ISSN 1027-5495. Functional Materials, 25, No.2 (2018), p. 258-266.
doi:https://doi.org/10.15407/fm25.02.258

Hot isostatic pressing of potassium-magnesium-phosphate materials for cesium immobilization

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Received September 17, 2017

High-density potassium-magnesium phosphates (PMP), produced by hot isostatic pressing (HIP) at temperature of 900°C and pressures of 200 and 400 MPa, are promising materials for the immobilization of radioactive cesium. The maximum density of PMP samples was obtained after HIP at pressure of 400 MPa, 900°C and holding time of 1 h, and PMP + 10 wt. % CsCl samples at 200 MPa, 900°C and 1 h. The resulted materials possess monophase monoclinic structure of potassium-magnesium monophosphate α-$KMgPO_4$. The possibility of PMP materials to incorporate cesium into its structure by substitution with potassium has been studied by X-ray phase analysis and laser mass spectrometry methods using. The homogeneous fine-crystalline structure of ceramic PMP and PMP + 10 wt.% CsCl samples after HIP was analyzed by scanning electron microscopy method.

Keywords: potassium-magnesium phosphate, cesium, hot isostatic pressing, X-ray phase analysis, electron microscopy, density.

Высокоплотные калий-магниевые фосфаты (КМФ), полученные горячим изостатическим прессованием (ГИП) при температуре 900°С и давлении 200 и 400 МПа, являются перспективными материалами для иммобилизации радиоактивного цезия. Максимальная плотность КМФ образцов получена после ГИП при давлении 400 МПа, температуре 900°С и времени выдержки 1 час, а КМФ + 10 вес.% CsCl образцов — при давлении 200 МПа, температуре 900°С и времени выдержки 1 час. Полученные материалы обладают монофазной моноклинной структурой калий-магниевого монофосфата α-$KMgPO_4$. Методами рентгеновского фазового анализа и лазерной масс-спектрометрии изучена возможность КМФ материалов по включению в свою структуру цезия путем замещения им калия. Показано методами сканирующей электронной микроскопии, что керамические КМФ и КМФ + 10 вес.% CsCl образцы после ГИПа обладают однородной мелкокристаллической структурой.

Гаряче ізостатичне пресування калій-магній-фосфатних матеріалів для іммобілізації цезію. *С.Ю.Саєнко, В.А.Шкуропатенко, Г.О.Холомєєв, О.В.Пилипенко, Г.В.Зикова, Н.Н.Бєлаш, Р.В.Тарасов, О.Є.Сурков, К.А.Улибкіна, К.В.Лобач, М.Савчак, М.Кміец.*

Високощільні калій-магнієві фосфати (КМФ), отримані гарячим ізостатичним пресуванням (ГІП) при температурі 900°С і тиску 200 і 400 МПа, є перспективними

матеріалами для іммобілізації радіоактивного цезію. Максимальна щільність КМФ зразків отримана після ГІП при тиску 400 МПа, температурі 900°С і часу витримки 1 година, а КМФ + 10 ваг.% CsCl зразків — при тиску 200 МПа, температурі 900°С і часу витримки 1 година. Отримані матеріали мають монофазну моноклінну структуру калій-магнієвого монофосфата α-$KMgPO_4$. Методами рентгенівського фазового аналізу і лазерної мас-спектрометрії вивчено можливість КМФ матеріалів з включення в свою структуру цезію шляхом заміщення ним калію. Показано методами скануючої електронної мікроскопії, що керамічні КМФ і КМФ + 10 ваг.% CsCl зразки після ГІПа володіють однорідною дрібнокристалічною структурою.

1. Introduction

Reliability of radionuclides immobilization into the matrices should be guaranteed by a complex of physical and chemical properties of the matrices [1]. The mechanical characteristics of the resulting matrices material have significant influence on the safety of the radionuclides disposal. The matrices containing radionuclides are exposed to different mechanical loads during processes of producing, storage, transportation, and immobilization into the geological environment. The insufficient mechanical properties (compressive strength, bending, etc.) of the matrices materials result in appearance of cracks and fractures of cured radioactive waste (RAW) and, as a consequence, to decrease of material chemical resistance [2]. High density of ceramic materials is one of the most important factors ensuring high mechanical properties. Simultaneously with the increase in density, the mechanical properties and thermal stability of ceramics are improved, and the rate of chemical reactions on the surfaces (dissolution, interaction with salt solutions) is decreased by reducing the specific surface [3].

