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Development of new generation of durable radio-luminescence emitters based on actinide-doped crystals

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Abstract

Development of actinide-doped materials with matrices that are chemically inert and resistant to radiation damage may significantly change the approaches to actinide immobilization. Durable crystalline actinide host phases would be considered as advanced materials which are prospective for safe use of actinides before their final disposal. One of prospective applications of such materials is fabrication of radio-luminescence emitters with extremely durable matrices based on self-glowing crystals. Single crystals of zircon, monazite and xenotime doped with different amount of luminescence ions such as Tb, Eu and actinides such as ^{239}Pu, ^{238}Pu, ^{241}Am, ^{237}Np have been grown using flux method. Non-radioactive crystals were studied first using cathodoluminescence method in order to identify optimal contents of Tb^{3+} and Eu^{3+}, which provide the highest intensity of luminescence emission. Then radioactive self-glowing crystals doped with the same content of luminescence ion and small admixture of actinide were grown. It was suggested that content of ^{238}Pu and ^{241}Am in self-glowing crystals should not exceed 0.1 wt. %. Intensively glowing crystals of zircon, xenotime and monazite were successfully obtained and studied. Principal features of these crystals are discussed.

Keywords : Plutonium; americium; neptunium; self-glowing crystals; luminescence ions; terbium; europium.

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1. Introduction

Some solids may emit luminescence under external or internal ionizing irradiation. This effect used to apply in first generation of radio-luminescence emitters consisted of separate parts: non-radioactive solid material doped with luminescence ion(s) and radionuclide in the form of sintered powder, ceramic or film [1]. Main disadvantage of regular light emitters is their short-term use (10-20 years) related to low resistance of luminescence material to radiation damage. Crystalline materials with high chemical resistance, mechanical durability, and stability under self-irradiation are very promising for development of new generation of radio-luminescence emitters. The most important requirement to such emitters is their durability in environment. In order to create environmentally friendly long-lived light-emitters we have suggested incorporating the actinides and non-radioactive luminescence ions in common durable crystalline matrix in the form of solid solution [2-6]. Durable radioactive crystals, which intensively glow in the dark, are advanced materials for use in optical couplers, robotics, medicine and other fields. Intensive radio-luminescence might be converted into electric current that allows development of reliable "nuclear" batteries. Such nuclear batteries can potentially be used in aggressive chemical media as well as for applications in space for dozens to hundreds of years. The main difficulty related to development of self-glowing crystals is to determine the optimal balance between the amounts of actinides initiating the glowing process and the non-radioactive luminescence ion supporting intensive scintillation [2-6]. Too high an admixture of luminescence ion can suppress scintillation. Similar behavior is also found for excessive admixture of actinides. In addition, a high content of radionuclides may cause more rapid radiation damage of crystalline structure that has a negative effect not only on glowing but also on the chemical and mechanical durability of crystal matrix. It was suggested that content of ^{238}Pu and ^{241}Am in self-glowing crystals in any case should not exceed 0.1 wt. %. Admixture of ^{239}Pu and ^{237}Np can be accepted at the level of several wt. %. Well known durable actinide host phases initially proposed for actinide immobilization [5] such as zircon, $(Zr,\ldots)SiO_4$; zirconia, $(Zr,\ldots)O_2$; monazite, $(Ln,\ldots)PO_4$ and xenotime, $(Y,\ldots)PO_4$, were selected for our research. It was demonstrated [2-6] that non-radioactive crystals doped with an optimal amount of luminescence ions can be used as starting precursors for the synthesis of self-glowing crystals. The use of cathodoluminescence (CL) method allows for the identification of the optimal amount and type of luminescence ion(s) incorporated in any non-radioactive crystals [2]. This paper summarizes results on synthesis and study of different single crystals such as zircon, monoclinic zirconia, monazite and xenotime doped with different amount of actinides (^{239}Pu, ^{238}Pu, ^{241}Am, ^{237}Np) and non-radioactive luminescence ions (Tb and Eu).

2. Experimental details, results and discussion

All single crystal samples were synthesized by the flux method [7] at temperature 1070°C in Pt-crucibles using a starting precursor that is based on MoO_3. Some crystals were selected from each batch, mounted in epoxy, polished and coated with carbon for electron microprobe analysis (EMPA) and CL investigations. CL spectroscopy was performed using an optical spectrometer [8] installed into a CAMECA Camebax electron microprobe. This spectrometer is characterized by a high sensitivity and spectral resolution of 0.1 nm in the optical region between 300 and 850 nm. The CL spectra were obtained from the same locations as the microprobe measurements which allow to understand the correlation between chemical composition and the CL intensity even in heterogeneous, zoned crystals. Zircon single crystals obtained from phosphor-bearing flux were characterized by intensive CL-emission. It was confirmed that a small addition of Zr-phosphate to the flux supports Tb and Eu incorporation into the zircon lattice (Fig. 1). At the same time, the addition of Zr-phosphate to the flux also caused the crystallization of zirconia as a minor phase.

