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Phosphate $Ca_{1/4}Sr_{1/4}Zr_2(PO_4)_3$ of the $NaZr_2(PO_4)_3$ structure type: Synthesis of a dense ceramic material and its radiation testing

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HIGHLIGHTS

- High density ceramics with NZP structure were prepared by Spark Plasma Sintering.
- Ceramic materials were irradiated in cyclotron by Xe ions with fluences 6×10^{10} to 1×10^{13} ions/cm^2.
- The conditions of transformation from metamict to crystalline state have been found.

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ABSTRACT

The powder of phosphate $Ca_{1/4}Sr_{1/4}Zr_2(PO_4)_3$ was synthesized by sol–gel processes in the presence of citric acid and ethylene glycol. Ceramic samples were prepared from this powder by Spark Plasma Sintering (SPS), their relative densities were found to be $99.5 \pm 0.3\%$ after the isothermal treatment at 860 °C for 3 min.

Sintered disc-shaped ceramic samples (d = 10 mm, h = 4 mm) were bombarded at 300 K by 167 MeV Xe^{26+} ions with fluences ranging from $6 \cdot 10^{10}$ to $1 \cdot 10^{13}$ ions/cm^2. It was found that exposure to the highest fluence (10^{13} ion/cm^2) led to a complete amorphization of the irradiated layer. The observed phase transition is ascribed to the formation of amorphous latent tracks via dense electronic excitations. Post-radiation heat treatment revealed that the transformation from metamict to crystalline form took place after annealing at T = 200, 300, 400, 500, 600 and 800 °C and t = 3, 13, 11, 5, 17 and 15 h, respectively.

1. Introduction

The development of durable crystalline ceramic forms for solidification of radioactive waste is an important problem for modern nuclear industry. Relevant to this task is the development of materials stable under extreme conditions and the improvement of the technology used in their fabrication.

Materials with crystal structures of natural minerals, including phosphates, are investigated in many scientific centers of the world as prospective candidates for the immobilization of hazardous radionuclides such as caesium, strontium, actinides and others. Several works summarize information on phosphates with different structure types for such applications [1–5]. An extensive series of investigations was dedicated to synthesis, structure formation and properties of phosphates with certain structural modifications: monazite $CePO_4$ [6–9], apatite–britholite $Ca_{10}(PO_4)_6(OH)_2$ and $Ca_9Nd(PO_4)_5(SiO_4)F_2$ [10–12], phosphate–diphosphate $Th_4(PO_4)_4P_2O_7$, together with monazite [10,13–16], brabantite $B^{II}M^{IV}(PO_4)_2$ (M^{IV}–actinides) [10,11], structure type of $NaTh_2(PO_4)_3$ [17–19], kosnarite $KZr_2(PO_4)_3$ [3,20,21], whitlockite [22], langbeinite [23–25].

A large group of compounds with tetrahedral oxyanions PO_4, SiO_4, SO_4, AsO_4 is represented by the family of isostructural analogues of $NaZr_2(PO_4)_3$ – NZP (the natural mineral kosnarite is a potassium zirconium phosphate $KZr_2(PO_4)_3$). The presence of several types of crystallographically inequivalent positions in the structure provides broad possibilities for iso- and heterovalent isomorphism of cations and anions in such compounds.

Theoretically possible cationic compositions of the NZP-structured phosphates were calculated in [26] using crystal chemical design principles. The implementation of such principles was demonstrated in [27] on the ceramic materials for certain types of wastes of one of the radiochemical plants.

NZP phosphates are known to possess high characteristics of durability. They are stable upon heating up to 1200–1700 °C, many of them have low thermal expansion with low thermal expansion

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anisotropy [28–31], resist to pressures of up to 60 MPa [32] and preserve their chemical and phase composition under external γ-irradiation up to $1.5 \cdot 10^8$ Gy [33]. The characteristics of radiation stability under the influence of internal α-irradiation were experimentally determined by doping the phosphate samples with 61% of plutonium (isotopic composition 100% ^{239}Pu or 20% ($^{239}Pu + ^{240}Pu$) and 80% ^{238}Pu) or ^{244}Cm (2%) [34,35]. The examined samples demonstrated high values of radiation stability and threshold doses: amorphization of phosphate $NaPu_2(PO_4)_3$ doped with ^{238}Pu occurred after the accumulation of $9.3 \cdot 10^{18}$ α-decay/g [21], which was two times higher than the values found for matrices based on zirconolite and perovskite minerals. The ceramics were also found to be stable under hydrothermal conditions (200, 400°C, duration up to 500 days), including preliminary γ-irradiated samples [36].

An important characteristic that determines the stability of ceramics with regard to physical and chemical impacts, including chemical durability and resistance to radiation damage, is density. The latter depends on the chosen preparation procedure.

According to basic kinetic concepts, the rate of a heterovalent reaction with participation of solids depends on the surface size and its reactivity, they in turn depend on the temperature and relative density of solid components.

Some recent papers present studies of the effect of microstructure (grain size, porosity) on the kinetic characteristics of the desorption process and radiation destruction [37–39]. The investigations were carried out for oxides $Ce_{1-x}Nd_xO_{2-x/2}$, $Th_{1-x}Ce_xO_2$, CeO_2 and SiO_2.

As to the relative density of the material, its value under the same microstructural factors depends on the preparation route.