The most famous methods for producing of high-density ceramic materials for RAW immobilization are cold pressing followed by sintering, hot pressing or hot isostatic pressing (HIP). To obtain high-density ceramic matrices by sintering in air, in a vacuum or an inert medium, higher processing temperatures and longer holding times are required. This process leads to the liberation of readily volatile radio nuclides from the matrices, and cesium in particular. The application of the hot pressing method in vacuum allows not only to achieve a reduction in the synthesis temperature and a decrease in the heat treatment time, but also to produce high density samples of the material. However, the process of hot pressing involves the use of graphite molds and the pressed material will inevitably be in a medium saturated with carbon. As is known, carbon is able to enter into the phosphates structure resulting in a degradation of crystallinity, increased solubility and decrease in the thermal stability [4]. Therefore, the application of the method of hot isostatic pressing, providing a high density of the pressed material and avoiding abovementioned disadvantages is fully justified.

Examples of the production by means of HIP method (temperature ~ 850°C, pressure 100 MPa) of sodalite-containing glass forms for the immobilising fission product-bearing waste KCl–LiCl pyroprocessing salts in the ANSTO (Australian Nuclear Science and Technology Organization) are known. The obtained samples were characterized by high density and showed high corrosion resistance in the process of conducting leaching tests in water [5].

There is an experience of successful application of the process of hot isostatic pressing for manufacture of mineral-like ceramic matrices of Synroc composition for high-level waste immobilization in NSC KIPT. This experience was used in the development of glass-ceramic mineral-like materials of aluminosilicate composition for application as protective elements in the encapsulation of spent nuclear fuel (SNF) [6].

Recently, potassium-magnesium phosphate $KMgPO_4 \cdot 6H_2O$ (PMP), which has a room temperature of synthesis, high corrosion properties and radiation resistance, is proposed for the immobilization of both separately isolated radionuclides and liquid radioactive wastes [7–10]. Its anhydrous form $KMgPO_4$ is of interest as an inorganic compound that can reliably hold the ^{137}Cs radioactive isotope and be used as a source of gamma radiation for medical purposes such as cancer treatment and diagnosis of heart disease. In addition, such a form of sources after the end of the service life allows to be stored without additional processing.

The aim of the paper was to study the hot isostatic pressing method for production of a high-density fine-grained ceramics based on potassium magnesium phosphate $KMgPO_4$ needed for immobilization of radioactive cesium.

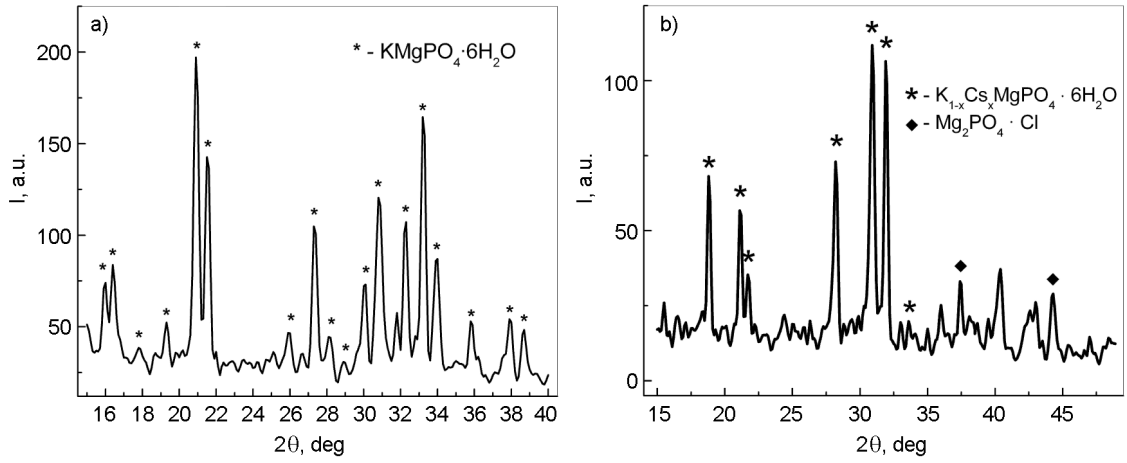


Fig. 1. XRD patterns of the samples: a — PMP, b — PMP + 10 wt. % CsCl.

2. Experimental

Hot isostatic pressing of PMP samples was carried out at NSC KIPT on a laboratory HIP installation GAUS-4/2000-35. The operating parameters of the installation are following: working gas — argon, maximum pressure — 400 MPa, maximum temperature — 2000°C. The dimensions of inside-furnace space were following: diameter 35 mm, height 170 mm. The gas pressure (up to 400 MPa) in the unit is created by the cryogenic thermocompressor KRIT-4L, which was designed and manufactured at the NSC KIPT.