CL imaging can be more sensitive to some chemical inhomogeneities defects compared to backscattered electron SEM imaging and optical microscopy (Fig. 2). CL spectroscopy is an important tool in determining the valence states of actinides incorporated into the crystalline structure of host-phases or dissolved into glass

matrices. CL spectra of anisotropic crystalline phases are a function of crystal orientation [5]. CL can be used to determine crystal orientation in actinide-bearing single crystals.

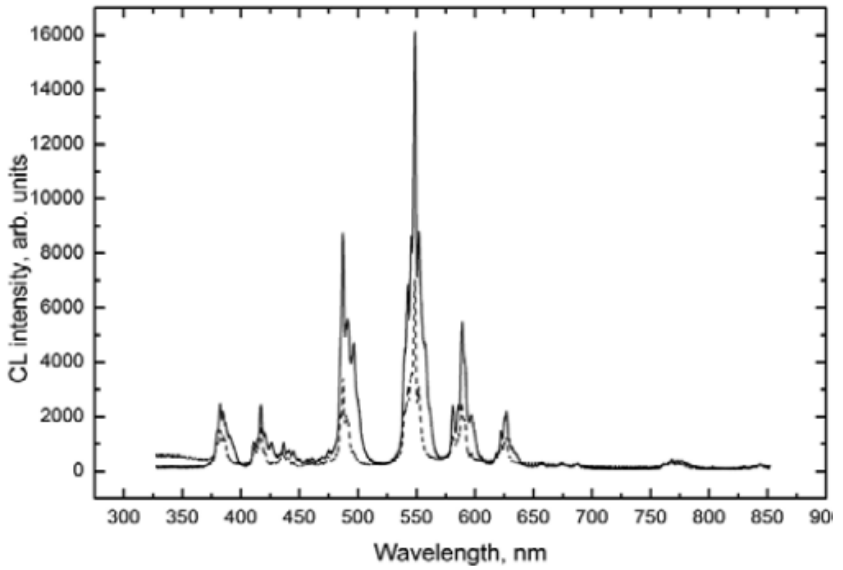

Fig. 1 Representative cathodoluminescence spectra of non-radioactive zircon doped with: 0.2 wt. % Tb (and no P) – broken line; 4.0 wt.% Tb and 0.2 wt. % P – unbroken line.

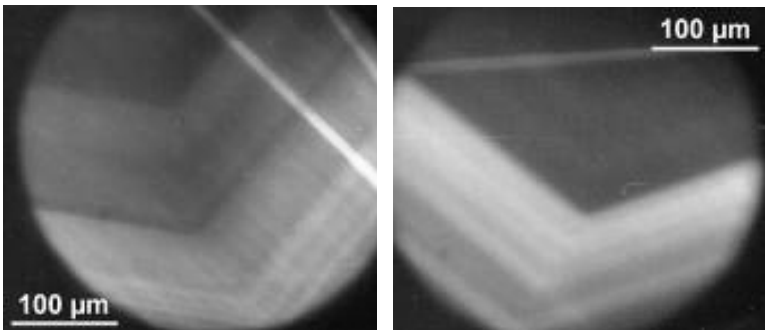

Fig.2. Cathodoluminescence images of zoned areas in crystals of ^{239}Pu doped zircon. Plutonium content ranged from 0.1 wt.% (in light zones) to 1.4 wt.% (in dark zones).

The EMP analyses of Tb, Eu and P were carried out using wave lenght-dispersive spectrometer MICROSPEC – 3PC. The acceleration voltage was 30 kV at a beam current of 100 nA. The error of measurements (at contents of Tb, Eu and P less than 1 wt. %) was 10 relative %. Actinide contents in the crystals were measured by precise gamma-spectroscopy using a Ge detector with Schlumberger EGP 20P11A. The relative self-glowing intensity of the different radioactive samples was evaluated visually (Fig. 3, 4). Principal features of synthesized crystals are summarized in Table I.

