ANALYSES OF FLUORAPATITE PREPARED BY BOTH CHEMICAL PRECIPITATION AND SOLID PHASE REACTION METHODS

S.Yu. Sayenko, V.A. Shkuropatenko, R.V. Tarasov, K.A. Prudyvus, S.A. Savina, A.V. Zykova

NSC "Kharkov Institute of Physics and Technology"

Ukraine

At the present study the possibility of obtaining two compositions of $Ca_{10}(PO_4)_6F_2$ and $Ca_9Sr(PO_4)_6F_2$ fluoroapatites by both chemical deposition from solutions of the initial components and reaction in the solid phase was investigated. Using X-ray diffraction (XRD) method was shown that the fluorapatite synthesis based on calcium pyrophosphate with the addition of strontium takes place at lower temperatures. Fluoroapatite formation obtained by precipitation process is the result of the reaction between initial component solutions. At the process of heat treatment of obtained powders by XRD method was found that compared with fluorapatite obtained by solid phase reaction, fluorapatite obtained by precipitation method include less content of TCP phase. Maximum density (~92 % of the theoretical value) is reached for the sample heat treated at 1250 °C with the exposure time up to 6 hours for fluorapatite obtained by precipitation and at a temperature 1200 °C with the exposure time up to 10 hours for fluorapatite prepared by reaction in the solid phase.

Keywords: structure modification, fluorapatite, X-ray diffraction, differential thermal analysis, radioactive wastes immobilization

АНАЛИЗ ФТОРАПАТИТА, ПОЛУЧЕННОГО МЕТОДАМИ ХИМИЧЕСКОГО ОСАЖДЕНИЯ И ТВЕРДОФАЗНОЙ РЕАКЦИИ

С.Ю. Саенко, В.А. Шкуропатенко, Р.В. Тарасов, Е.А. Прудывус, С.А. Савина, А.В. Зыкова

В данной работе исследовалась возможность получения фторапатита двух составов $Ca_{10}(PO_4)_6F_2$ и $Ca_9Sr(PO_4)_6F_2$ методом химического осаждения растворов исходных компонентов и реакцией в твердой фазе. С помощью рентгенофазового анализа (РФА) показано, что с добавлением стронция синтез фторапатита на основе пирофосфата кальция проходит при более низких температурах. Образование фторапатита, полученного осаждением происходит в результате реакции между растворами исходных компонентов. При термообработке полученных порошков методом РФА установлено, что по сравнению с фторапатитом, полученным с помощью твердофазной реакции, фторапатит, полученный осаждением содержит меньшее количество ТКФ. Максимальное значение плотности (~92% от теоретической) достигнуто для образцов термообработанных при температуре 1250 °C и времени выдержки 6 часов для фторапатита, полученного осаждением и при температуре 1200 °C и времени выдержки 10 часов для фторапатита, полученного реакцией в твердой фазе.

Ключевые слова: радиоактивные отходы, иммобилизация, фторапатит, рентгенофазовый анализ, дифференциально-термический анализ.

АНАЛІЗ ФТОРАПАТИТУ, ОТРИМАНОГО МЕТОДАМИ ХІМІЧНОГО ОСАДЖЕННЯ ТА ТВЕРДОФАЗНОЇ РЕАКЦІЇ

С.Ю. Саєнко, В.А. Шкуропатенко, Р.В. Тарасов, С.О. Савіна, К.А. Прудивус, А.В. Зикова

У даній роботі досліджувалася можливість отримання фторапатиту двох складів $Ca_{10}(PO_4)_6F_2$ та $Ca_9Sr(PO_4)_6F_2$ методом хімічного осадження розчинів вихідних компонентів і реакцією в твердій фазі. За допомогою рентгенофазового аналізу (РФА) показано, що з додаванням стронцію синтез фторапатиту на основі пірофосфата кальцію проходить при нижчих температурах. Утворення фторапатиту, отриманого осадження відбувається в результаті реакції між розчинами вихідних компонентів. При термооброцці отриманих порошків методом РФА встановлено, що у порівнянні з фторапатитом, отриманим реакцією в твердій фазі, фторапатит, отриманий осадженням містить меншу кількість ТКФ. Максимальне значення щільності (~92% від теоретичної) досягнуте для зразків термооброблених при температурі 1250 °C і часі витримки 6 годин для фторапатиту, отриманого осадженням і при температурі 1200 °C і часі витримки 10 годин для фторапатиту, отриманого реакцією в твердій фазі.

