

Synthesis and study of the synthetic hydroxyapatite doped with aluminum

M Goldberg^{1,*}, V Smirnov¹, O Antonova¹, A Konovalov¹, A Fomina¹,
V S Komlev¹, S Barinov¹, A Rodionov², M Gafurov² and S Orlinskii²

¹ A.A. Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, 49 Leninsky Pr., Moscow, Russia

² Kazan Federal University, 18 Kremlevskaya Str., Kazan, Russia

E-mail: margo.goldberg@yandex.ru (Goldberg Margarita), Tel.: +7-929-651-63-31.

Abstract. Powders of synthetic hydroxyapatite doped with aluminium (Al) ions in concentrations 0 and 20 mol. % were synthesized by the precipitation method from the nitrate solutions and investigated by atomic emission spectrometry with inductively coupled plasma (AES-ICP), X-ray diffraction (XRD), scanning electron microscopy (SEM), gas absorption and conventional electron paramagnetic resonance (EPR). It is shown that for the chosen synthesis route an introduction of Al provokes formation of highly anisotropic phase, leads to the decrease in the crystallinity while no significant changes in the EPR spectra of the radiation-induced defects is observed. The results could be used for understanding the structural transformations with Al doping of the mineralized materials for geological and biomedical applications.

1. Introduction

The element phosphorus is widely distributed in the earth's crust, but because of its great affinity for oxygen is not found in nature in a free or uncombined state. In the form of orthophosphate (PO_4) phosphorus also combines readily with a number of cations, chiefly calcium, to form numerous phosphate minerals. There is known to be more than 150 phosphate minerals but only the calcium phosphates, mainly those of the apatite group, and, to a very limited extent the aluminium (Al) phosphates, are generally found in phosphate deposits of commercial importance [1].

Phosphate minerals containing significant amounts of aluminium (and/or iron) are to be found mainly in tropical or subtropical regions where they are formed by intensive lateritisation of phosphatic bedrock. An understanding of the structural complexity of mineralized materials and their transformations under the influence of the environmental factors such as soil pH, soil hydrology, temperature, etc. is fundamental for exploration into the field of diagenesis. For example, unusual replacement of biogenic apatite in dinosaur teeth by aluminium and iron phosphates as a result of fossil diagenetic processes was observed in Spain [2].

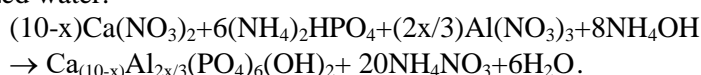
During recent years there have been efforts in developing synthetic calcium phosphate to enhance their biological and mechanical properties for use in biomedical applications that can be mainly achieved by cationic substitutions of calcium ions [3]. Aluminium can serve as one of the substituents but the biological effect of Al remains controversial (both positive and negative functions of the element in human bone metabolism have been reported) while introduction of Al ions can lead to the



significant lattice distortions [5]. In our previous work we have demonstrated enhanced solubility of Al in the β -tricalcium phosphate matrix synthesized by precipitation method [6]. In present paper we use the same reaction route to synthesize aluminum substituted hydroxyapatite (Al-HA) powders and to investigate them by different analytical methods to follow the changes caused by aluminum introduction.

2. Materials and Methods

Samples of Al-HA with the chemical formula $\text{Ca}_{10-x}\text{Al}_{2x/3}(\text{PO}_4)_6(\text{OH})_2$ were synthesized with $x = 0; 0.2$ by the precipitation method according to the following reaction using reactants of analytical grade and deionized water:



Calcium and aluminum nitrate solutions were mixed with a diammonium hydrogen phosphate solution in the corresponding ratios. The pH value of the reaction mixture was maintained at a level of 9.0–9.5 by adding aqueous ammonia. Powders were ripened at mother solution during 21 days at temperature of 25°C for full crystallization of precipitate [7]. The obtained powders were filtered, washed and dried at 60°C for 24 h. The powders were heat treated at 300°C for 3 h in air to remove ammonium nitrate, an impurity phase.

