorapatite into the fluorapatite is fully implemented, as it is shown on the refined XRD spectrum (Figure 2).

Figure 3 shows the nearest neighbours of F\(^{-}\) ion in the structure of carbonate fluorapatite. It is noted that there are three Ca\(^{2+}\) located near F\(^{-}\) ion at a distance of 2.3 Å.
These CaII$^{2+}$ ions form the vertices of an equilateral triangle with F$^-$ ion in the center. There are three CaII$^{2+}$, P$^{5+}$, and O$^{2-}$ ions in the second coordination sphere, which mutually form the vertices of triangles. The distance between F$^-$ and P$^{5+}$ is 3.6 Å, and between P$^{5+}$ and O$^{2-}$(1) is 3.9 Å. There are O$^{2-}$(3) ions above and below the plane containing F$^-$ and CaII$^{2+}$. The oxygen ions occupy the vertices of a dodecahedron. The distance between F$^-$ and O$^{2-}$(3) ions is 3.1 Å, whereas between P$^{5+}$ and O$^{2-}$(3) ions it is 1.5 Å. Figure 2 shows a fragment of the crystal lattice compared with the unit cell. According to the research of Pandaet al. CaII$^{2+}$ has larger atomic size compared to CaI$^{2+}$. When OH$^-$ ions are substituted with F$^-$, there is greater distortion in the structure due to the larger size of the ionic radius of F$^-$. At the end of the mechanochemical synthesis process, F$^-$ ion occupies large space in the center of the lattice forming a stable fluorapatite structure.

According to the research of Jokanovic et al. [24] (OH$, F$ $)$, in addition to the three types of [OH$-$], the chain of apatite also contains the fourth type with different vibrational energies. It is observed in this study that if the criteria for displacement of free vibration OH$^-$ is taken as the criteria for quantifying the changes of OH$^-$ with F$^-$, then it is indicated that about 50% of OH$^-$ groups are modified with F$^-$, while the system, with almost completely changed OH$^-$ groups with F$^-$ (for pure fluorapatite), provides the value of the wave number of 758 cm$^{-1}$ (Figure 4 and Table 1).

**THE METHOD OF SYNTHESIZING WITH ADDITIONAL LOW-TEMPERATURE THERMAL TREATMENT**

Another method of mechanochemical synthesis using the precursors Ca(OH)$_2$, P$_2$O$_5$, NH$_4$F and surfactant of vinyl acetate / versatate, shows that mechanochemical process only can not form fluorapatite. That is why it is necessary to carry out an additional low-temperature treatment.

Table 1. Assignment of IR absorption bands

| Mod     | FA (t = 6 h) | FA (t = 9 h) | FA (t = 6 h, 1100 C) | FA (t = 9 h, 1100 C) |
|---------|--------------|--------------|----------------------|----------------------|
| $\nu$(O-H) | 3430         | 3430         | 3430                 | 3430                 |
|         | 2926         | 2926         | 2926                 | 2926                 |
| $\delta$(O-H) | 1626        | 1626         | 1626                 | 1626                 |
| $\nu$(CO$_3^{2-}$) | 1455      | 1455         | -                    | -                    |
| $\nu$(PO$_4^{3-}$) | 1092   | 1092         | 1093                 | 1093                 |
| $\nu$(PO$_4^{3-}$) | 1046   | 1042         | 1043                 | 1043                 |
| $\nu$(CO$_3^{2-}$) | 963    | 962          | 963                  | 963                  |
| $\nu$(F) | 726          | 726          | -                    | 726                  |
| $\nu$(OH) | -            | -            | 630                  | -                    |
| $\nu$(PO$_4^{3-}$) | 603    | 603          | 603                  | 603                  |
| $\nu$(PO$_4^{3-}$) | 571    | 571          | 571                  | 571                  |
| $\nu$(PO$_4^{3-}$) | 473    | 473          | 473                  | 473                  |

FTIR method (Figure 5) proved to be the most suitable method for monitoring the synthesis. In order to obtain complete picture of phase transitions that occur in materials during mechanochemical and low-temperature treatment, the method of X-ray diffraction [23] can be used in addition to FTIR method.