Ключові слова: радіоактивні відходи, іммобілізація, фторапатит, рентгенофазовий аналіз, диференціально-термічний аналіз.

INTRODUCTION

The surface and bulk material structure modifications are effective methods of modern innovative material development. Various technologies such as sintering, hot pressing, chemical precipitation and others are used for obtaining new materials with tailored properties.

The problem of radioactive waste accumulation is one of the long-term and hazardous consequences of nuclear programs. The most dangerous for the biosphere are high-level wastes (HLW). The concept of fractionation of HLW is developed according to the fact that the half-life, biological hazards and chemical properties of the HLW components vary greatly. The concept of radioactive waste immobilization into the crystalline matrices is based on a matrices using such as mineral phases, which have a natural analogs stable over long geological time.

Recently experts from different countries carried out multidisciplinary research of more than 30 such crystalline compounds for immobilization of HLW. There are durable and chemical stable minerals such as zircon, pyrochlore, magnesium-aluminum spinel, rare earth garnets, zirconolite, apatite, monazite, etc. [1]. In different countries, the application of a variety of rocks for geological disposal of the immobilized HLW is expected, so often, for the same radionuclides different waste forms were used for next compatibility with the disposal mineral phases and the immobilization matrices.

The immobilization waste forms based on apatite ceramic are considered as promising materials for the immobilization of high-level waste due to a wide range of iso- and heterovalent substitutions, high chemical and radiation resistance. Minerals and synthetic compounds with apatite structure type form a large family: $A_{10}(BO_4)_6X_2$ (A – Ca, Sr, Ba, Pb, Na, Cd, Fe, K, Li, rare earth elements; B – P, Si, As, Cr , V, S; X – F, Cl, OH, O, Br, CO_3) [2].

One of the famous examples showing the chemical and radiation resistance of apatite in nature is uranium deposit in Oklo (Gabon, Africa). The chain reaction of uranium fission in the mineral formation took place some two billion years ago. The crystals of apatite are located in this place, characterized by abnormal enrichment of ^{235}U and fission products. Consequently, the apatite-like compounds can maintain the crystalline structure within a very long time.

Apatite materials have also found an application in many other fields, including biology, medicine, electronics, etc. There are various technologies of fluorapatite synthesis such as solid phase reactions, precipitation from solution, sol-gel, hydrothermal methods, and others. The aim of the present study was to obtain calcium fluorapatite and fluorapatite with strontium content by means of the solid phase reaction and the precipitation of initial components solutions

MATERIALS AND METHODS

For fluoroapatite $Ca_{10}(PO_4)_6F_2$ preparation by means of the solid phase reaction the following components such as calcium pyrophosphate $Ca_2P_2O_7$, calcium fluoride, CaF_2, calcium carbonate $CaCO_3$, phosphoric acid H_3PO_4 were taken in the required stoichiometry. Process of preparation of fluorapatite was made by the following reaction [3]:

$$2Ca_2P_2O_7 + CaF_2 + 2H_3PO_4 + 3SaSO_3 \rightarrow$$
$$\rightarrow Ca_{10}(PO_4)_6F_2 + 3H_2O + 5SO_2\uparrow. \qquad (1)$$
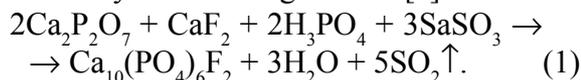
To obtain fine powder of calcium pyrophosphate grinding carried out in a planetary mill Mono "Pulverisette 6" with isopropyl alcohol.