Preliminary heat treatment of potassium-magnesium-phosphate samples was carried out in air at 700°C for 1 h in a Nabertherm L5/13/B180 (Germany) furnace.

The phase composition of the PMP materials was studied by X-ray diffraction analysis (XRD) (DRON-4-07 in copper Cu–Kα radiation using a Ni selectively absorbing filter). The ASTM diffraction data base was used to identify the obtained phases.

Elemental analysis of PMP samples with the addition of 10 wt. % CsCl was performed on a high-resolution laser mass spectrometer EMAL-2.

To determine the processes occurring during the heating of the PMP samples, a differential thermal and thermo-gravimetric analysis (DTA/TG) was performed on the SDT Q600 thermal analyzer in the temperature range (20–1300)°C at a heating rate of 10°C/min.

A study of the structure of the obtained ceramic materials and X-ray spectrometric measurements of the composition was carried out on a scanning electron microscope Zeiss EVO 40 and JEM-7001 F equipped with an X-ray EDX microanalyzer PentaFET-x3 (Oxford INCA) at an accelerating voltage of 20 kV. X-ray spectra were processed using Oxford Instruments INCA 4.11.

Raman spectra were obtained on the Raman spectroscopy scientific equipment "Renishaw in Via". 3D tomography was performed on 3D XRD Tomography (Phoenix micromex DXR-HD, GE Sensing & Inspection Technologies GmbH, Germany).

The density of the samples after HIP was determined by hydrostatic weighing.

The synthesis of potassium-magnesium phosphate $KMgPO_4 \cdot 6H_2O$ was carried out at room temperature using the following reagents:

— magnesium oxide MgO;

— potassium dihydrogen phosphate KH_2PO_4;

— distilled water.

PMP was produced as a result of an acid-alkaline reaction between MgO and KH_2PO_4 in water [7]:

$$MgO + KH_2PO_4 + 5H_2O = KMgPO_4 \cdot 6H_2O. \quad (1)$$

The simulator of radioisotopes ^{137}Cs and ^{134}Cs in the synthesis of cesium-containing PMP samples was Cs^+, which was introduced as cesium chloride CsCl.

The PMP phase composition studies by X-ray phase analysis (XRD) showed that the PMP samples, both containing cesium and without cesium, mainly consist of hexahydrate of potassium and magnesium double orthophosphate $KMgPO_4 \cdot 6H_2O$ of rhombohedral structure (ASTM 35-0812) (Fig. 1a, b). On the diffractogram of the PMP sample + 10 wt. % CsCl there were also lines of magnesium chloride phosphate Mg_2PO_4Cl (Fig. 1b).

After adding of 10 wt. % CsCl, a small shift of the main X-ray lines $KMgPO_4 \cdot 6H_2O$ toward smaller angles was observed. The shift is explained by the partial substitution of potassium atoms by cesium atoms with large ionic radii. According to this fact, the obtained material of PMP samples with cesium (90 wt. % PMP + 10 wt% CsCl) can be represented as $K_{1-x}Cs_xMgPO_4 \cdot 6H_2O$.

In the HIP technology, cylindrical capsules are usually made of stainless steel with a thickness of a few tenths of a millimeter. To avoid excessive deformation of the resulting blanks in order to increase the density of the feed material before the process of HIP, preliminary sintering of the initial powders in air is necessary [6]. In the case of potassium-magnesium phosphate, which contains bound water, preliminary heat treatment is also necessary to remove water. As is known, in the process of heat treatment dehydration of potassium-magnesium phosphate occurs in accordance with the following reaction [11]:

$$KMgPO_4 \cdot 6H_2O \rightarrow KMgPO_4 + 6H_2O. \quad (2)$$

Using DTA/TG analysis, it was found that the endothermic peak at a temperature of 120°C corresponds to the dehydration of the PMP sample (Fig. 2a). This fact is confirmed by a weight loss (~ 40 %) on the TG curve, which corresponds to the removal of the stoichiometric amount of bound water. Above the temperature of ~ 250°C, the weight of the PMP sample does not change. In contrast to the PMP sample, a weight loss of ~ 30 % of the PMP sample with the addition of cesium chloride up to a temperature of 700°C is observed (Fig. 2b). Above the temperature of 700°C, the sample weight practically does not change. Therefore, in order to avoid the removal of water or gas release in the process of HIP, the thermal treatment of PMP samples with both cesium chloride addition and without additives at temperature of 700°C for 1 h was carried out. After heat treatment, an elemental analysis of the PMP samples with the addition of 10 wt. % CsCl was carried out on an EMAL-2 laser mass spectrometer. The results of elemental analysis of PMP + 10 wt. % CsCl are shown in Table 1. From the presented data, it can be concluded that the thermal treatment at 700°C for 1 h does not lead to a decrease in the cesium amount in samples of PMP + 10 wt. % CsCl composition.