For determination of Al content in the precipitates, powders were heat treated at 900 °C for water removing, dissolved in HCl – HNO₃ mixture and analyzed by atomic emission spectrometry with inductively coupled plasma (AES-ICP, HORIBA Jobin Yvon, ULTIMA 2). The powder materials were characterized by the X-ray diffraction (XRD) method (Shimadzu XRD-6000, CuK α radiation) with identification of phase composition according to JCPDS and PCPDFWIN databases. The particle morphology of synthesized powders was assessed by scanning electron microscopy (SEM) (Tescan VEGA II microscope, secondary electron imaging, accelerating voltage of 20kV). The specific surface area (S) of powders was determined by low-temperature nitrogen adsorption measurements (BET, Micromeritics TriStar analyzer).

Continuous wave (CW) EPR spectra of the samples were obtained using table-top Labrador (Ekaterinburg, Russia) and ESP-300 (Bruker) spectrometers. operating at 9.4 – 9.9 GHz (X-band) microwave frequency. PC concentration was estimated at room temperature in the double cavity ER4105DR of ESP-300 by comparing the integrated intensities of the spectra of a test sample and a reference samples (Cu-DETC solution and Mn²⁺ in MgO powder). X-ray irradiation of the synthesized powders was provided by using URS-55 tube (U = 55kV, I = 16mA, W anticathode) at room temperature with the estimated dose of 5 kGy to create stable paramagnetic centers in the nominal pure material.

3. Results and Discussion

Data on Al content in the investigated species are presented in Table 1 which shows that the chemical composition of synthesized materials is close to the predetermined one.

Table 1. Powder composition and surface area for the investigated species.

Ca substitution by Al, mol. %	Stoichiometric formulae	Al theoretical, mol. %	Al theoretical, wt. %	Al measured, wt. %	S, m ² /g
0	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	0	0	$< 10^{-4}$	91±1
20	$\text{Ca}_8\text{Al}_{1.33}(\text{PO}_4)_6(\text{OH})_2$	20	3.629	3.62 ± 0.04	90±1

According to the XRD analysis, both powders consist of apatite-like phases with the low crystallinity degree (Figure 1). The only detected phase in both samples was hydroxyapatite (JCPDS

#9-432). The shape of triplet between 30.5° and 33.5° of HA sample became smoother and transformed into the duplet with introduction of Al due to decrease of crystallinity degree of powders in correspondence with ref. [8].

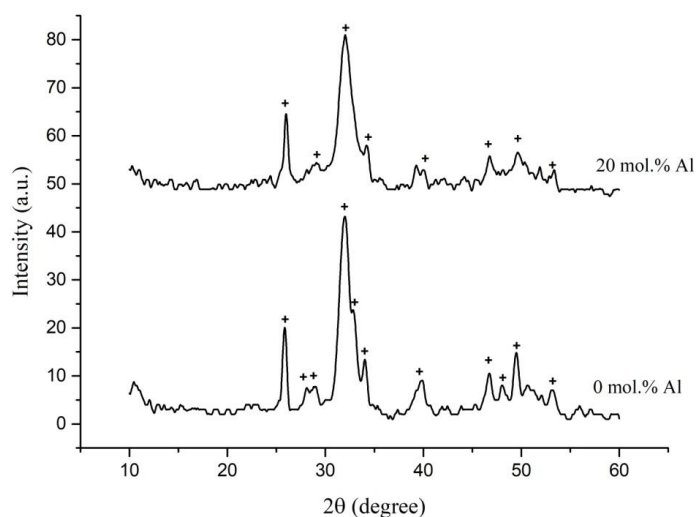


Figure 1. XRD spectra of Al-substituted HA powders. Peaks marked with “+” correspond to HA (JCPDS No: 9 -432).