Calcium pyrophosphate, calcium carbonate and calcium fluoride were mixed in a mill environment in isopropyl alcohol and dried at a temperature of 100 °C to a residual moisture content 3 – 5%. Fluoroapatite dried mixture was screened through a sieve with a mesh size of 100 microns. For strontium adding in the fluorapatite mixture the strontium nitrate $Sr(NO_3)_2$ as an aqueous solution was used. Thus, an uniform distribution of strontium nitrate in the fluorapatite mixture was provided. Strontium fluorapatite $Ca_9Sr(PO_4)_6F_2$ was obtained by reaction:

$$2Ca_2P_2O_7 + CaF_2 + 2H_3PO_4 + 4CaCO_3 +$$
$$+Sr(NO_3)_2 \rightarrow Ca_9Sr(PO_4)_6F_2 + 3CO_2\uparrow + 4H_2O +$$
$$+ 2NO_2 + (1/2)O_2. \qquad (2)$$
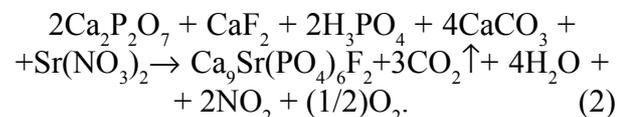
For fluorapatite preparation by solutions precipitation method the following components such as calcium nitrate $Ca(NO_3)_2 \cdot 4H_2O$, disodium hydrogen phosphate $(NH_4)_2HPO_4$, ammonium fluoride NH_4F were taken in the required stoichiometry. The preparation of $Ca_{10}(PO_4)_6F_2$ was performed according to the following reaction:

$$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 2NH_4F +$$
$$NH_4OH + (1/2)O_2 \rightarrow Ca_{10}(PO_4)_6F_2 +$$
$$+ 14NN_4NO_3 + +5,5H_2O + 7NO_2\uparrow. \qquad (3)$$
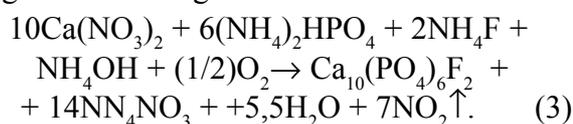
The process of calcium fluoroapatite preparation by chemical precipitation method comprises the following steps [4]:

– Preparing of the aqueous solutions of the initial components required concentration. A sample of $Ca(NO_3)_2 \cdot 4H_2O$ in distilled water was dissolved. Separately, the samples of $(NH_4)_2HPO_4$ and NH_4F in distilled water were dissolved.

– Mixing the initial solutions. A solution of $(NH_4)_2HPO_4$ (0.3 M) and NH_4F by drops, with constant stirring, was poured in warm $Ca(NO_3)_2 \cdot 4H_2O$ (0,5 M) (50 °C) solution with pH = 9 – 9.5 adjusted by adding ammonium hydroxide NH_4OH.

– Preparing of a calcium fluorapatite powder. Flushing the precipitate, drying in air, grinding and heat-treating of the obtained powder was carried out in the temperature range 900 – 1250 °C for 1 hour.

The strontium incorporation into fluorapatite structure was made by strontium nitrate $Sr(NO_3)_2$ adding to a solution of $Ca(NO_3)_2 \cdot 4H_2O$. The preparation of strontium containing fluorapatite was carried out analogously to the preparation of calcium fluorapatite:

$$9Ca(NO_3)_2 + Sr(NO_3)_2 + 6(NH_4)_2HPO_4 +$$
$$+ 2NH_4F + NH_4OH + (1/2)O_2 \rightarrow$$
$$\rightarrow Ca_9Sr(PO_4)_6F_2 + 14NN_4NO_3 + 5.5\ H_2O +$$
$$+ 7NO_2\uparrow. \qquad (4)$$
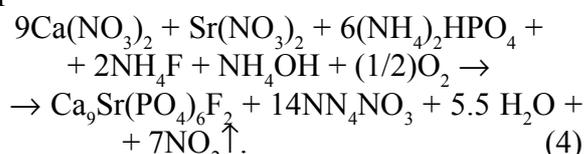
The heat treatment of the powders was made in air furnaces SUOL–0.25.1/12 – M1 and MP – 2U. Thermogravimetric and differential thermal analysis (TGA/DTA) was performed on derivatograph Q – D 1500 at a temperature range 20 – 1000 °C, with heating rate about 12 °C/min and termoanalizatore SDT Q600 V20.9 Build 20 in the temperature range 50 – 1300 °C, with heating rate about 10 °C/min. The phase analysis was made by the phase X-ray diffraction method (XRD) (DRON – 1.5 with Cu radiation using a nickel selective filter). Samples were prepared in the form of tablets with diameter of 14 mm and height of 5 – 7 mm by double-side axial fluorapatite powder cold pressing method in a hydraulic press. Pressing was carried out in the pressure range 124 – 247 MPa.

The sintering of synthesized fluorapatite samples in air was performed in the temperature range 900 – 1250 °C. The apparent bulk density (ρ_{ap}) of the samples after sintering was determined by hydrostatic GOST 2409 – 95.

RESULTS AND DISCUSSION

Fluoroapatite obtained by solid phase reaction. According to results of XRD analysis, only lines of calcium pyrophosphate $Ca_2P_2O_7$ after mixing of the initial components were found (fig. 1a).
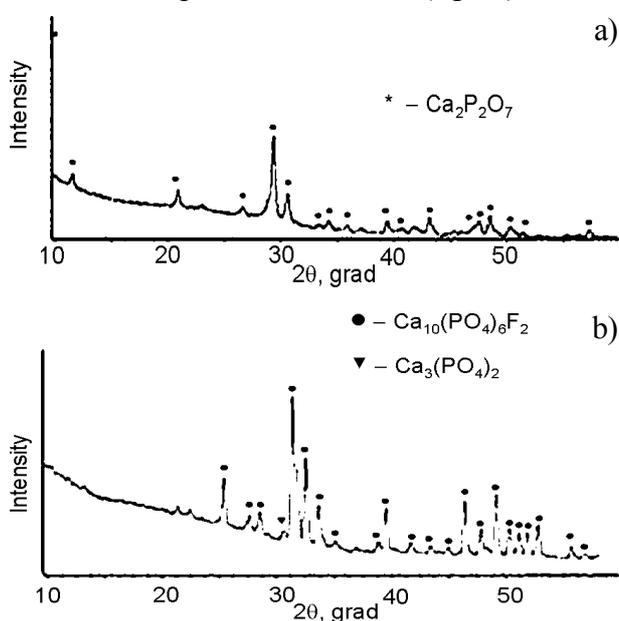
Fig. 1. Diffraction peaks of $Ca_{10}(PO_4)_6F_2$ obtained by solid phase reaction: a) – initial mixture; b) – termal treatment at: $T = 1000$ °C, $\tau = 1$ hour.

