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Development and synthesis of durable self-glowing crystals doped with plutonium

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A B S T R A C T

Different crystalline materials doped with plutonium and other alpha-emitting radionuclides are characterized by self-glowing. Some of these materials, in particular, monocrystalline ones, which are highly chemically resistant, mechanically durable, and stable under radiation damage are promising for application in optical couplers, robotics and medicine. They might be used for a long time (from tens to hundreds years) in aggressive chemical media and space. Crystals with low content of radionuclides (less than 0.1 wt%) but intensive self-glowing are main subject of interest. Phosphate and silicate single crystals with zircon structure: xenotime, (Y,...)PO_4 and zircon, (Zr,...)SiO_4, were doped with ^{238}Pu, ^{237}Np and non-radioactive elements: Eu^{3+}; In^{3+} and Tb^{3+}. The most intensive self-glowing was obtained for xenotime crystals doped with 0.1 wt% ^{238}Pu and Eu; and for zircon crystals doped with 0.01 wt% ^{238}Pu and coupled admixture of In and Tb.

1. Introduction

Admixture of alpha-emitting radionuclides in some glasses and crystals or just external alpha-irradiation of some solids may initiate scintillation of their matrices [1]. In our previous research we have observed self-glowing of highly radioactive zircon single crystals doped with 2–3 wt% ^{238}Pu [2]. The intensive glowing might be converted into electric current [3–5]. However, only materials with low content of radionuclides but intensive self-glowing are prospective for industrial scale application. An important requirement to the wide use of self-glowing materials is their durability in environment. The crystalline materials with high chemical resistance, mechanical durability, and stability under radiation damage are very promising for long-term work in optical couplers, robotics and medicine. They might be used from tens to hundreds years in aggressive chemical media and space. The disposal of demolished or spent self-glowing crystalline materials does not cause any essential ecological consequences if these materials are analogues of natural extremely durable accessory minerals.

We have chosen to study phosphate and silicate crystalline materials with zircon-type crystalline structure: xenotime, YPO_4 and zircon, $ZrSiO_4$. The choice of zircon is based on previous proposal to use it as a durable host-phase for immobilization of weapon plutonium and other actinides [6,7]. The results obtained from previous study of self-glowing xenotime crystals doped with plutonium were promising [8].

Scintillation is a process in which a material produces luminescence following absorption of radiation, such as alpha. The luminescence centres might be produced by activating elements, for example, rare-earth ions (Eu, Ce, Tb, Mn, Gd, Nd, Er, Yb, Dy, etc) or intrinsic defects, caused by different reasons such as chemical admixtures (In, etc.). We use the term 'phosphors' to call all chemical elements, which are responsible for luminescence centres.

In principle, there is a range in which concentration of the alpha producer is proportional to the luminescence intensity. Single alpha particle is characterised with energy which is high enough to excite dozens of luminescence centres. If there is too much alpha activity, then the crystalline material may glow without doping with any non-radioactive phosphor [2]. At the same time high content of alpha-emitter causes radiation damage of crystalline structure and finally, decrease of glowing intensity. The use of proper admixture of phosphor(s) allows essential increasing of glowing intensity and decreasing of radionuclide content [3,8]. However, if content of phosphor is too high the self-glowing is also suppressed.

The results obtained from our previous study [8] have demonstrated that the use of cathodoluminescence (CL) method allows identifying optimal content of phosphor(s). Such content is similar for intensive luminescence of non-radioactive samples and intensive self-glowing of radioactive crystals. However, optimal content of alpha-emitter can be understood only from numerous experiments on synthesis of the samples doped with different content of radioactive element.

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Table 1
Main features of self-glowing crystals doped with ^{238}Pu.

