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The use of cathodoluminescence for development of durable self-glowing crystals based on solid solutions YPO_4–$EuPO_4$

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Local cathodoluminescence spectroscopy has been suggested for development of durable self-glowing crystals based on crystalline solid solutions $(Y,Eu)PO_4$. Nonradioactive ions of Eu^{3+} in these crystals cause strong luminescence in visible range initiated by small admixture (less than 1 wt%) of α-radioactive ^{238}Pu. The intensity of self-glowing depends on Y : Eu ratio and ^{238}Pu content. Optimal Y : Eu ratio responsible for the most intensive luminescence was identified. Principal features of cathodoluminescence emission in $(Y,Eu)PO_4$ crystals of various chemical compositions are being discussed.

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1. Introduction

Self-glowing compounds based on mixtures of nonradioactive powdered phosphor and radionuclide or „activator“ are well known light emitters used in different measurement instruments and equipment [1]. However, the most phosphor materials are unstable under $\beta-\alpha$-irradiation from „activator“ and are not chemically durable. This disadvantage limits the use of radioactive light emitters during long time. Also, there is a possibility of radionuclide release into environment from corroded sources. We have suggested development of self-glowing low radioactive monocrystalline materials, which are characterized by high chemical resistance, mechanical durability and stability under radiation damage. Such crystals are prospective for wide use in optical couplers, robotics and medicine. They might be used for a long time (from tens to hundreds of years) in aggressive chemical media and space. Crystal matrix durability provides safe handling of self-glowing crystals. Such handling meets the requirements of work with sealed sources of irradiation. The disposal of demolished or spent crystals does not cause any essential ecological consequences because these crystalline materials are analogues of natural accessory low radioactive minerals, which demonstrate extremely high durability for millions of years.

The main goal of our investigation was the search for optimal compositon of self-glowing crystals doped with ion responsible for luminescence and $\beta-\alpha$-radioactive element initiating glowing. The following activating admixtures have been selected: nonradioactive europium and α-radioactive plutonium-238 with half-life 87.7 years. Solid solutions based on $(Y,Eu)PO_4$ with structures of xenotime (YPO_4) and monazite ($EuPO_4$) have been chosen as matrices. In these structures europium occurs in trivalent state which supports intensive luminescence under irradiation by ultraviolet light, X-rays, electron beam, etc. as well as self-glowing in visible range of spectrum. It was necessary to take into account that the crystals with low content of radionuclide but intensive self-glowing were the main subject of interest.

Moreover, the amount of experiments with plutonium-238 was limited for economical reasons. Therefore, at the first stage of the research we determined ratio Y : Eu, which was optimal for the highest luminescence. Investigation of optimum plutonium content is the subject of further research.

Either nonradioactive crystals $(Y,Eu)PO_4$ or radioactive crystals $(Y,Eu,Pu)PO_4$ with different ratio Y : Eu were grown and studied. The cathodoluminescence emission features depending on crystal structure and chemical composition were studied.

2. Experimental methods

All crystals were grown by flux method using similar procedure as for Pu-doped zircon single crystals [2]. Selected crystals were mounted in acrylic resin and polished to reveal their interiors. Polished samples were studied by electron microprobe analysis (EMPA) using wavelength-dispersive electron microprobe Camebax (Cameca) under the following conditions: beam current — 10 nA; accelerating voltage — 10 kV. Crystal structures and unit cell parameters were determined by powder X-ray diffraction analysis (XRD) using diffraction system D/max-RC (Rigaku, Japan) at CoK_α irradiation (wavelength $\lambda = 1.789$ Å); current — 60 mA, tube voltage — 40 kV, scan speed — 1.5 deg/min, step size — 0.01 deg. The content of ^{238}Pu in all radioactive samples was measured by precise γ-spectrometry method

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Average results of EMPA and bulk XRD