XRD spectra of samples (Figure 6) show very intense peaks of portlandite (P), while $\beta$-Ca$_3$P$_2$O$_7$(CP) peaks are also visible. In addition, CaCO$_3$ (C) and CaF$_2$ (CF) peaks are strongly emphasized. All the characteristic diffraction peaks for FA are almost negligible, and some of them absent [29].

After 5 minutes of milling, the most intense peaks belong to Ca(OH)$_2$, and typical peaks for $\beta$-Ca$_3$P$_2$O$_7$, CaF$_2$ and CaCO$_3$ are clearly visible. The peak corresponding to Ca(OH)$_2$ is clearly visible and shows low rate of reaction for forming fluorapatite. Consequently, the amount of synthesized FA in the mixture is negligible.
There were identified changes in the structure from amorphous to crystalline, for all thermally treated samples. The typical peaks of FA confirmed transformation that took place in almost all samples (Figure 7). The amount of residual CaCO₃ and CaF₂ was still significant only in the sample milled for 5 minutes. The emphasized peaks of these phases indicate that parts of the samples remained unchanged, despite the high energy involved in the mechanochemical treatment during the preparation of the precursors mixture (Figure 7a).

As shown in Figure 7 a-c, clearly emphasized and sharp peaks typical for FA are present as a result of an adequate mixing of samples for 2 hours and particularly milling for 8 hours. The sample milled for 5 minutes shows that the transformation of the reaction mixture in fluorapatite was only partial, despite the thermal treatment at 550°C for 3 hours. In addition to FA peaks, there are also CaCO₃ and CaF₂ peaks. This proves that even though the inside of the micelle of a surfactant contains the components of the building blocks of precursors phase that can be easily transformed into the pure fluorapatite, they still remain unchanged.

On the contrary, the mixture that was milled for at least 2 hours and additionally thermally treated for 3 hours is completely transformed into the pure fluorapatite. Similar was for a sample that was milled for 8 hours. The peak corresponding to FA only moves towards the greater angles of diffraction. This means that the content of OH groups was reduced during the milling of the sample and that FA finally became predominant phase (possibly mixed with a small amount of hydroxyapatite).

**REACTION MECHANISM**

During 5 minutes and 2 hours of milling, the reactions in which β- Ca₃P₂O₇ and CaF₂ are formed are dominant, while Ca(OH)₂ part remains unchanged. This has a strong influence on the synthesis rate of FA, which is very slow and cannot be completed only by milling (even after 8 hours of milling). This low rate comes from a very slow diffusion and rearrangement of certain ions that are necessary for FA formation. The exchange and incorporation of Ca²⁺ ions in β- Ca₃P₂O₇ and CaF₂ pre-formed cells is strongly inhibited by the presence of EVA/EVV. Therefore, in order to provide bigger reaction rate of formation of FA, crystal structure of β- Ca₃P₂O₇ and CaF₂ must firstly be transformed to amorphous by additional milling (2 – 8 hours). This procedure provides good mixing, which reduces the diffusion paths of different ions.

The second stage of the formation of FA started after low temperature treatment of the samples at 550°C for 3 hours. In this step, according to certain researches, the reactions can be initiated on the surface of the dominant phase β- Ca₃P₂O₇ through the surface diffusion of additional Ca²⁺ and F⁻ ions in its volume. According to the diffraction peaks, it is evident that the process of formation of FA during these thermal treatments is very intense. The only exception was a sample milled for 5 minutes. Despite conducted thermal treatment, short milling time was not
enough to obtain a single-phase system (FA). However, the milling of at least 2 hours led to the formation of pure FA phase. The presence of almost negligible peak typical for $\beta$-Ca$_2$P$_2$O$_7$, proves that this milling time is the border time for obtaining the single-phase FA.

