

Original article

In print article

<https://doi.org/10.26565/2222-5617-2023-38-02>

UDC 576.3/7.002:531/534

PACS numbers: 81.35. +k

## STRUCTURAL CHANGES IN CERAMIC CARBONIZED HYDROXYAPATITE AS A RESULT OF LONG-TERM STORAGE AT ROOM TEMPERATURE

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Received on April 12, 2023. Reviewed on May 14, 2023.

Accepted for publication on May 22, 2023.

Carbonated hydroxyapatite (CHA) is the basic mineral component of animal and human bone. Therefore, it is widely used in medicine to repair bone defects. In orthopedic surgeries, ceramic implants are usually used as a biologically active defect filler. In the lattice of CHA carbonate ions can occupy two non-equivalent positions - A and B. A position corresponds to the position of OH<sup>-</sup> anions in the lattice of hydroxyapatite (HA), and B - PO<sub>4</sub><sup>3-</sup>. It is well known that substitution of B-positions with carbonate groups leads to significant distortions of HA lattice, which causes microstresses and crystalline defects in it. Therefore, CHA ceramics as a result of sintering is characterized by significant internal stresses whose relaxation at room temperature can lead to a change in both its phase composition and biological activity. By methods of chemical and X-ray structural analysis, infrared spectroscopy and electron scanning microscopy the ageing process of pressed CHA at room temperature, sintered in an atmosphere of dry carbon dioxide at temperatures 800÷1200 °C was studied. The phase composition and structure of freshly prepared and aged for two years ceramic samples were compared. It is shown that relaxation of internal stresses arising during sintering of presses causes plastic deformation of crystallites accompanied by redistribution of carbonate ions from B to A-position. As a result, displacement of OH<sup>-</sup> ions from channel (A) positions and decomposition of B-type CHA on CaO and A-type CHA becomes energetically advantageous.

**Keywords:** carbonated hydroxyapatite, internal stresses, ageing process, bioactive ceramics.

**In cites:** M.V. Tkachenko. *Structural Changes in Ceramic Carbonized Hydroxyapatite as a Result of Long-Term Storage at Room Temperature*. The Journal of V.N. Karazin Kharkiv National University. Series "Physics" Iss. 38, 2023; 15-20. <https://doi.org/10.26565/2222-5617-2023-38-02>.

### INTRODUCTION

Among calcium phosphates, which have recently been widely used in medicine to restore bone defects formed in various osteopathologies, carbonated hydroxyapatite (CHA) occupies a special place, since it is the basis of the mineral component of animal and human bones. Due to a number of reasons associated with physiological processes leading to the "washout" of the implanted material from the defect, during operations, not powder, but ceramic implants are usually used as a biologically active defect filler. In this regard, when preparing ceramics, biological materials science is faced with the problem of retaining carbonate groups in the structure of hydroxyapatite, since, as is known, CO<sub>3</sub><sup>2-</sup> ions at temperatures above 800 °C become unstable and

decompose with release from the sample in the form of carbon dioxide. On the other hand, diffusion processes leading to a significant compaction of carbonate-containing hydroxyapatite compacts, depending on the initial content of carbonate groups in the samples and the atmosphere in which sintering is carried out, are activated at temperatures above 900 °C. For this reason, carbonate-substituted hydroxylapatite ceramics with satisfactory density and mechanical properties can only be obtained in a dry or humid atmosphere of carbon dioxide [1–5]. Moreover, carbonate ions can occupy two non-equivalent places in the CHA lattice: when OH<sup>-</sup> groups are replaced, A-type CHA is formed (in this case, one carbonate group replaces two hydroxyl ions), when the PO<sub>4</sub><sup>3-</sup> group is replaced, we deal with CHA B- type (in this case, to

maintain the charge balance, a charged vacancy arises in the cationic sublattice during substitution). When replacing B positions, carbonate groups create significant lattice distortions on the mirror plane of phosphate tetrahedra [6], microstresses, and crystal defects [7]. Numerous CHA studies have shown that, upon A-type substitution, the lattice parameter  $a$  increases, while  $c$  decreases slightly relative to the stoichiometric value for hydroxyapatite. Conversely, the substitution of carbonate ions for orthophosphorus groups  $\text{PO}_4^{3-}$  is accompanied by a significant decrease in the parameter  $a$  and some increase in the parameter  $c$  [8, 9]. In the case of AB-type CHA, the values of unit cell parameters are affected by the degree of substitution of A and B positions. However, the generally accepted picture can be disturbed by the presence of structural water, as a result of which a significant increase in the parameter  $a$  is observed due to the replacement of vacancies in the channel, oxygen tetrahedra, and, probably, calcium positions by water molecules [9, 10].