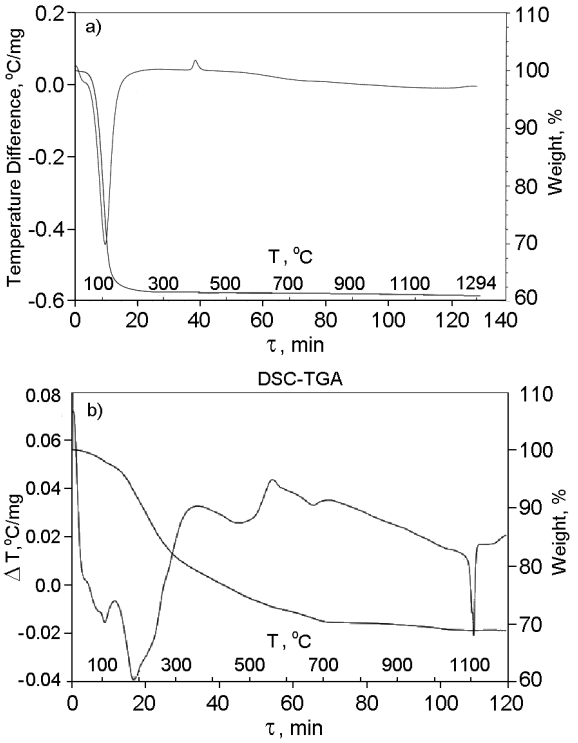


Fig. 2. DTA/TG analysis of the samples: a — PMP, b — PMP + 10 wt % CsCl.

Isostatic treatment of PMP and PMP + 10 wt. % CsCl samples was carried out on a laboratory gas-static unit GAUS-4/2000-35 at temperature of 900°C and pressures of 200 and 400 MPa for 1 hour. Capsules with samples 50–60 mm in length and 10 mm in diameter were placed with special equipment in the working zone of the gas-stove oven. After HIP, the material was extracted from the steel shell mechanically and the composition, structure and properties of the obtained samples were studied (Fig. 3).

3. Results and discussion

After hot isostatic compaction at temperature of 900°C and pressure of 200 MPa for 1 h, lines of potassium-magnesium mo-

Table 1. Element composition of PMP + 10 wt. % CsCl samples after heat treatment

Temperature, time of heat treatment	Element composition, wt. %										
	K	Mg	P	O	Cs	Cl	Na	Al	Si	Ca	S
700°C, 1 h	9.9	24.1	14.6	30.8	10.27	5.9	3.5	0.02	0.17	0.07	0.67

Fig. 3. The view of capsules with PMP samples: a — after HIP, b — after extraction from the capsules shell.

nophosphate α-$KMgPO_4$ of a monoclinic structure (ASTM 089-4675) are observed on the X-ray diffraction pattern of the sample (Fig. 4a). With an increase in the pressure of the HIP up to 400 MPa at a temperature of 900°C, there were no polymorphic transformations in PMP sample (Fig. 4b). However, as follows from the analysis of the diffractograms, there are quite noticeable differences in the magnitudes of the intensities of reflections. Such changes in the intensity of the reflections, along with the small broadening, are apparently caused by the deformation of the PMP particles during the HIP processing, which is accompanied by the accumulation of linear defects.

The increase in the distortions of the crystal structure of the PMP samples with increasing of the HIP pressure is also indicated by the Raman spectrometry data (Fig. 5). The main lines of the Raman spectra of samples after HIP at the temperature of 900°C and pressure of 200 MPa (Fig. 5a) are analogous to the previously published Raman spectra of $KMgPO_4$ samples obtained by solid-phase synthesis at a temperature of 830°C for 10 h. The highest intensity of the lines is observed at a Raman shift of 975 and 1000 cm^{-1}, which corresponds to the vs (PO_4^{3-}) oscillation lines in the potassium-magnesium phosphate spectrum of $KMgPO_4$ [12]. With an increase in the HIP pressure up to 400 MPa at the same temperature, the number of lines with a noticeable intensity of the Raman spectrum decreases sharply up to two lines: 956 and 981 cm^{-1} (Fig. 5b).