#	Crystal	Phosphor	Content of ^{238}Pu (wt%)	Relative intensity of self-glowing
1	Zircon (Fig. 1a)	None	2.4-2.7	Weak
2	Zircon (Fig. 1b)	Eu	0.007	Weak
3	Zircon	In	0.02	Weak
4	Xenotime	Eu	0.002	Weak
5	Xenotime (Figs. 1c and 3a)	Eu(optimal content from CL study)	0.1	Very high
6	Zircon (Fig. 3b)	In(optimal content from CL study)	0.01	High
7	Zircon (Figs. 2 and 3c)	In + Tb(optimal content from CL study)	0.01	Very high

Therefore, main goal of our research was identifying optimal contents of non-radioactive phosphor(s) and alpha-radioactive element initiating glowing of zircon-structured crystals.

2. Experimental

All crystals of zircon and xenotime were grown by flux method using the same procedure as previously reported [2]. Desired contents of admixtures varied in the crystals matrices in the following ranges: ^{238}Pu – from 0.001 to 0.1 wt%; ^{237}Np – from 2 to 3 wt%; phosphor(s) – from 0.001 to 10 wt%. Selected crystals were mounted in acrylic resin and polished to reveal their interiors. Polished samples were studied by electron microprobe analysis (EMPA) using electron probe microanalyser Camebax (Cameca) with wavelength-dispersive spectrometers under the following conditions: beam current – 10 nA; energy of electron beam – 10 keV. The content of ^{238}Pu and ^{237}Np in all radioactive samples was measured by the precise γ-spectrometry method using a HPGe solid-state photon detector (ORTEC). All crystals were studied using local cathodoluminescence (CL) The original spectrometer [9] was installed into the optical port of the Camebax electron probe microanalyser. The CL spectra were acquired under the following conditions: energy of electron beam – 10 keV; beam current – 10 nA.

3. Results and discussion

Weak self-glowing of phosphor-free zircon #1 doped with 2.4–2.7 wt% ^{238}Pu (Table 1) was observed. However, as stated above the ^{238}Pu content was too high and it has to be optimized. Preliminary experiments on use of Eu and In as phosphors allowed us to decrease ^{238}Pu content in self-glowing crystals at least 100 times in comparison with phosphor-free zircon #1 (Table 1). Intensity of self-glowing for all these relatively low-radioactive samples #2, 3, 4 doped with Eu and In remained at similar level to highly radioactive phosphor-free sample #1 (Table 1). As expected, incorporation of phosphors into crystal structure changes the colour of self-glowing (Fig. 1).

Next step of our research was identifying optimal content of phosphor(s) which is responsible for the highest intensity of luminescence and self-glowing of non-radioactive and Pu-doped crystals, respectively. At first we applied CL method for non-radioactive samples doped with broad range of phosphor(s) content taking into account that amount of radioactive experiments was limited for economic reasons. Then we synthesized radioactive samples doped with similar (optimal) content of phosphor(s) and varying ^{238}Pu content from 0.1 wt% and less.

Among crystals doped with optimal amount of Eu the highest intensity of self-glowing was observed for xenotime with 0.1 wt% ^{238}Pu (Fig. 1c, Table 1, sample #5). Such glowing of orange-red colour was visually observed in the dark and it looked like cigarette light.

Self-glowing of similar very high intensity was not achieved for crystals doped with optimal amount of In (for instance, sample #6 in Table 1). We have succeeded in essential increase of self-glowing intensity when applied coupled doping with In and Tb simultaneously. Optimal content of (In + Tb) was determined from the study of non-radioactive zircon samples. Radioactive crystals of zircon synthesized with similar content of (In + Tb) and 0.01 wt% ^{238}Pu (sample #7, Table 1) demonstrated very intensive self-glowing comparable to the intensity of the best Eu-doped xenotime (sample #5, Table 1). The colour of self-glowing of this In + Tb