The results of thermal analysis of the fluoroapatite $Ca_{10}(PO_4)_6F_2$ mixture are shown in fig. 2.
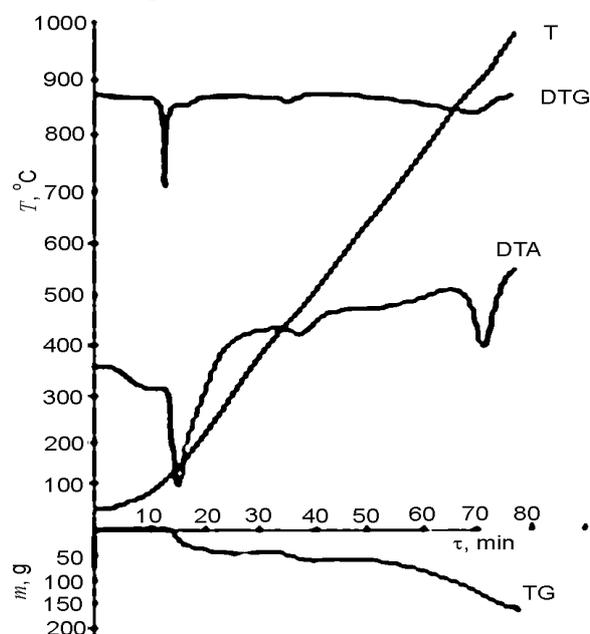
Fig. 2. TG/DTA analysis of $Ca_{10}(PO_4)_6F_2$.

Heat treatment of the original mixture up to 500 °C, according to X-ray studies, does not change the phase composition. According to TG/DTA analysis in the temperature range 120 – 280 °C there

is a strong endothermic effect, which is associated with the removal of adsorbed water and evidenced by weight loss in the TG curves, and also lack of visible change in the phase composition. Second small endothermic peak in the DTA curve in the temperature range 440 – 520 °C, apparently associated with the start of decomposition of calcium carbonate which is in a small amount in the mixture. At the difractogram of the powder, which was heat-treated at 600 °C, there is the appearance of lines fluorapatite. At temperature about 700 °C, there is a significant number of lines of fluorapatite, and reducing the intensity of the lines $Ca_2P_2O_7$. Total synthesis of the fluorapatite with $Ca_2P_2O_7$ destruction proceeds in the temperature range 900 – 1000 °C (fig. 1b). On the DTA curve at such temperature range there is a fairly strong endothermic effect. Furthermore the line of tricalcium phosphate $Ca_3(PO_4)_2$ (TCP) appears in addition to the lines of the synthesized fluorapatite in the diffraction peaks.

The research of phase formation of fluorapatite with strontium content demonstrate that heat treatment of fluorapatite mixture up to 500 °C similar to the case of the calcium fluoroapatite, does not affect on the mixture phase composition. Also, similar to the case of calcium fluoroapatite, on the DTA curve endothermic peaks were observed, which associated with removal of adsorbed water and the start of decomposition of calcium carbonate. Intensive synthesis of fluorapatite runs at 600 °C. Total synthesis of fluorapatite with the initial phases destruction occurs in the temperature range 800 – 900 °C (fig. 4) and is accompanied by the endothermic effect at the DTA curve. Similar to the calcium fluoroapatite case the diffraction lines of TCP appear, and its intensity decreases with increasing temperature up to 1000 °C (fig. 3).

The sintering in air at the temperature range 1100 – 1200 °C for 600 minutes residence time is

performed. The data of the relative density measurements of the sintered samples in air are shown in fig. 4.
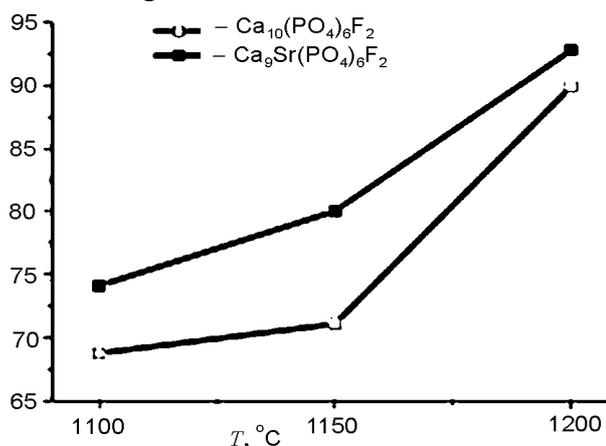
Fig. 4. The dependence of relative density of fluorapatite samples obtained by solid phase reaction on sintering temperature ($\tau = 600$ min).