Photographs of the microstructure of samples of potassium-magnesium phosphate $KMgPO_4$ obtained after hot isostatic pressing at a temperature of 900°C and a pressure of 200 MPa and 400 MPa for 1 h are shown in Fig. 6. The microstructures of the samples demonstrate the presence of generally well-faceted grains in PMP samples after HIP (pressure of 200 MPa, Fig. 6a) compared with the absence of a clear grain faceting in PMP samples after the HIP (pressure of 400 MPa, Fig. 6b). This is apparently due to the fact that at higher pressures, the grains are brought closer together and rearranged, leading to an increase in the intergrain contacts. This process, in turn, leads to an increase in mass transfer, change in the shape of the grains, and a more dense structure formation.

As can be seen from the PMP + 10 wt.% CsCl diffractograms, the samples after HIP treatment at the temperature of 900°C (pressures of 200 and 400 MPa) consist of a single phase of $K_{1-x}Cs_xMgPO_4$ (Fig. 7). As well as in the case of X-ray diffraction patterns of samples without cesium chloride additions, changes in the intensities of reflections are observed with an increase in pressure from 200 to 400 MPa. However,

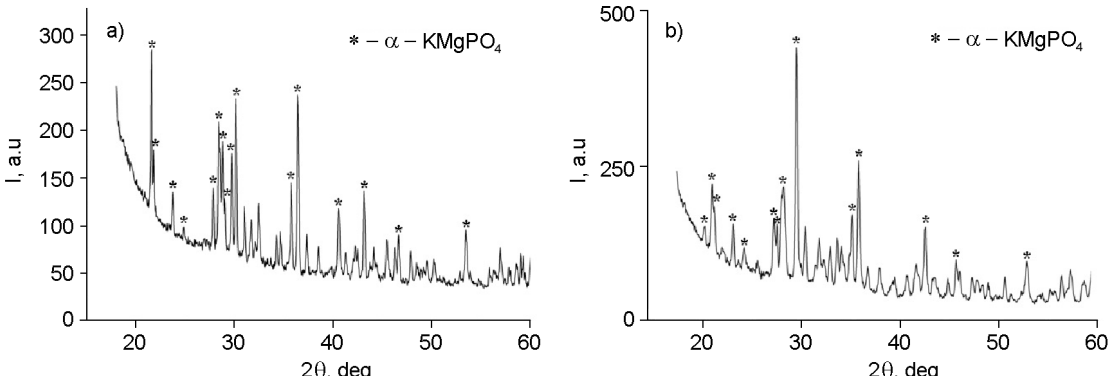


Fig. 4. XRD patterns of the PMP samples after HIP: a — 900°C, 200 MPa, b — 900°C, 400 MPa.

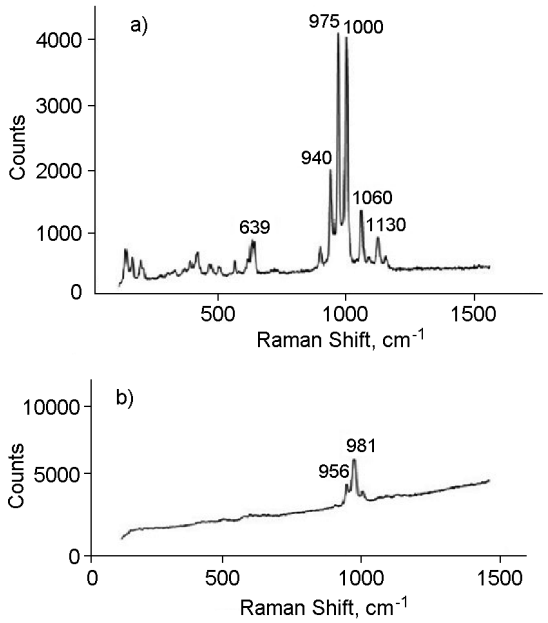


Fig. 5. Raman spectra of $KMgPO_4$ samples after HIP: a — 900°C, 200 MPa, b — 900°C, 400 MPa.

the presence of cesium leads to significant distortions in the crystal lattice of potassium-magnesium phosphate (Fig. 7b). There are also significant changes in the Raman spectra of PMP + 10 wt. % CsCl samples with an increase in the HIP pressure from 200 to 400 MPa (Fig. 8). The highest intensity of the lines of the Raman spectrum of samples after HIP at the temperature of 900°C and pressure of 200 MPa is observed at a Raman shift of 982, 1011 and 1044 cm^{-1} (Fig. 8a). With an increase in the pressure, the Raman spectrum significantly changes: the Raman shift lines of 957 and 1064 cm^{-1} are characterized by the maximum intensity values (Fig. 8b).