It is important to emphasize that, no matter how long the samples were milled; this reaction wouldn’t be possible without the thermal treatment. With the extended milling time (up to 3 hours or more), the system became amorphous. The reaction did not progress even during the longest milling time (8 hours), which was confirmed by XRD. The progress was observed only in the amorphous samples (milled for at least 2 hours), which were subjected to subsequent thermal treatment. The mechanism of the process, which took place during milling, was possibly significantly activated by the water present in Ca(OH)$_2$. The explanation provided by some researchers shows that smaller Ca(OH)$_2$ particles, during milling under the influence of shearing forces, tend to grow, causing further disintegration [29-31], so that the exchange of different ion species becomes more efficient.

During milling, the distortion of Ca$^{2+}$-O polyhedra is much more prominent in comparison with P$^{5+}$-O tetrahedra. The distortion led to displacement of cations from the center of its coordination sphere. It has a strong impact on the diffusion rate of the remaining amount of Ca$^{2+}$ and F$^{-}$ ions and consequent destruction of $\beta$-Ca$_2$P$_2$O$_7$ during milling. Thus, the “empty” space in $\beta$-Ca$_2$P$_2$O$_7$ is increasingly filled with these ions, until $\beta$-Ca$_2$P$_2$O$_7$ cell is completely destroyed. It should be noted that the capacity of dissolution of Ca$^{2+}$ and F$^{-}$ ions within $\beta$-Ca$_2$P$_2$O$_7$ is very high. Accordingly, the smaller size of CaF$_2$, and especially Ca(OH)$_2$, crystallites is suitable for further propagation reaction of the formation of FA. Although crystallization of amorphous phase cannot be achieved through milling, the distribution of ions provides very rapid crystallization of the samples in FA in the next step of a very low thermal treatment (at 550 °C for 3 hours).

Therefore, it seems that there is enough space within $\beta$-Ca$_2$P$_2$O$_7$ structure for F$^{-}$ anions to be placed in large gaps, and within the network of calcium and phosphate ions. In addition to F$^{-}$ ions, very small CaF$_2$, nanoparticles are placed randomly in the gaps within $\beta$-Ca$_2$P$_2$O$_7$, lattices, which produce significant changes in its symmetry, causing the corresponding chemical changes responsible for the transformation of mixture into fluorapatite during the next thermal treatment. This treatment can significantly accelerate the processes of diffusion, causing degradation of EVA/EVVE micellar cages and supporting small ion redistribution by distortion in $\beta$-Ca$_2$P$_2$O$_7$ structure induced by shear forces, until the final transformation of the mixture into fluorapatite.

CONCLUSION

Mechanochemical process of fluorapatite synthesis is based on the use of two kinds of precursors: calcium hydroxide, phosphorus pentoxide and calcium fluoride, or calcium hydroxide, phosphorus pentoxide and ammonium fluoride with the addition of surfactant vinyl acetate/verstat. On the basis of XRD and FTIR analysis it was observed that fluorapatite has significant advantages in comparison with hydroxyapatite. These benefits are related to its greater stability, lower solubility and especially better protection against cavities.

APPRECIATION

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project no. 172026).

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Strukturne karakteristike i mehanizmi mehanohemijske sinteze fluorapatita

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KRATAK SADRŽAJ
U radu su analizirani mehanizmi mehanohemijske sinteze fluorapatita i njegove strukturne karakteristike. Suština istraživanja čine istraživanja V. Jokanovića i saradnika objavljena u odgovarajućim časopisima i knjizi Nanomedicina, najveći izazov 21. veka. Karakteristike dobijenih materijala pokazuju njihove brojne biološke prednosti, koje su povezane sa specifičnostima strukturnog dizajna materijala tokom procesa sinteze.

Kao osnove za proučavanje procesa sinteze i mehanizma nastajanja fluorapatita korišćene su metode rendgenske difracije (XRD) i infracrvene spektroskopije sa Furijeovom transformacijom (FTIR).