The results demonstrate that the sintering temperature increasing in air leads to increase in density and there is the maximum value of relative density for all investigated fluorapatite compositions at the temperature 1200 °C.

Fluoroapatite obtained by chemical precipitations method. Fig. 5 shows XRD data of powders obtained by co-precipitation of solutions of the initial components, $Ca_{10}(PO_4)_6F_2$ calcium and $Ca_9Sr(PO_4)_6F_2$ with strontium content fluorapatites. At all diffraction lines are present only one phase – $Ca_{10}(PO_4)_6F_2$ (fig. 1a) and $Ca_9Sr(PO_4)_6F_2$ (fig. 1b), respectively. Previously the necessity of heat treatment of resulting powder at 800 – 1000 °C for 1 hour for fluorapatite solid-phase synthesis by calcium pyrophosphate $Ca_2P_2O_7$ using, as a main component, was shown. In contrast to fluorapatite, obtained by reaction in the solid phase, the formation
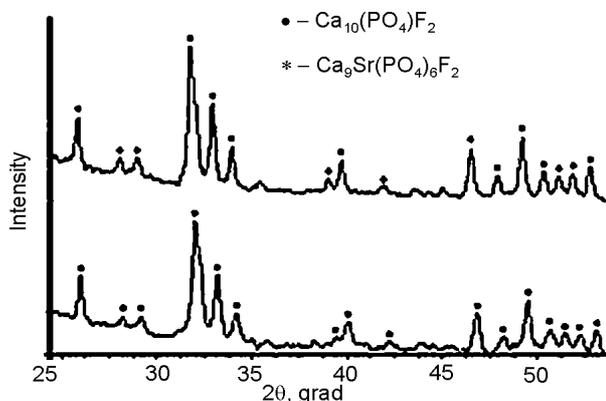
Fig. 5. Diffraction peaks of initial powders $Ca_{10}(PO_4)_6F_2$ (a) and $Ca_9Sr(PO_4)_6F_2$ (b) obtained by chemical precipitation method.

Fig. 3. Diffraction peaks of $Ca_9Sr(PO_4)_6F_2$ obtained by solid phase reaction $T = 1000$ °C, $\tau = 1$ hour.

of fluorapatite by chemical precipitation is directly resulting of the reaction of the initial component solutions.

The only endothermic peaks with minimum at 100 °C which correspond to remove adsorbed water was observed at the DTA curve obtained by chemical precipitation of powders $Ca_{10}(PO_4)_6F_2$ and $Ca_9Sr(PO_4)_6F_2$.

A small endothermic peak at the temperature range 900 – 1000 °C in fig. 6 is observed and probably associated with the start of thermal decomposition reaction for fluoroapatite [5]:

$$Ca_{10}(PO_4)_6F_2 \rightarrow 3Ca_3(PO_4)_2 + CaF_2. \quad (5)$$
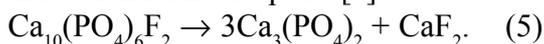
DTA data are confirmed by XRD data of fluorapatite heat-treated powders obtained by chemical precipitation from solutions The line of tricalcium phosphate with low intensity was observed after heat treatment of the powder of calcium fluoroapatite at 900 °C.
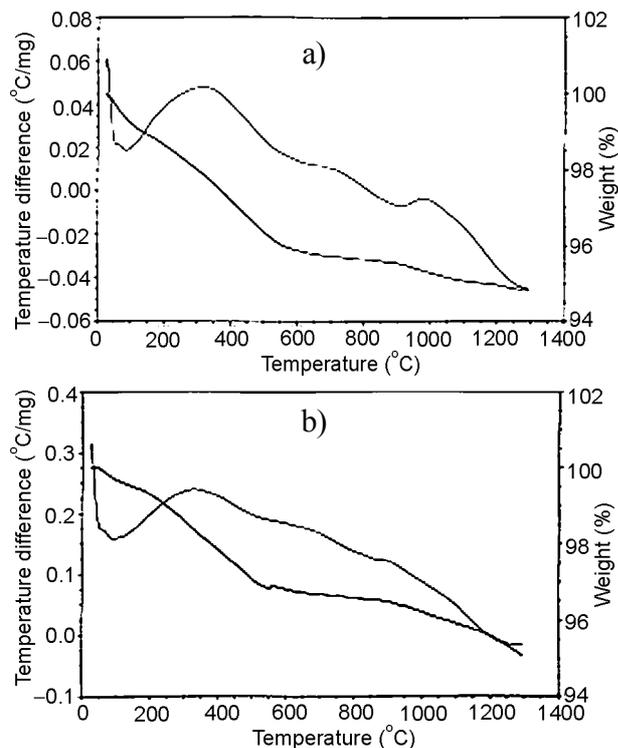
Fig. 6. TG/DTA analysis of $Ca_{10}(PO_4)_6F_2$ (a) and $Ca_9Sr(PO_4)_6F_2$ (b).