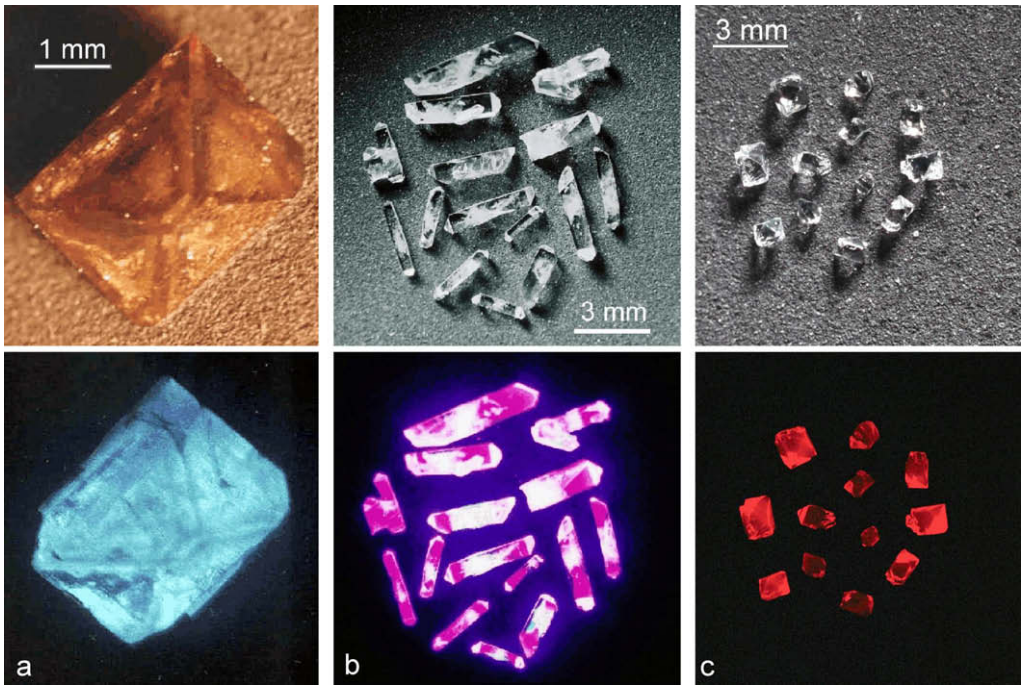

Fig. 1. Self-glowing crystals in transmitted light (top row) and in the dark (lower row): (a) phosphor-free zircon containing 2.4–2.7 wt% ^{238}Pu (sample #1); (b) zircon doped with 0.007 wt% ^{238}Pu and Eu (sample #2); (c) xenotime doped 0.1 wt% ^{238}Pu and optimal Eu content (sample #5).