Kljучне реčи: fluorapatit; mehanоhемijsка синтеза; дифракција X зрака; инфрачервена спектроскопија; тремат ниском температуром

UVOD
Fluorapatit (FA), hemijske formule Ca10(PO4)6(F,OH)2, najstabilniji je, najmanje rastvorljiv i najtvrdiji kalcijum-ortofosfatni mineral (tvrdoča po Mosu 5). Takve osobine fluorapatita povezane su sa specifičnom pozicijom F- jona u centru Ca2+ trougla, njegove kristalne strukture. Tehnine sinteze su slične kao kod hidroksiapatita, sa tim što sinteza podrazumeva prisustvo F- jona, koji se unose u sintezu preko CaF2, NaF ili NH4F. Za razliku od hidroksiapatita (HA) deficijentnog kalcijuma, nema podataka o fluorapatitima deficijentnim kalcijumom. Hemijska formula fluorapatita je Ca10(PO4)6(F,OH)2, zbog toga što je labilniji u konzistenciji, količina fluorida je najčešće smanjena u odnosu na steklohitrajnu količinu. Zbog svoje slabe rastvorljivosti (brzine degradacije) retko se koristi kao zamenik kostiju.

Poslednjih godina fluorohidroksiapatit/fluorapatit (FHA/FA) koristi se u kliničkoj restauraciji, jer mu je zahvaljujući kvalitetnom i mehaničkoj stabilnosti smanjena rastvorljivost i unapredena funkcionalnost. FHA/FA se koristi u kliničkoj restauraciji, jer mu je zahvaljujući efikasnom i redukcijom labilnosti F- jona, lakše teško rastvorljiv u mineralnom stanju.
MEHANIZMI SINTEZE FLUORAPATITA

Tipični mehanizmi sinteze fluorapatita prikazani su na primjeru naječesće primjenjivih postupaka mehanohemijske sinteze iz najčešće korišćenih prekursora kao što su kalcijum-hidroksid – Ca(OH)2, fosfor-hidroksid – P2O5 i kalcijum-fluorid – CaF2. Sinteza iz najčešće korišćenih prekursora kao što su kalcijum-fluorid – P2O5, i amonijum-fluorid – NH4F, uz dodatak površinskoj kordinaciji F- smetici, rezultira transformati polaznih reaktanata u fluorhidroksiapatit, sa sve manjim i manjim udaljenim OH grupe i sve većim i većim udaljenim lima F naustvarjenih OH grupe, sve do potpune transformati sistema u fluorapatit.

Reakcija se u osnovi odvija sa nepotpunom stehiometrijom, pri čemu se vrednost x, koja definiše odstupanje od potpune stehiometrije u fluorapatitu, nalazi u intervalu x1<x<xk, pri čemu se vrednost x, koja definiše odstupanje od potpune sistema u fluorapatitu.

KINETIKA I MEHANIZAM REAKCIJE ZA DOBIJANJE FHA/FA I DRUGE FASE

Parametri mlevenja, kao što su brzina rotacije, prečnik i broj kugli, maseni odnos kugle – praha, bili su konstantni, dok je uticalj vremena mlevenja na sastav faze veoma pažljivo određen. Kinetika i mehanizam reakcije za dobijanje FHA/FA i druge prelazne faze su ispitivani koristeći XRD i FTIR spektroskopiju.

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Zbog toga, cilj ovog rada je bio da se predstavi suština metode sinteze nanopraha fluorhidroksiapatita/fluorapatita metodom mehaničkog legiranja.

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Osnovna reakcija je:

\[
\text{Ca}^{10+}(\text{PO}_4)_{1-y}(\text{CO}_3)^{y-}(\text{PO}_4)_{5-y}(\text{OH})^{2-2x} + (2-2x)\text{HF} \rightarrow \text{Ca}^{10+}(\text{PO}_4)_{1-y}(\text{CO}_3)^{y-}(\text{PO}_4)_{5-y}(\text{OH})^{2-2x} + 2x\text{H}_2\text{O} + (x-1)\text{HF} + \text{H}_2\text{O}.
\]

pri čemu x i y može imati maksimalnu vrednost 1 a x i y minimalnu vrednost 0.