The increasing of the thermal treatment temperature up to 1150 °C does not affect on the phase composition of calcium fluoroapatite. In contrast to the diffractogram of strontium containing fluorapatite which has demonstrated the increasing of the $Ca_3(PO_4)_2$ lines number as compared to $Ca_9Sr(PO_4)_6F_2$, heat-treated at 900 °C. The next temperature increasing up to 1250 °C leads to the

disappearance of the tricalcium phosphate lines in the diffraction pattern of calcium fluorapatite and the reducing of intensity and number of lines in the diffraction pattern of strontium containing fluorapatite (fig. 7). It is known that chemical durability of phosphate materials decreases during process of fluoroapatite $\rightarrow$ hydroxyapatite $\rightarrow$ tricalcium phosphate transformation [6].
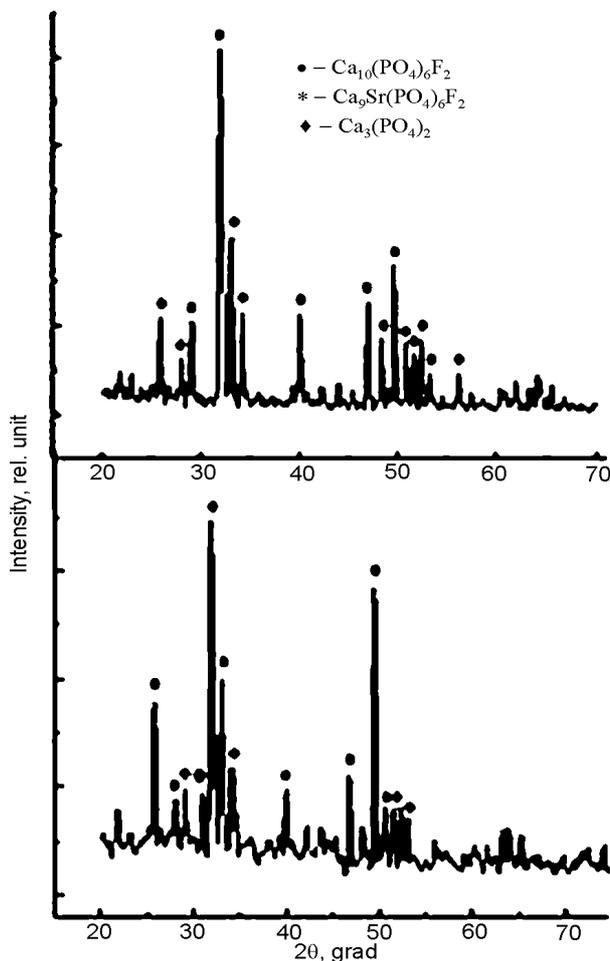
Fig. 7. Diffraction peaks of $Ca_{10}(PO_4)_6F_2$ (a) and $Ca_9Sr(PO_4)_6F_2$ (b) $T = 1250$ °C, $\tau = 1$ hour.