SEM data demonstrate formation of powders agglomerates for both species. As it can be seen, HA are formed by agglomerates of uniaxial and prismatic particles with average sizes of 50-100 nm (Figure 2). Materials with 20 mol.% of Al are formed by compact agglomerates consisted of 100-250 nm needle-like and prismatic crystals. Thus, doping of HA by Al provokes formation of highly anisotropic phase.

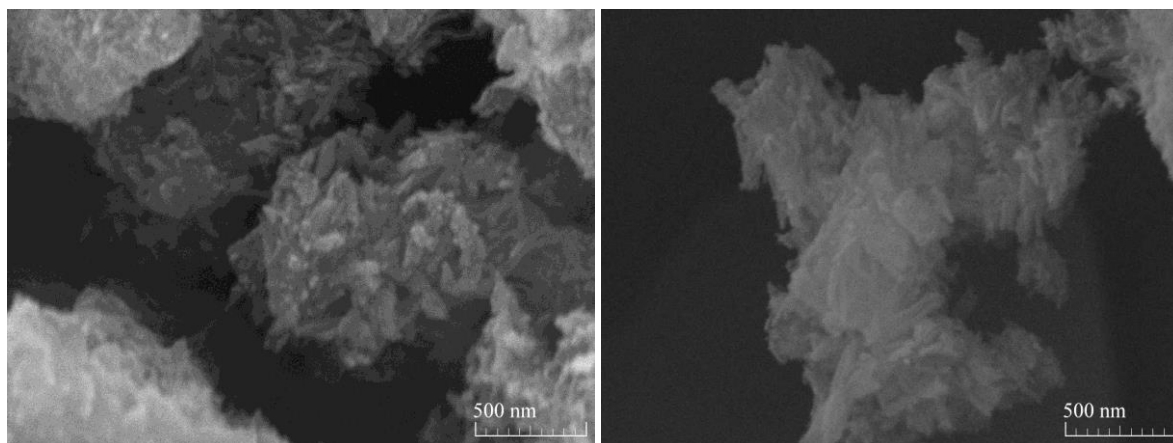


Figure 2. Microphotographs of HA with 0 mol.% (left panel) and 20 mol. % of Al (right panel).

According to the gas absorption data, aluminum introduction does not change the specific area of the synthesized powders that is in the range of 90-91 m²/g (Table 1).

Pure HA and Al-HA samples are supposed to be EPR silent. Indeed, in the investigated species no EPR signals within the sensitivity limits of our equipment was found that confirms the purity of the initial reagents and proper synthesis treatment [9]. The paramagnetic centers appear after the X-ray irradiation (Figure 3). The EPR patterns are very close to each other and mainly are due to the known in HA synthesized by the wet precipitation technique from the nitrate containing reagents CO_3^{2-} and NO_3^- stable radicals [10]. As we have shown previously in refs [9], introduction of even non-paramagnetic impurities can lead to the significant changes of the relaxation and spectroscopic parameters of the radiation induced defects. From the presented EPR results it follows that the spectroscopic parameters of the obtained radiation-induced defects do not change with the aluminum doping and, therefore, gives an opportunity to follow electron-nuclei interactions with the Al nuclei in the way similar to the previously described for other aluminum containing matrices [12].