Forced retention of carbonate ions in the structure of hydroxyapatite (HA), provided by sintering presses in an atmosphere of carbon dioxide, leads to the formation of CGA ceramics with significant internal stresses, which relaxation at room temperature can lead to aging of the material, that is, changes in both the phase composition of samples, and their biological activity. This issue, to our knowledge, has not been studied in the literature so far, although it is important both from the point of view of the conditions and time of storage of implanted materials, and from the point of view of fundamental research to elucidate the mechanisms of aging of CHA ceramics.

In this regard, the task is to study the phase and structural changes that occur in CHA ceramics during its exposure to ambient conditions at room temperature for two years.

## MATERIALS AND METHODS

### *Sample preparation*

The precipitate was formed by the wet method using the reaction between calcium carbonate and phosphoric acid. Finely dispersed  $\text{CaCO}_3$  powder (Merck, Darmstadt, Germany, analytical purity) and  $\text{H}_3\text{PO}_4$  solution (Merck, Darmstadt, Germany, analytical purity) were used, which were quickly poured into the  $\text{CaCO}_3$  suspension with further continuous stirring of the reaction medium at  $45\text{ }^\circ\text{C}$  for a day. The weight ratio of the reagents was chosen in such a way as to obtain stoichiometric HA [11].

From the powder obtained by drying the precipitate in an oven at  $90\text{ }^\circ\text{C}$  by pressing in a steel mold at a pressure of 120 MPa, compacts were prepared in the form of tablets 3 mm high and 8 mm in diameter. The average porosity of the compacts was 51%. The compacts were fired in a flow of dry  $\text{CO}_2$  (4 ml/min) at  $800\text{--}1200\text{ }^\circ\text{C}$  in increments of  $100\text{ }^\circ\text{C}$  for 2 hours at each temperature [12]. Five batches of annealed compacts were prepared (10 samples per batch).

### *Structural studies*

Structural measurements were performed on a Philips APDW 40C diffractometer in copper  $\text{K}\alpha$  radiation ( $\lambda = 0.154056\text{ nm}$ ) with a nickel filter in the range of diffraction angles  $2\theta$   $20\text{--}70$ , scanning step  $0.01\text{ deg.}$  and a scan time of  $0.6\text{ s.}$

### *Spectroscopic analysis and electron microscope studies*

IR spectra were recorded using a Bruker-Vortex 70 spectrometer operating in the transmission mode of wavenumbers between  $400\text{--}4000\text{ cm}^{-1}$ , averaged over 200 scans, with a resolution of  $2\text{ cm}^{-1}$  using the KBr technique. The morphology and microstructure of the samples were studied using an ESEM Quanta 400FEG scanning electron microscope. To remove the charge induced by the action of electrons, the samples were sputtered with gold. We analyzed micrographs of fractures of freshly prepared samples obtained at different sintering temperatures, and of the same samples, but aged for two years.