Sample #	Element content from EMPA						Structure (angle β for monazite)	Unit cell parameters, Å		
	wt%			at%						
	Eu	Y	P	Eu	Y	P		*a*	*b*	*c*
1	–	48.4	16.8	–	16.6	16.6	Xenotime	6.883(2)		6.018(2)
2	0.7	48.6	16.7	0.1	16.8	16.5	Xenotime	6.880(1)		6.019(2)
	0.4	48.4	16.6	0.1	16.8	16.5				
	1.1	46.4	17.3	0.2	15.9	17.0				
	2.7	46.7	16.4	0.5	16.3	16.5				
3	5.4	43.8	16.6	1.1	15.4	16.7	Xenotime	6.892(1)		6.021(2)
	6.8	43.1	16.3	1.4	15.3	16.6				
4	7.9	40.6	17.1	1.6	14.2	17.2	Xenotime	6.897(1)		6.023(2)
5	31.9	22.2	15.0	7.3	8.7	16.9	Xenotime	6.941(1)		6.066(2)
6	52.4	7.7	13.0	13.6	3.4	16.6	Monazite (104.04(3) deg)	6.647(2)	6.844(2)	6.342(2)
7	61.5	–	12.5	16.6	–	16.6	Monazite (103.95(4) deg)	6.665(3)	6.867(2)	6.353(5)

using HPGe solid-state photon detector (ORTEC). All crystals were studied using cathodoluminescence (CL) spectroscopy. The original spectrometer [3] was installed into optical microscope port of the Camebax electron microprobe. The CL spectra were acquired under following conditions: accelerated voltage — 10 kV, beam current — 10 nA.

3. Results and discussion

Principal features of the crystals obtained are summarized in Table. Crystals of pure YPO_4 and $(Y,Eu)PO_4$ with Eu content less than 35 wt% were characterized by tetragonal xenotime structure. Crystals of pure $EuPO_4$ and $(Eu,Y)PO_4$ with Eu content higher than 48 wt% had monoclinic monazite structure. Chemical compositions of different crystals grown from the same precursor in one crucible slightly varied due to dynamic of flux evaporation. It is interesting to note that the use of starting precursor $50\,YPO_4 : 50EuPO_4$ caused formation of $(Y,Eu)PO_4$ crystals of both structures (xenotime and monazite) during the same synthesis process (Table).

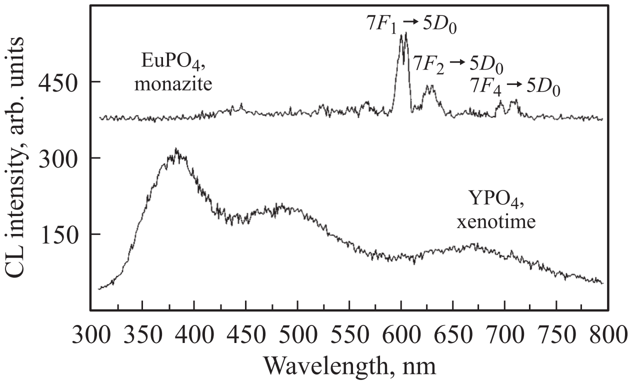

Figure 1. General CL spectra of non-doped crystalline xenotime, YPO_4, and monazite, $EuPO_4$.

CL emission of pure YPO_4 and $EuPO_4$ is characterized by weak intensity (Fig. 1). Spectrum of xenotime, YPO_4, has three broad bands. In CL spectrum of monazite, $EuPO_4$, there are three main bands at 584.80 nm (2.12 eV), 621.12 nm (1.99 eV) and 699.31 nm (1.77 eV) related to $7F_0 \rightarrow 5D_0$, $7F_2 \rightarrow 5D_0$ and $7F_4 \rightarrow 5D_0$ electron transitions in Eu^{3+}.