Known methods of synthesis of NZP ceramics include: (1) two-stage process of cold pressing with subsequent sintering; (2) one-stage process of hot pressing; (3) microwave sintering. Among the disadvantages of these methods are: formation of ceramics with low densities in most cases; longer duration of processes (10–40 h) [40–42]; high reaction temperatures (above 1100–1300 °C) [30,43]; the use of high pressures (150–500 MPa) [42].

An alternative way to obtain SYNROC material, developed for radioactive waste immobilization, was described in [44]. The authors applied the method of Spark Plasma Sintering to obtain high-density polyphase ceramic material.

The potential of using this technique to fabricate oxide ceramics for similar applications was also discussed in [45]. The SPS method is known to produce dense ceramics and is based on the rapid heating of both sample and pressing mold by the pulsed DC current of high power [46]. The technique combines different factors such as high heating speed, vacuum and hydrostatic pressure applied to the sample.

The use of SPS method for the phosphates with NZP structure was earlier shown in [47–49]. In [47] ceramics based on the compositions $Ca_{1/2}Zr_2(PO_4)_3$ and $NaFeNb(PO_4)_3$ with relative densities of 99.1% and 99.9% were obtained by sintering the powders for 12 and 3 min at 1100–1200°C and 880 °C, respectively.

In the present work the SPS method was applied to fabricate the ceramic NZP type material $Ca_{1/4}Sr_{1/4}Zr_2(PO_4)_3$. Another objective of the study was the estimation of radiation stability of the prepared ceramic samples under exposure to swift heavy ions. It should be noted that the irradiation by heavy ions in a charged particle accelerator creates severe conditions of radiation exposure, thus providing accelerated evaluation of the radiation stability of the material.

The information on the behavior of phosphate $Ca_{1/4}Sr_{1/4}Zr_2(PO_4)_3$ in radiation fields, along with its high thermal and thermochemical stability and near-zero thermal expansion anisotropy [28,50], might be useful for the development of structural materials for nuclear and space applications, and materials for solidification of radionuclides, such as strontium and many others.

2. Experimental

2.1. Synthesis of a powder sample and ceramics

The synthesis of powders was carried out by a sol–gel procedure with the use of citric acid as a complexing agent and ethylene glycol [51].

The initial 1 M solutions of reagent grade metal salts $Ca(NO_3)_2$ and $Sr(NO_3)_2$ were added to a 0.5 M solution of $ZrOCl_2$ in a stoichiometric proportion. Then, crystalline citric acid $C_6H_8O_7$ was introduced. The molar ratio of citric acid (CA) to metal (M) was CA:M = 15:1, where M = ν(Ca and Sr) + ν(Zr). The obtained suspension was mixed with a magnetic stirrer at the temperature of around 85 °C until the citric acid was completely dissolved. Next, the solutions of ammonium dihydrogen phosphate $NH_4H_2PO_4$ and ethylene glycol $C_2H_6O_2$ were added simultaneously and gradually under constant stirring. The molar ratio of citric acid and ethylene glycol (EG) was CA:EG = 1:4. In order to ensure homogeneous distribution of the metal ions among micelles the stirring was continued for another 15 min. The gel so prepared was dried at 135 °C (24 h) and heated at 350 °C (48 h). The quantity of powder obtained was about 50 g. The powder was ground in a vibrational mill for 30 min (at 150 Hz), heated at 600 °C, 700 °C, 800 °C and 900 °C for 24 h at each stage with intermediate grinding for 30 min between the stages.

Ceramic samples were produced by Spark Plasma Sintering using a Dr. Sinter Model-625 apparatus (SPS SYNTEX INC. Ltd., Japan). The fabrication of ceramics was carried out in vacuum (3 Pa) under the mechanical load of 70 MPa in the solid phase sintering domain (at temperatures of up to 1200 °C).

The heating and cooling rates and the duration of isothermal dwell were determined experimentally.

2.2. Radiation testing procedure

Irradiation experiments were carried out by using xenon ions with energies of 167 MeV at the IC-100 cyclotron of the Flerov Laboratory of Nuclear Reactions (Joint Institute for Nuclear Research, Dubna). The samples were fixed to a copper holder using thermally- and electrically-conducting bi-adhesive. The ion flux was about 10^9 cm^{-2} s^{-1}. The temperature of the samples during irradiation did not exceed 30 °C. Ion beam homogeneity over the irradiated surface (that was achieved using beam scanning in the horizontal and vertical directions) was better than 5%. The accuracy of the ion flux and fluence measurements was 15%.

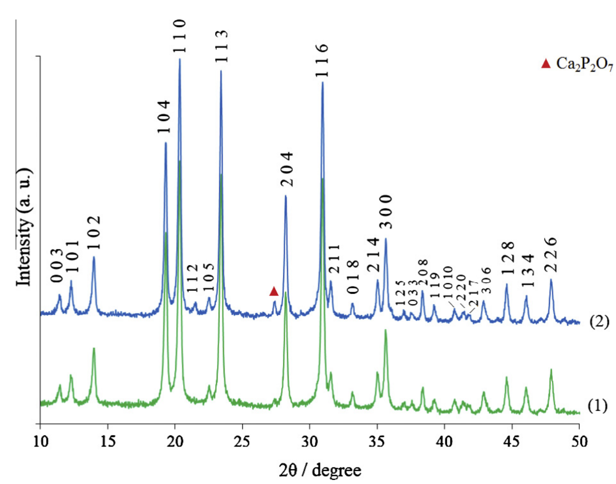

Fig. 1. XRD patterns of phosphate $Ca_{1/4}Sr_{1/4}Zr_2(PO_4)_3$ (powder) after thermal treatments at 800 °C (1) and 900 °C (2).