Therefore, the content of TCP in the fluorapatite matrices materials for next HLW immobilization should be minimal. The samples were sintered in the temperature range 1000 – 1250 °C for 6 hours in air. Fig. 8 shows the relative density fluoroapatite $Ca_{10}(PO_4)_6F_2$ (a) and $Ca_9Sr(PO_4)_6F_2$ depending on the sintering temperature.

The density measurement results found that at the temperature 1250 °C the maximum value of the relative density (90 – 92%) was observed both for calcium fluoroapatite and fluorapatite containing strontium.
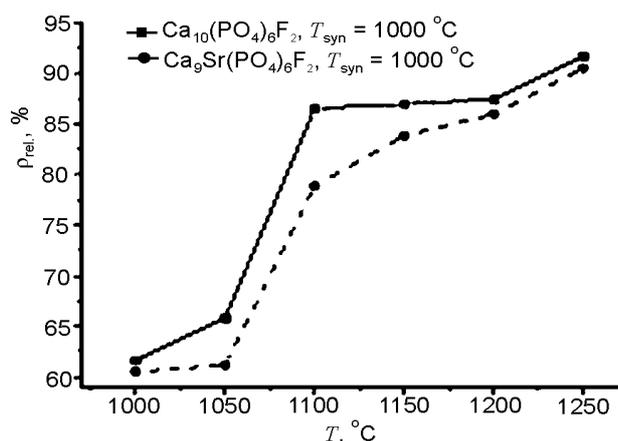
Fig. 8. The dependence of relative density of $Ca_{10}(PO_4)_6F_2$ (a) and $Ca_9Sr(PO_4)_6F_2$ on the sintering temperature.

CONCLUSIONS

1. The fluoroapatite compositions $Ca_{10}(PO_4)_6F_2$ and $Ca_9Sr(PO_4)_6F_2$ were prepared by both the reaction in the solid phase and chemical precipitation methods.

2. Found that in contrast to solid phase synthesis, the formation of fluorapatite by chemical precipitation method is directly resulted on the initial component solutions reaction.

3. According to XRD and DTA/TG analysis using was shown that heat treatment of obtained by precipitation from solutions fluorapatite at a temperature above 900 °C leads to formation of a small amount of TCP.

4. By sintering in air at temperatures of 1200 – 1250 °C the samples of calcium fluoroapatite and strontium containing fluoroapatite with low content of TCP and acceptable relative density of 90 – 92% both in the case of solid phase reaction and chemical precipitation were prepared.

5. The resulting material based on fluoroapatite structures may be used as effective matrices for strontium radionuclide immobilization.

REFERENCES

6. Omelyanenko B.I., Yudintsev S.V., Nikonov B.I., etc. Mineralogy and geochemistry of matrices preserving high-level waste//Geol. ores. deposits. – 1997. – T. 39, № 3. – P. 211-228.

7. Shpak A.P., Karbovskiy V.L., Trachevsiky V.V. Apatites. – K.: Academperiodika, 2002.

8. Shkuropatenko V.A., Tarasov R.V., Prudyvus E.A., etc. Synthesis of strontium fluorapatite on the basis of calcium pyrophosphate//Problems of Atomic Science and Technology. Series: physics of radiation damage and radiation material. Issue – 2012. – Vol. 5 (81). – P 98-105.

9. Hossein Eslami. Synthesis and characterization of nanocrystalline fluorinated hydroxyapatite powder by a modified wet-chemical process. Mehran Solati-Hashjin and Monhammadreza Tahriri//J. of Ceramic Processing Research 3. – 2008. – Vol. 9. – P. 224-229.

10. Chaikin M.V. Mechano-chemical processes and the mechanism of energy conversion indentation of single crystals//Chemistry for Sustainable Development. – 2009. – Vol.17. – P. 653-666.

11. Kanazawa T. Inorganic phosphate materials. – K.: Naukova Dumka, 1998. – 98 p.