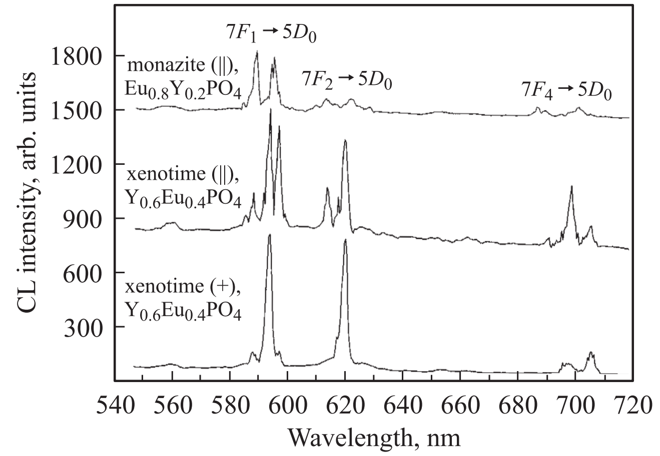

Figure 2. General CL spectra of solid solutions $(Y,Eu)PO_4$ with monazite and xenotime structures: (||) — along crystal axis; (+) — across crystal axis.

General CL emission of solid solutions $(Y,Eu)PO_4$ with xenotime and monazite structures is also initiated by ions Eu^{3+}. Despite crystal structure type main CL bands of $(Y,Eu)PO_4$ are similar to those of pure $EuPO_4$. However,

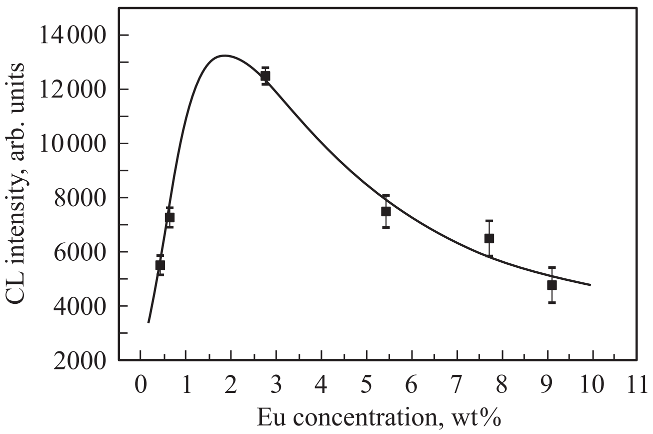

Figure 3. The intensity of CL emission as a function of Eu content in xenotime crystals, $(Y,Eu)PO_4$.

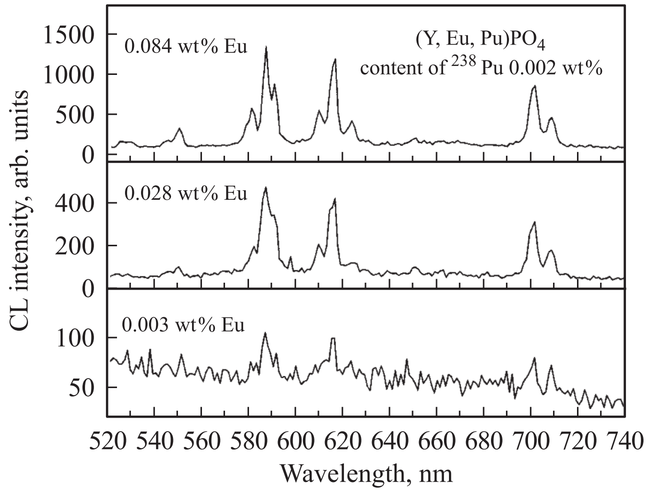

Figure 4. CL spectra of $(Y,Eu,Pu)PO_4$ doped with 0.002 wt% ^{238}Pu and with different Eu content.

some features of these CL bands such as fine structure and intensity depend on Y : Eu ratio (Fig. 2). CL intensity of monazite-type crystals is essentially less than of crystals with xenotime structure. The CL bands at 621.12 and 699.31 nm in monazite are weak and the intensive band at 584.80 nm is characterized by fine structure.