Dakle, sumarna reakcija, kod reakcije sa potpunom stehiometrijom, imala bi oblik:

\[
\text{Ca}^{10+}(\text{PO}_4)_{1-y}(\text{CO}_3)^{y-}(\text{PO}_4)_{5-y}(\text{OH})^{2-2x} + 3\text{P}_2\text{O}_5 + \text{CaF}_2 \rightarrow \text{Ca}^{10+}(\text{PO}_4)_{1-y}(\text{CO}_3)^{y-}(\text{PO}_4)_{5-y}(\text{OH})^{2-2x} + 3\text{H}_2\text{O} + 9\text{HF} + x=1
\]

Na osnovu rendgenske difrakcije utvrđeno je da je već posle 1 h mehanohemijskog tretmana došlo do amorfizacije sistema/mešavine.

Naime, zbog izuzetno visoke koncentracije mehaničkih naprezanja na veoma maloj površini (kontakti koji se ostvaruju kada dvije mehanički deformirane čestice se u presijecaju), javlja se traka na 963 cm\(^{-1}\), koja je karakteristična za HPO\(_4\)\(^{2-}\) i OH\(^{-}\) grupe, a kod kalcijum-hidroksihidrofluorapatita javlja se traka na 963 cm\(^{-1}\), koja je karakteristična za HPO\(_4\)\(^{2-}\) i OH\(^{-}\) grupe. Glavna razlika u primjeni termičkih procesa spojena s oblikom mnogih reaktivacija je pravilo: sa izuzetno visokim stupnjem mehaničke aktivacije sistema, veoma visokim dubinama promene, veoma brzim, primetnim izmjenama proizvoda, i inicijalnim primetnim izmjenama reaktanta.

To ukazuje da je realno pretpostaviti da se reakcija u većim i manjim polaznim česticama sistema odvija na različit način i da u različitim vremenskim intervalima doseže ravnotežne uslove za krajnju reakciju transformacije fluorapatita. U velikim česticama vezovih reakcija na površini teče redom između površini i prve reakcije sa polaznim česticama.

Reakcija se odvija brzo, u srednjim česticama i posebno u velikim česticama, već je prije reakcije pomazanih česticama sistema među-fazni proces tretiranje svakih polaznih česticama.

Rastojanje temena jednakostraničnog trougla sa F- jonom u centru. Rastojanje temena jednakostraničnog trougla sa F- jonom u centru.

Opterećenja, tako da ne mogu da se učvrstiju u fluorapatitu.

Nekadašnji teški suvasti, pri čemu je veoma koristeći XRD i FTIR spektroskopiju.

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између $F-$ i $P^{5+}$ je 3,6 Å, a између $P^{5+}$ i $O^{2-}(1)$ je 3,9 Å. $O^{2-}(3)$ jona nalaze se ispod i iznad ravni koja sadrži $F-$ i $Ca^{II2+}$. Kiseonična vrednost talasnog broja od 758 cm$^{-1}$ (Slika 4 i tabela 1).

Drugi postupak mehanohemijske sinteze, koji je izveden pri-










Kao najadekvatnija metoda za praćenje same sinteze pokazala se kao i u prethodnom primeru FTIR metoda (Slika 5).Radi dobijanja kompletna slike o faznim prelазима koji se događaju u materijalu tokom mehanohemijskog i niskotemperaturnog tretmana, pored FTIR metode korишćena je i metoda rendgenske difракcije, koje su detaljno opisane u referenci 23.

XRD spekttri uzoraka (Slika 6) pokazuju vrlo intenzivne pikove portlandita (P), dok su pikovi $\beta$-$Ca_{3}P_{2}O_{7}$(CP) takođe vidljivi. Osim toga, veoma su naglašeni i pikovi $Ca(OH)_{2}$ (C) i $CaF_{2}$(CF).

Svi karakteristični difraksioni pikovi za FA su gotovo zanemarljivi, a neki od njih su odsutni [29].

Posle pet minuta mlevenja, najintenzivniji vrhovi pripadaju $Ca(OH)_{2}$, $\beta$-$Ca_{3}P_{2}O_{7}$ i $CaF_{2}$. Pikovi karakteristični za $\beta$-$Ca_{3}P_{2}O_{7}$ i $CaF_{2}$ jasno su vidljivi, dok je za $Ca(OH)_{2}$ jedino vidljiv sukob brzina reakcije formiranja fluorapatita.