The presence of cesium atoms in the lattice is evidenced by the fact that the lattice parameters *a* and *b* of PMP + 10 wt.% CsCl after the HIP (T = 900°C, P = 200 MPa) increase in comparison with the α-$KMgPO_4$ single crystal lattice parameters. The α-$KMgPO_4$ single crystal lattice parameters data were obtained by the hydrothermal method under pressure 90 MPa at a temperature of 500°C for 2 days (Table 2) [13]. With an increase in the HIP pressure up to 400 MPa, an insignificant increase in the parameters *a* and *b* and a more substantial increase in the *c* lattice parameter of PMP + 10 wt. % CsCl were indicated.

The structure of PMP containing cesium after HIP is homogeneous and fine-crystalline (Fig. 9). As well as in the case of PMP

Table 2. Crystalline lattice parameters of the $KMgPO_4$ + 10 wt.% CsCl after HIP

Sample	Phase composition	Lattice parameters, Å
$KMgPO_4$ + 10 wt.% CsCl, HIP:900°C, 200 MPa,1 hour	α-$K_{1-x}Cs_xMgPO_4$	a = 8.594, b = 5.097, c = 18,938, β = 91.51°
$KMgPO_4$ + 10 wt.% CsCl, HIP:900°C, 400 MPa, 1 hour	α-$K_{1-x}Cs_xMgPO_4$	a = 8.602, b = 5.103, c = 19.008, β = 91.76°
α-$KMgPO_4$ hydrothermal-grown single crystal	α-$KMgPO_4$	a = 8.549(2), b = 5.078(1), c = 18.996(2), β = 91.68(1) [13]

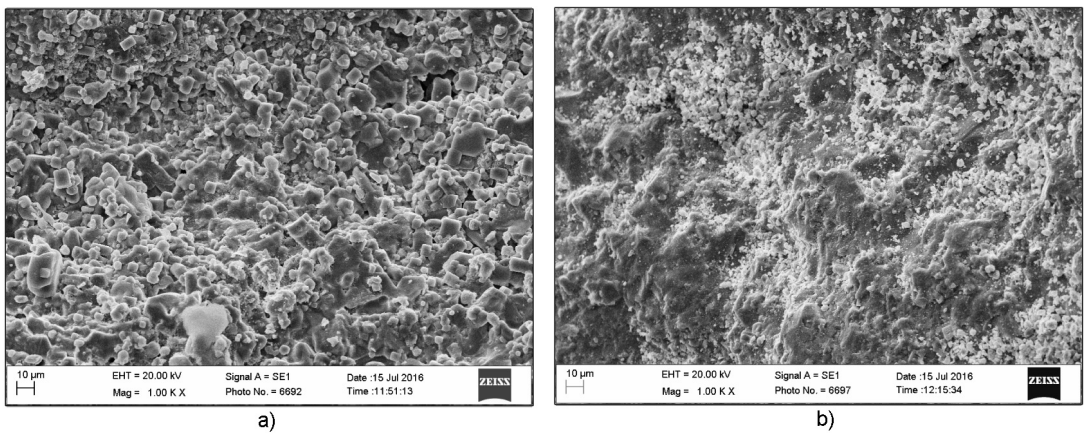


Fig. 6. SEM images of $KMgPO_4$ samples after HIP: a — 900°C, 200 MPa, b — 900°C, 400 MPa.

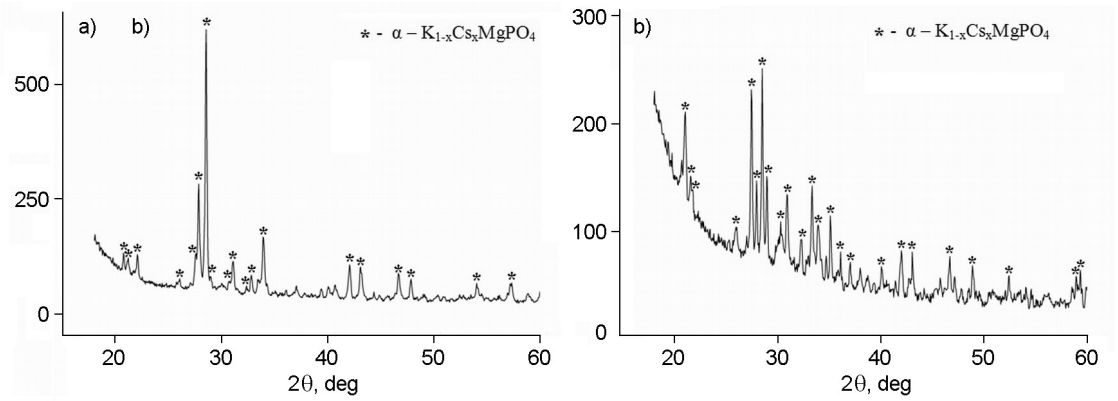


Fig. 7. Diffractograms of the PMP + 10 wt. % CsCl samples after HIP: a — 900°C, 200 MPa, b — 900°C, 400 MPa.