Cathodoluminescence of xenotime crystals depends on crystal orientation. The CL emission across crystal axis is more intensive than observed along the axis. The structure of CL spectrum across the crystal axis is characterized by two intensive bands at 584.80 and 621.12 nm without fine structure (Fig. 2). Three intensive bands at 584.80, 621.12 and 699.31 nm are observed in xenotime CL spectrum obtained along the crystal axis. All these bands have fine structure.

The difference of CL spectra allows to express distinguishing solid solutions $(Y,Eu)PO_4$ with xenotime structure from those with monazite structure avoiding the use of other methods. Essential anisotropy of xenotime CL emission might be also used for identifying crystal orientation.

On the basis of CL data obtained the xenotime-structure solid solutions $(Y,Eu)PO_4$ have been chosen as the most promising compounds for development of self-glowing materials. The CL intensity of xenotime crystals has been studied as a function of Eu content (Fig. 3). It was found out that optimal Eu content, which provides the most intensive CL emission and, as assumed, the most intensive self-glowing of ^{238}Pu-doped, is about 2.7 wt%. It is necessary to note, that these data are related only to CL emission excited along xenotime crystal axis. Up to the present only three different self-glowing samples doped with ^{238}Pu have been obtained. These are:

— monazite, $(Eu,Pu)PO_4$ containing 4.9 wt% ^{238}Pu;

— xenotime, $(Y,Eu,Pu)PO_4$ containing about 1.7 wt% Eu and doped with 0.1 wt% ^{238}Pu;

— xenotime, YPO_4 doped with 0.03 wt% Eu and 0.002 wt% ^{238}Pu.

Plutonium doped monazite was characterized by very weak intensity of self-glowing as well as CL emission. This result correlates with weak CL emission of pure monazite $EuPO_4$ (Fig. 1).

Xenotime doped with smallest admixtures of Eu and Pu also demonstrated weak CL emission and self-glowing. CL imaging allowed us to observe inhomogeneous distribution of Eu inside crystal matrices Europium content in these crystals was less than the detection limit of microprobe analysis (0.2 wt%). It was possible to evaluate roughly low Eu content using the intensity of CL band at 584.80 nm and admitting linear correlation between Eu content and CL intensity (Fig. 3,4). According to calculations done Eu content varied from 0.001 to 0.08 wt%.

Bright self-glowing of xenotime $(Y,Eu,Pu)PO_4$ containing about 1.7 wt% Eu was visually observed in the dark. Glowing of glass ampoule with these crystals has orange-red color resembling cigarette light. It is interesting to note that CL intensity of this xenotime was at least two times higher in comparison with nonradioactive sample $(Y,Eu)PO_4$ containing similar Eu content. However, the structure of CL spectrum and positions of CL bands were similar in Pu-doped and nonradioactive samples.

4. Conclusion

The results obtained allow us to make the following preliminary conclusions.

1) CL emission of solid solutions $(Y,Eu)PO_4$ is affected by the type of their crystalline structure and crystal orientation.

2) The most intensive CL emission was observed in non-radioactive xenotime-structure $(Y,Eu)PO_4$ with Eu content $\sim (2-3)$ wt%.

3) CL method allows to make quantitative measurements of Eu admixture in $(Y,Eu)PO_4$ at level at least 0.001 wt%.

4) Plutonium doping of xenotime-structure $(Y,Eu)PO_4$ with Eu content $\sim$ 2 wt% causes at least two times increase of CL intensity.

5) Bright self-glowing crystals of xenotime-structure solid solution (Y,Eu,Pu)PO_4 containing 1.7 wt% Eu and 0.1 wt% ^{238}Pu have been successfully synthesized. The search of optimal Pu content providing the most intensive self-glowing is the subject of current research.

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