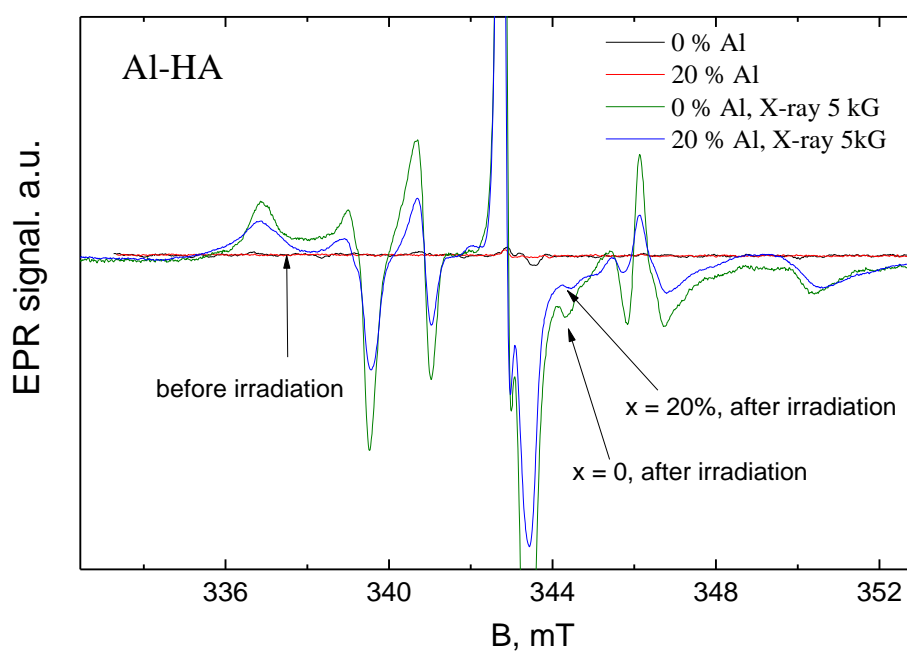


Figure 3. EPR spectra of Al-HA samples before and after X-ray irradiation.

4. Conclusion

Calcium phosphates are compounds of interest to many fields of science, including geology, chemistry, biology and medicine due to their abundance in the nature and presence in the living organism. A huge number of publications were and are devoted to the cationic and anionic substitutions in the hydroxyapatite – they can significantly affect the properties of the material even in very low concentrations. Despite the large number of the studies performed, many important problems related to anionic and cationic substitutions in HA are not thoroughly investigated. Data of different studies contradict one another. The most inconsistent information is associated with the sites of the ions localization in biomineral, synthetic and nanosized samples, influence of dopant onto the biologically relevant properties [9]. We hope that our study is the first step in revealing the role aluminum doping, location of Al ions in the HA lattice and the influence of Al on the local environment in HA structure.

Acknowledgements

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References

- [1] Notholt A, Highley D, Slansky M 1979 *Dossiers IV. Phosphate. Raw Materials Research and Development*, (Cedex: Commission of the European Communities) p 234
- [2] Bauluz B, Gasca J, Moreno-Azanza M, Canudo J 2014 *Lethaia* **47** 556
- [3] Barinov S 2010 *Russ. Chem. Rev.* **79** 13
- [4] Laskus A, Kolmas J 2017 *Int. J. Mol. Sci.* **18** 2542
- [5] Wang M, Wang L, Shi C, Sun T, Zeng Y, Zhu Y 2016 *Phys. Chem. Chem. Phys.* **18** 21789
- [6] Goldberg M, Smirnov V, Protsenko P, et al. 2017 *Ceram. Int.* **43** 13881
- [7] Goldberg M, Smirnov V, Ievlev V, et al. 2012 *Inorg. Mater.* **48** 181
- [8] Kolekar T, Thorat N, Yadav H, Magalad V, Shinde M, Bandgar S, Kim J, Agawane G 2016 *Ceram. Int.* **42** 5304
- [9] Murzakhanov F, Gabbasov B, Iskhakova K, et al. 2017 *Magn. Reson. Solids* **19** 17207
- [10] Gafurov M R, Biktagirov T B, Mamin G V, Shurtakova D V, Klimashina E S, Putlyayev V I and Orlinskii S B 2016 *Phys. Solid State* **58** 469
- [11] Biktagirov T, Gafurov M, Mamin G, Klimashina E, Putlayev V, Orlinskii S 2014 *J. Phys. Chem. A* **118** 1519
- [12] Herklotz F, Lavrov E, Weber J, Mamin G, Kutin Y, Volodin M, Orlinskii S 2011 *Phys. Status Solidi B* **248** 1532
- [13] Mukhambetov I, Lamberov A, Yavkin B, Gafurov M, Mamin G, Orlinskii S 2014 *J. Phys. Chem. C* **118** 14998