Upotrebom dodatnih Ca$^{2+}$ i F$^{-}$ jona u njenu zapreminu. Prema difrakcionim pikovima, evidentno je da je proces formiranja FA tokom tih termičkih tretmana veoma intenzivan. Jedini izuzetak bio je uzorak mleven pet minuta. Upotrebom primenjenog termičkog tretmana, tako kratak vreme mlevenja nije bilo dovoljno da se dobije monofoznaj sistem (FA). Međutim, mlevenje od najmanje 2 h dovelo je do formiranja čiste FA faze. Prisustvo gotovo zanemarljivog pika karakterističnog za $\beta$-$Ca_{3}P_{2}O_{7}$ dokazuje da je ovo vreme mlevenja granično vreme za dobijanje mono faze FA.

Veoma je važno naglasiti da bez obzira na to koliko su uzorci mleveni, bez termičkog tretmana ne bi došlo do ove reakcije. Sa produženim vremenom mlevenja (do 3 h ili duže), sistem je postao amorfniji. Reakcija nije napredovala čak i tokom najdužeg vremena mlevenja (8 h), što je potvrdeno pomoću XRD. Napredak je primećen samo u amorfnijim uzorcima (mlevenim dužeg vremena). Reakcija nije napredovala čak i tokom najdužeg vremena mlevenja (8 h), što je potvrdeno pomoću XRD. Napredak je primećen samo u amorfnijim uzorcima (mlevenim dužeg vremena). Reakcija nije napredovala čak i tokom najdužeg vremena mlevenja (8 h), što je potvrdeno pomoću XRD. Napredak je primećen samo u amorfnijim uzorcima (mlevenim dužeg vremena).

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Treba napomenuti to da je kapacitet rastvaranja Ca$^{2+}$-i F jona unutar β-Ca$_2$P$_2$O$_7$ veoma visok. Shodno tome, manje veličine CaF$_2$, a naročito Ca(OH)$_2$ kristaliti, prikladni su za dalju propagaciju reakcije formiranja FA. Iako se kristalizacija amorfnih faza ne može postići kroz mlevenje, raspodela jona omogućava vrlo brzu kristalizaciju uzoraka u FA u sledećem koraku veoma slabog termičkog tretmana (na 550°C tokom 3 h).

Stoga, čini se da unutar β-Ca$_2$P$_2$O$_7$ strukture ima dovoljno prostora za F anjone da se postave u velike praznine, unutar mreže kalcijumovih i fosfatnih jona. Pored F jona, veoma male nanočestice CaF$_2$ smeštaju se nasumice u praznine u β-Ca$_2$P$_2$O$_7$, rešetki, koje proizvode značajne promene u njoj simetriji, izazivajući odgovarajuće hemijske promene koje su odgovorne za transformaciju smešta u fluorapatit tokom naredne termičke obrade. Ovaj tretman, kako je dokazano u ovim istraživanjima, može značajno ubrzati procese difuzije, uzrokujući degradaciju EVA/EVV micelarnih kaveza i podrške malim jonskim preraspodelama distorzijom u strukturi β-Ca$_2$P$_2$O$_7$, izazvanoj silama smicanja, do konačne transformacije mešavine u fluorapatit.

**ZAKLJUČAK**

Mehanohejmjski postupak sinteze fluorapatita bazira se na primeni dve vrste prekursora: kalcijum-hidroksida, fosforpentoksida i kalcijum-fluorida, odnosno kalcijum-hidroksida, fosfor-pentoksida i amonijum-fluorida uz dodatak površinski aktivne supstance vinil acetat/verstata. Na osnovu XRD i FTIR analize, kao mehanizma formiranja FA, uočeno je da fluorapatit ima značajne prednosti u poređenju sa hidroksiapatitom. Te prednosti su vezane za njegovu bolju stabilnost, nižu rastvorljivost i pre svega bolju zaštitu od karijesa.

**ZAHVALNOST**

Ovaj rad je podržan od strane Ministarstva prosvete, nauke i tehnološkog razvoja Republike Srbije (projekat br. 172026).