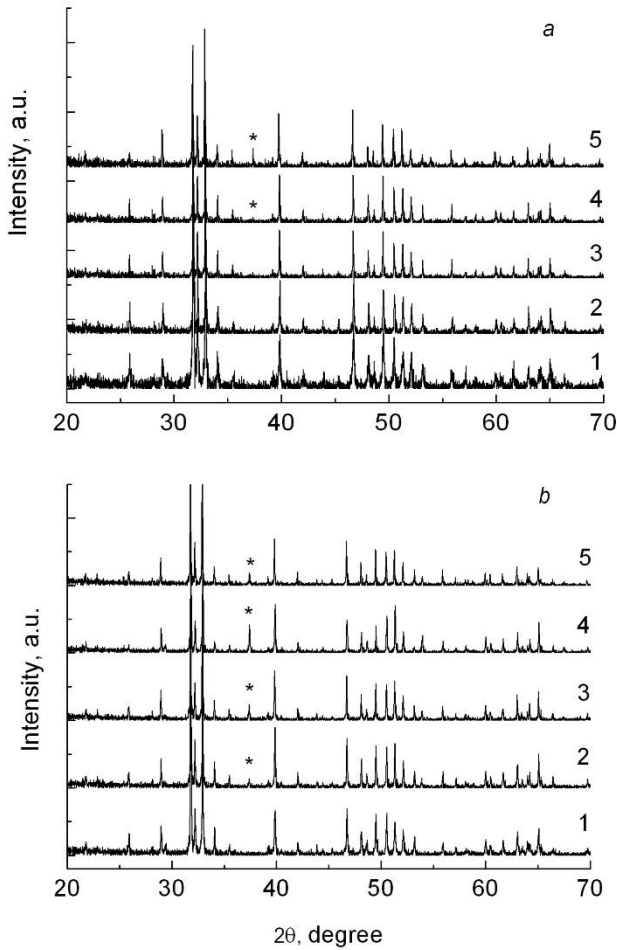
### *Chemical analysis*

The amount of calcium in the samples was determined by atomic absorption spectroscopy (Thermo Electron Corporation, M-series AA spectrometer). The corresponding amount of orthophosphates was found by colorimetry using the molybdenum blue method (Varian Cary Win UV spectrophotometer,  $\lambda = 725\text{ nm}$ ). Carbon and hydrogen were determined by standard ashing analysis using an EA 1110 spectrophotometer (CE Instruments). All experiments on the study of elements were performed twice.

## RESULTS AND DISCUSSION

The studies included: comparison of diffractometric, IR spectroscopic and electron microscopic measurements, as well as chemical analysis of two batches of samples - freshly prepared and aged for two years. The phase composition and lattice constants of ceramics were determined from diffraction patterns, the type of carbonate substitution was determined from IR spectra, and the change in the microstructure during aging was determined from electron microscopy measurements.

Fig. 1 shows the diffraction patterns of freshly prepared (a), obtained at different temperatures, and aged (b) ceramic samples. It can be seen that in the initial samples, as the synthesis temperature increases, the intensity is redistributed between the lines (211), (112), (300), which is apparently associated with the appearance of a texture during sintering. In addition, ceramics obtained at temperatures below  $1100\text{ }^\circ\text{C}$  is single-phase, and above  $1100\text{ }^\circ\text{C}$  a line ( $2\theta = 37.347\text{ }^\circ$ ) appears on the diffraction patterns, which in the literature [1] is associated with calcium oxide. After two years, the diffraction patterns of the same ceramics differ significantly. First, the redistribution of line intensity becomes less pronounced and the diffractograms are more in line with the JCPDS-ICDD PDF-2 Data Base (Sets 1-46). Secondly, the phase

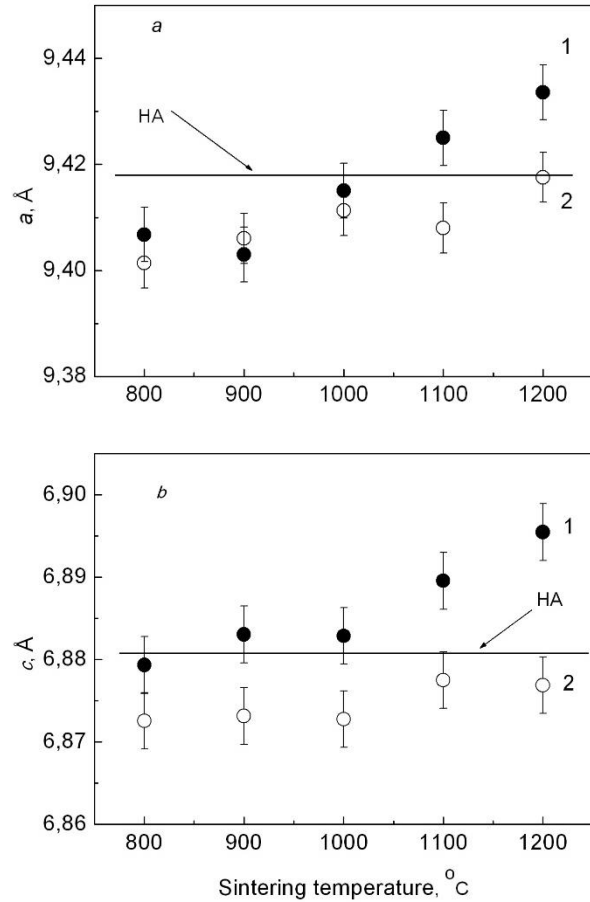


**Fig. 1.** X-ray diffraction pattern of freshly prepared (a) and aged for two years (b) samples sintered at different temperatures:

1 - 800 °C; 2 - 900 °C; 3 - 1000 °C; 4 - 1100 °C; 5 - 1200 °C.

associated with CaO already appears in samples obtained at lower temperatures (900 °C). Those, the aging process of CHA ceramics is accompanied by the breakdown of the CHA structure with the formation of calcium oxide. Comparison of these data with previously published data [7], where it was shown that the loss of carbonate ions from the B positions leads to the formation of CaO, gives reason to conclude that carbonate groups are preferentially isolated from the B positions of the studied CHA.