samples without the addition of CsCl, a grains of the PMP + 10 wt. % CsCl samples after the HIP (T = 900°C, P = 200 MPa) have a clearer faceting than the grains of the PMP + 10 wt. % CsCl samples after the HIP with pressure of 400 MPa. The grain size of the PMP + 10 wt. % CsCl samples after the HIP (T = 900°C, P = 200 MPa) is advantageously 2–2.5 μm, although the presence of smaller and larger grains is noted. Increasing the pressure of the HIP up to 400 MPa does not lead to a significant growth of the grains, and the average diameter is 2.5–3 μm. At the same time, denser packing of the grains with a rounded shape is observed after the HIP (T = 900°C, P = 400 MPa, Fig. 9).

The increase in the relative density of the PMP samples was detected with an increase in the HIP pressure at 900°C. The maximum is 99 % of the theoretical value (Table 3) at the pressure of 400 MPa. It is known that the calculated density of monophosphate α-$KMgPO_4$ is 2.55 g/cm^3 [13]. For PMP + 10 wt. % CsCl samples after HIP with a pressure of 200 MPa, an increase in the apparent density is observed compared with the PMP samples due to the presence of heavier cesium atoms. The decrease in the apparent density of PMP + 10 wt. %. CsCl samples with an increase in the HIP pressure appears to be due to the presence of a small amount of chlorine magnesium phosphate Mg_2PO_4Cl, which is dechlorinated, decomposed and formed additional pores at such HIP parameters (T = 900°C, P = 400 MPa).

Confirmation of the decrease in the apparent density of PMP + 10 wt.% CsCl samples with an increase in the HIP pressure is given by 3D analysis data. In a single part (V = 222.7 mm^3) of PMP + 10 wt. %

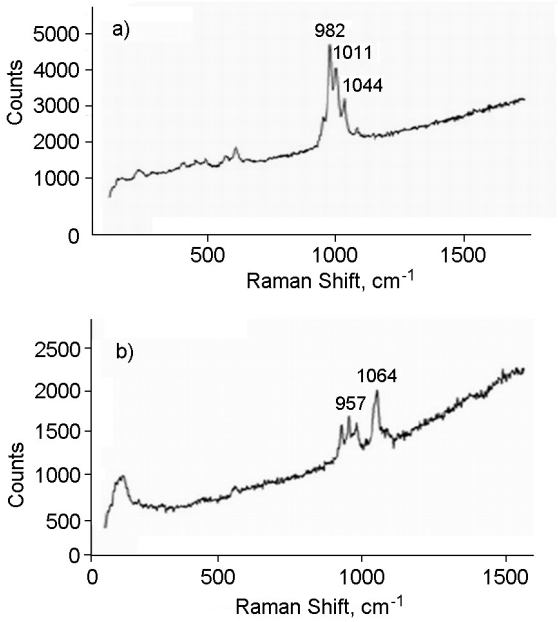
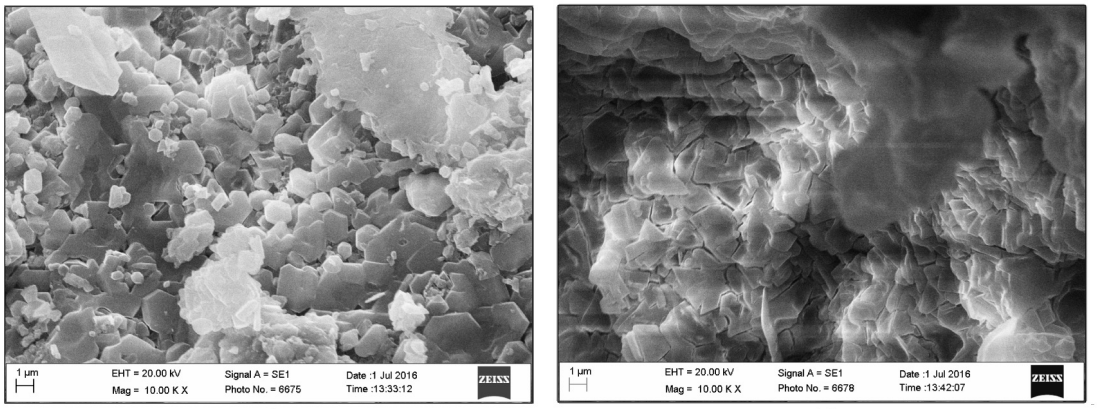