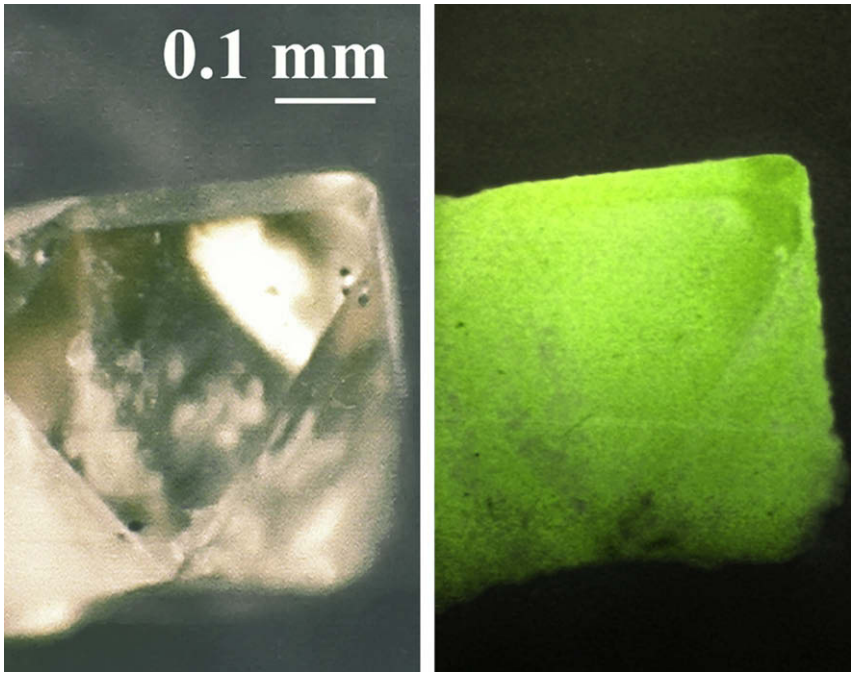

Fig. 2. Self-glowing zircon doped 0.01 wt% ^{238}Pu and optimal In + Tb content (sample #7) in transmitted light (left) and in the dark (right).

doped crystal was yellow–green (Fig. 2). For comparison, the CL spectra of samples #5, 6, 7 are shown at Fig. 3(a)–(c).

We made an attempt to synthesize self-glowing crystals doped with ^{237}Np instead of Pu. The advantages of using ^{237}Np are related to its extremely long half-life (2.14 million years in comparison to 87.7 years for ^{238}Pu) and absence of nuclear proliferation concern in contrast to ^{239}Pu (half-life 24 thousand years). However, activity of ^{237}Np is essentially less than ^{238}Pu (2.6×10^7 Bq/g and 6.3×10^{11} Bq/g, respectively). This is why content of ^{237}Np in our samples was 2–3 wt%. The zircon crystals doped with optimal In content and 3 wt% of ^{237}Np (sample #8) demonstrated insignificant self-glowing correlated with very weak CL emission (Fig. 3(d)).

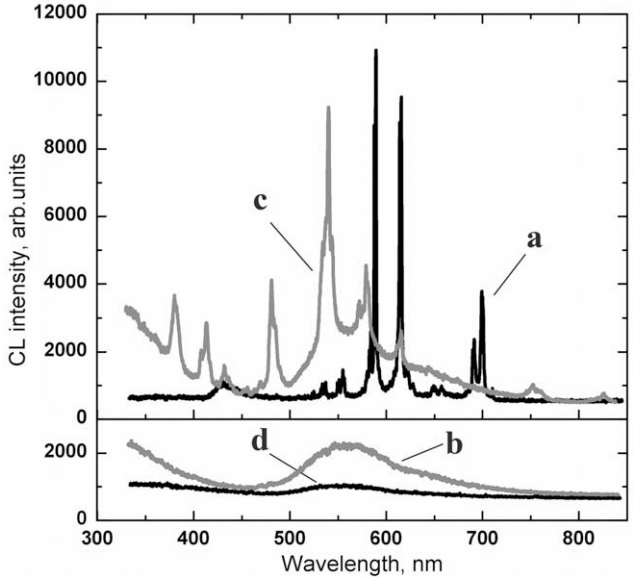

Fig. 3. CL spectra of self-glowing crystals. (a) Xenotime doped 0.1 wt% ^{238}Pu and optimal Eu content (sample #5); (b) zircon doped 0.01 wt% ^{238}Pu and optimal In content (sample #6); (c) zircon doped 0.01 wt% ^{238}Pu and optimal In + Tb content (sample #7); (d) zircon doped 3 wt% ^{237}Np and optimal In content (sample #8).

Development of new intensively self-glowing crystals doped with plutonium isotopes and other actinides is the subject of our further research.

4. Conclusions

The results obtained allowed us to make the following conclusions:

1. Samples of zircon-structured ^{238}Pu-doped crystals with intensive self-glowing were successfully synthesized. Content of ^{238}Pu admixture initiating self-glowing did not exceed 0.1 wt%.
2. Admixture of phosphor(s) dramatically increase intensity of self-glowing and allows decreasing ^{238}Pu content at least 100 times in comparison with phosphor-free crystals.
3. CL method is an important tool for evaluation optimal content of phosphor(s).

Acknowledgments

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