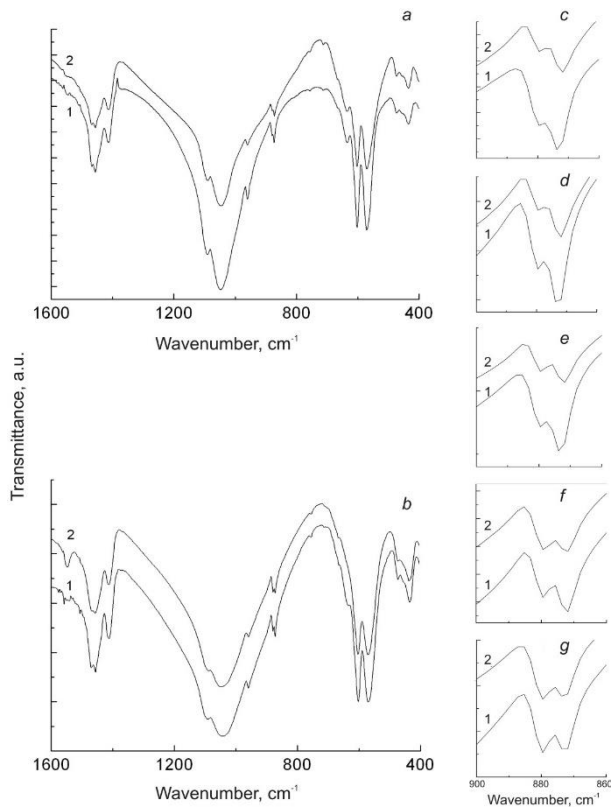
Such changes in the phase composition of the apatite matrix, depending on the synthesis temperature and aging time, affect the behavior and values of its lattice parameters. So, in freshly prepared samples, an increase in the values of parameters  $a$  and  $c$  is observed with increasing sintering temperature (Fig. 2), which indicates an increase in the volume of the unit cell and, accordingly, internal stresses, and with aging, due to the relaxation of internal stresses, the lattice volume decreases, tending to the equilibrium value.



**Fig. 2.** Lattice parameters ( $a$  and  $c$ ) of freshly prepared (1) and aged (2) samples as a function of sintering temperature.

The observed structural changes are also manifested at the molecular level, as evidenced by the IR spectra of the samples under study. Fig. 3 shows the characteristic fragments of the spectra in the wavenumber range 400–1600  $\text{cm}^{-1}$  of freshly prepared (1) and aged (2) samples sintered at 900 °C (a) and 1100 °C (b) and the spectra in the wavenumber range 860–900  $\text{cm}^{-1}$  of all studied samples (c-g), sintered at temperatures of 800–1200 °C. The last range of wave numbers most clearly reflects the type of carbonate substitution in the HA lattice. It can be seen from the IR spectra that all the studied ceramic samples belong to the carbonized HA of the mixed AB type. Both in freshly prepared and aged samples, the degree of substitution of A positions ( $\text{OH}^-$  ions) by carbonate ions increases with an increase in the sintering temperature, which perfectly correlates with changes in the lattice parameters (Fig. 2). Comparison of the IR spectra shows that during the aging of ceramics sintered at the same temperature, the intensity of the band at 880  $\text{cm}^{-1}$  increases with a simultaneous decrease in the intensity of the band at 631  $\text{cm}^{-1}$ , characteristic of the absorption of the OH.