Fig. 8. Raman spectra of $KMgPO_4$ + 10 wt % CsCl samples after HIP: a — 900°C,

Table 3. Dependences of apparent density of PMP and PMP + 10 wt. % CsCl samples on the HIP pressure

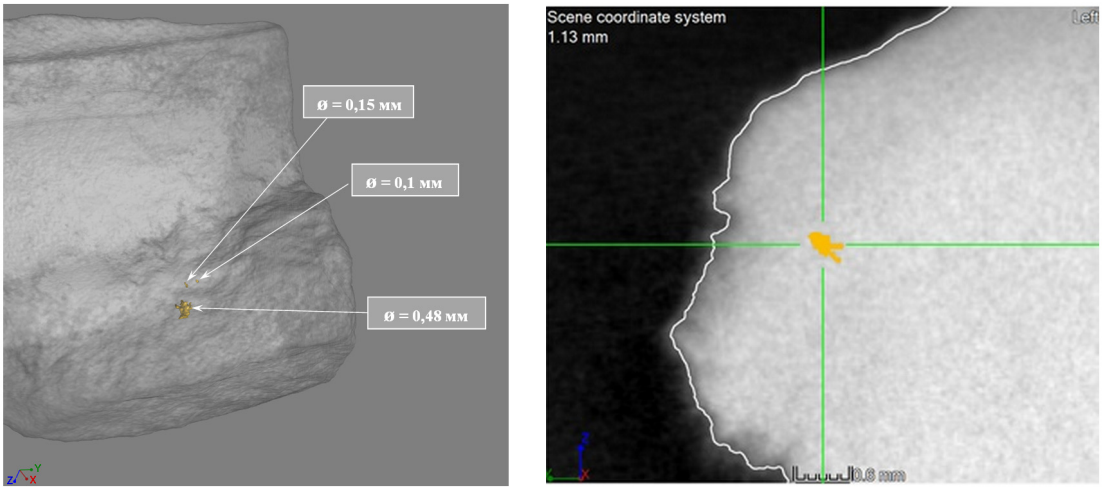
Sample	Apparent density, g/cm^3 HIP, 900°C, 1 h	
	200 MPa	400 MPa
PMP	2.38	2.52
PMP + 10 wt. % CsCl	2.61	2.49

CsCl sample obtained after HIP (T = 900°C, P = 200 MPa) process 3 pores were detected: one large diameter 0.48 mm and two smaller with diameters of 0.15 and 0.1 mm (Fig. 10a). At the same time, larger pores with a diameter >1 mm are present in PMP



a) b)

Fig. 9. SEM images of $KMgPO_4$ + 10 wt % CsCl samples after HIP: a — 900°C, 200 MPa, b — 900°C, 400 MPa.



a) b)

Fig. 10. 3D images of $KMgPO_4$ + 10 wt % CsCl samples after HIP: a — 900°C, 200 MPa, b — 900°C, 400 MPa.

+ 10 wt.% CsCl sample after HIP (T = 900°C, P = 400 MPa) process (Fig. 10b).

The high-density samples of cesium-containing potassium-magnesium phosphate were produced by hot isostatic pressing at pressure of 200 MPa, temperature of 900°C and holding time of 1 h. The development of manufacturing methods and new materials capable for cesium retaining is challenging after the nuclear accident at the Fukushima nuclear power plant. ^{137}Cs, characterized by high activity, high solubility and leaching rate, is one of the main heat-generating isotopes in radioactively contaminated wastewaters. Recently, a large number of materials have been proposed which are capable of efficiently recovering, and then, in the cured form, retaining readily volatile cesium [14, 15]. The presented results on the production of high-density potassium-magnesium-phosphate materials containing cesium can be useful for the further development of materials and methods of radioactive cesium reliable isolation.

4. Conclusions

High-density samples of potassium-magnesium phosphate and potassium-magnesium phosphate with cesium were produced by hot isostatic pressing method. The obtained materials have monophase monoclinic structure of potassium-magnesium monophosphate α-$KMgPO_4$.

Ceramic PMP and PMP + 10 wt. % CsCl samples after hot isostatic pressing demonstrate a homogeneous fine-crystalline structure. The maximum apparent density of PMP samples after HIP at the pressure of 400 MPa, temperature of 900°C and holding time of 1 h was 2.52 g/cm^3, and PMP + 10 wt. % CsCl samples after HIP at a pres-

sure of 200 MPa, 900°C and holding time 1 h — 2.61 g/cm^3.

The obtained high-density ceramic potassium-magnesium-phosphate materials are promising for use as a material for medical cesium sources of γ radiation and for immobilization of radioactive cesium.

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