Table I Principal features of self-glowing crystals

Crystal	Simplified formula	Average content of luminescence ion, wt. %	Content of actinide, wt. %	Relative intensity of self-glowing
zircon	$(Zr,Tb,Pu)(Si,P)O_4$	Tb – 0.2-0.3 (optimal content confirmed by CL method)	^{238}Pu – 0.02	very high
	$(Zr,Eu,Pu)(Si,P)O_4$	Eu – 0.1	^{238}Pu – 0.02	weak
		Eu – 0.1	^{238}Pu – 0.01	weak
		Eu – 0.3 (optimal content confirmed by CL method)	^{238}Pu – 0.01	high
	$(Zr,Eu,Pu)(Si,P)O_4$	Eu – 0.1	^{238}Pu – 0.01	weak
	$(Zr,Eu,Pu)(Si,P)O_4$	Eu – less 0.01	^{239}Pu – 8-10	no
	$(Zr,Am,Np)SiO_4$	no	^{237}Np – 0.35; ^{241}Am – 0.01	weak
	$(Zr,Np)SiO_4$	no	^{237}Np – 1.9	no
	$(Zr,Tb,Eu,Am)(Si,P)O_4$	Tb – 0.2-0.3 Eu – less 0.1	^{241}Am – 0.002	weak
baddeleyite	$(Zr,Tb,Pu)O_2$	Tb – 0.02	^{238}Pu – 0.03	weak
(monoclinic zirconia)	$(Zr,Eu,Pu)O_2$	Eu – 0.4	^{238}Pu – 0.01	weak
xenotime	$(Y,Eu,Pu)PO_4$	Eu – 1.8 (optimal content confirmed by CL method)	^{238}Pu – 0.1	very high
	$(Y,Eu,Pu)PO_4$	Eu – 0.03	^{238}Pu – 0.002	weak
monazite	$(Eu,Am)PO_4$	Eu – main element	^{241}Am – 0.04	high
	$(Eu,Pu)PO_4$		^{238}Pu – 4.9	weak
	$(Eu,Am)PO_4$		^{241}Am – 0.39	high

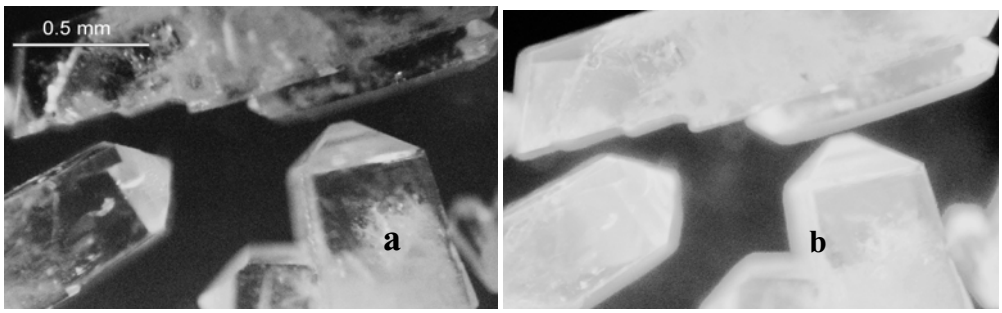

Fig. 3 Self-glowing crystals of zircon, $(Zr,Tb,Pu)SiO_4$, doped with 0.2-0.3 wt. % Tb and 0.02 wt. % ^{238}Pu, under binocular a) in the light and b) glowing in the dark.

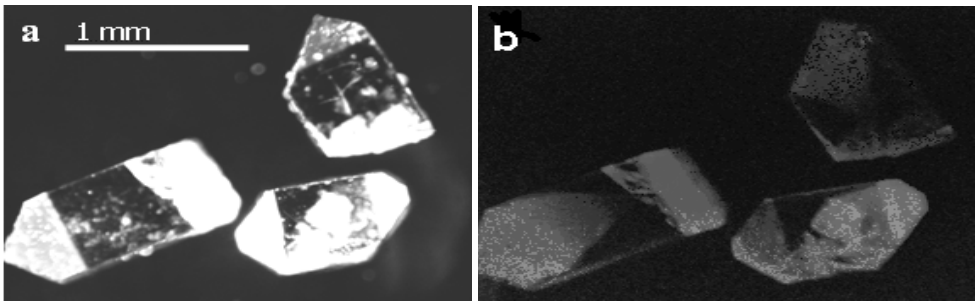

Fig. 4 Crystals of zircon $(Zr,Pu,Eu)(Si,P)O_4$, doped with 0.3 wt. % Eu and 0.01 wt. % ^{238}Pu, under binocular: a) in the light and b) self-glowing in the dark.

3. Conclusions

This research confirmed that actinide-doped zircon, monoclinic zirconia, monazite and xenotime are prospective materials not only for ceramic waste forms but also for the development of durable and safe radioactive light-emitters. Such light emitters can be used for very long time (many dozens of years at least) before their final disposal in the initial form (without reprocessing). The following results were obtained:

1. Intensively glowing crystals of zircon, xenotime and monazite were successfully obtained. Contents of ^{238}Pu or ^{241}Am in these crystals did not exceed 0.1 wt.%.
2. The most durable and intensively self-glowing actinide-doped crystals of zircon, (Zr,Tb,Pu)(Si,P)O4, were successfully synthesized by the flux method. Contents of ^{238}Pu, Tb, and P were (in wt.%): 0.02; 0.2 to 0.3; 0.2 to 0.3, respectively.
3. Crystals doped with ^{237}Np or ^{239}Pu were not characterized with self-glowing.
4. CL-spectroscopy is an efficient tool that allows identifying optimal content of luminescence ion in non-radioactive crystals. The same content of luminescence ion should be incorporated into radioactive crystals in order to provide highest intensity of self-glowing.

Acknowledgements

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