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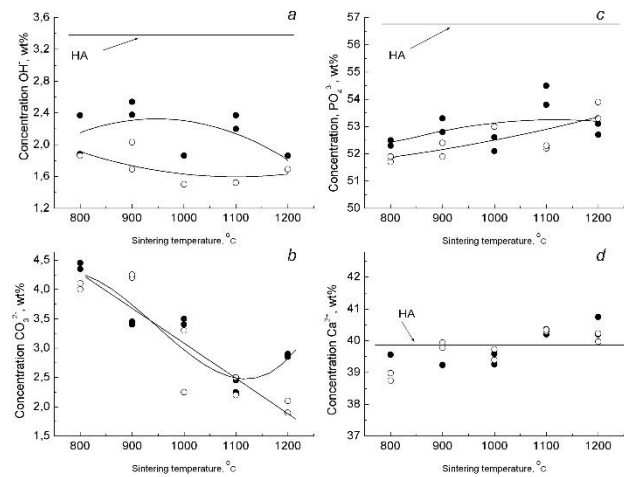


**Fig. 3.** IR spectra of freshly prepared (1) and aged for two years (2) samples sintered at different temperatures: *c* – 800 °C; *a* and *d* – 900 °C; *e* – 1000 °C; *b* and *f* – 1100 °C; *g* – 1200 °C.

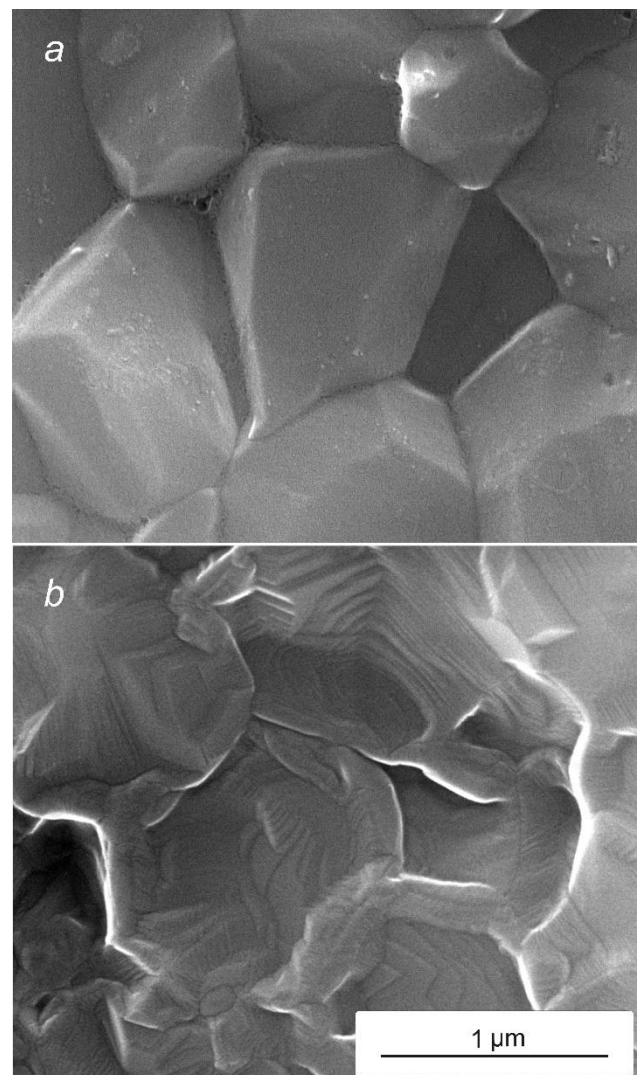
This may primarily indicate a redistribution of carbonate ions from B to A positions and a decrease in the OH<sup>-</sup> concentration in the structure. The process of redistribution of carbonate ions was observed earlier in [6], where it was found that when carbonized B-type apatites are heated in the temperature range from 480 to 800 °C, the position of CO<sub>3</sub><sup>2-</sup> ions changes: some of them move from PO<sub>4</sub> in the OH position (the appearance in the IR spectrum of bands from CO<sub>3</sub><sup>2-</sup>, replacing OH<sup>-</sup> ions).

The HA line corresponds to the stoichiometric concentration of ions in the HA structure.

It can be seen from the results of chemical analysis (Fig. 4) that in the samples obtained at the same temperatures, the concentration of Ca<sup>2+</sup>, PO<sub>4</sub><sup>3-</sup> and CO<sub>3</sub><sup>2-</sup> ions practically does not change during aging (the exception is the change in the concentration of CO<sub>3</sub><sup>2-</sup> ions at 1200 °C temperature). Those. the degree of carbonization of ceramics is preserved. Only the content of OH<sup>-</sup> ions changes, which are located in the channel positions of the HA structure and have facilitated conditions for leaving the lattice.



**Fig. 4.** The results of chemical analysis for the content of: *a* – OH<sup>-</sup>; *b* – CO<sub>3</sub><sup>2-</sup>; *c* – PO<sub>4</sub><sup>3-</sup>; *d* – Ca<sup>2+</sup> in freshly prepared (○) and aged (●) ceramic samples synthesized at different temperatures.



**Fig. 5.** Electron microscopic images of freshly prepared (a) and aged for two years (b) ceramics.

The above research results allow us to state that the preservation of carbonate groups in ceramics sintered at temperatures exceeding the decomposition temperature of  $\text{CO}_3^{2-}$  ions, provided by the atmosphere of carbon dioxide, leads to a nonequilibrium substitution of A and B positions in the CHA structure. As a result, the apatite lattice experiences large internal stresses, the relaxation of which causes the appearance of shear stresses that exceed the critical stress for the start of dislocation slip, mainly in the basal plane, which has the largest number of slip systems. Plastic deformation begins in crystallites, which can be judged by the presence of characteristic slip bands and shifts of slip planes relative to each other, observed in electron microscope images (Fig. 5). Moreover, during aging, the concentration of carbonate groups in ceramics does not change, therefore, the resulting structural changes lead to a redistribution of carbonate ions over the A and B positions, as well as the decomposition of CHA with the formation of CaO.

It has been found that the intensity of the process of structural and phase transformations increases with an increase in the sintering temperature of the compacts. Ceramic specimens sintered at temperatures exceeding 1000 °C are more susceptible to aging.

#### CONCLUSION

The studies allow assuming that the chain of phase and structural changes during aging is as follows: relaxation of internal stresses causes plastic deformation in grains favorable for sliding, which results in energetically advantageous redissolution of  $\text{CO}_3^{2-}$  ions from B to A positions and displacement of  $\text{OH}^-$  ions from channel (A) positions. This process is accompanied by decomposition

of B-type CHAs into CaO and A-type CHAs. Displacement of carbonate from B-positions leads to formation of CaO in hydroxyapatite matrix which is observed in X-ray diffraction analysis (Fig. 1). Since the number of carbonate ions in the channel positions (A), is limited by the number of hydroxyl ions in these positions, the observed redistribution of carbonate ions leads to the displacement of  $\text{OH}^-$  ions from the CHA structure, which is confirmed by the data of chemical analysis (Fig. 4).

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## СТРУКТУРНІ ЗМІНИ КЕРАМІЧНОГО КАРБОНІЗОВАНОГО ГІДРОКСИАПАТИТУ ВНАСЛІДОК ТРИВАЛОГО ЗБЕРІГАННЯ ПРИ КІМНАТНІЙ ТЕМПЕРАТУРІ

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Надійшла до редакції 12 квітня 2023 р. Переглянуто 14 травня 2023 р.  
Прийнято до друку 22 травня 2023 р.

Карбонізований гідроксилапатит (КГА) є основою мінеральної складової кістки тварин і людини. Тому його широко застосовують у медицині для відновлення кісткових дефектів. Під час ортопедичних операцій як біологічноактивні заповнювачі дефектів зазвичай застосовують керамічні імплантати. У решітці КГА карбонатні іони можуть займати дві нееквівалентні позиції А і В. А позиція відповідає положенню  $\text{OH}^-$  аніонів у ґратці гідроксилапатиту (ГА), а В -  $\text{PO}_4^{3-}$ . Добре відомо, що заміщення В-позицій карбонатними групами призводить до суттєвих спотворень ґратки ГА, які спричиняють виникненню в ній мікронапружень та кристалічних дефектів. Тому КГА кераміка в результаті спікання характеризується значними внутрішніми напруженнями, релаксація

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яких при кімнатній температурі може призвести до зміни як її фазового складу, так і біологічної активності. Методами хімічного та рентгенівського структурного аналізу, інфрачервоної спектроскопії та електронної скануючої мікроскопії досліджено процес старіння пресовок карбонізованого гідроксилапатиту (КГА) за кімнатної температури, спечених в атмосфері сухого двоокису вуглецю при температурах 800÷1200 °С. Проведено порівняння фазового складу та структури свіжовиготовлених і зістарених протягом двох років керамічних зразків. Показано, що релаксація внутрішніх напружень, які виникають під час одержання кераміки, визиває пластичну деформацію кристалітів, яка супроводжується перерозподілом карбонатних іонів із В в А-позиції. В результаті цього енергетично вигідним стає витіснення з каналних (А) позицій іонів  $\text{OH}^-$  і розпад КГА В-типу на  $\text{CaO}$  і КГА А-типу.

*Ключові слова:* вуглекислий гідроксиапатит, внутрішні напруження, процес старіння, біоактивна кераміка.