Development of nuclear electric batteries based on durable actinide-doped crystals

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The subject of this lecture is an elaboration of the joint work with the Radium Institute aimed at the search and development of chemically, mechanically and radiation-resistant crystalline materials for the immobilization of the heavy fraction of radioactive waste. But the heavy fraction of radioactive waste could be not just immobilized but used as an energy source. The search for new energy sources is one of the priority problems of science and technology.

The main idea of our research is the following. The radionuclide acting as the source of alpha radiation should be immobilized as an impurity in a crystal lattice containing active optical luminescence centers as well. In this case, the crystal becomes self-glowing. The time of its self-glowing is determined by the lifetime of the radionuclide and can be tens or hundreds of years. The content of the radionuclide will be selected in such a way as to ensure ecologically safety and technically simple handling of self-glowing materials. It can be less than 0.2% weight. Photovoltaic converters based on semiconductor with high efficiency (~50%) and high radiation resistance will be used as converters of optical energy into electric current. This idea was proposed for the first time in the world and partially experimentally implemented in Ioffe and Khlopin Institutes.

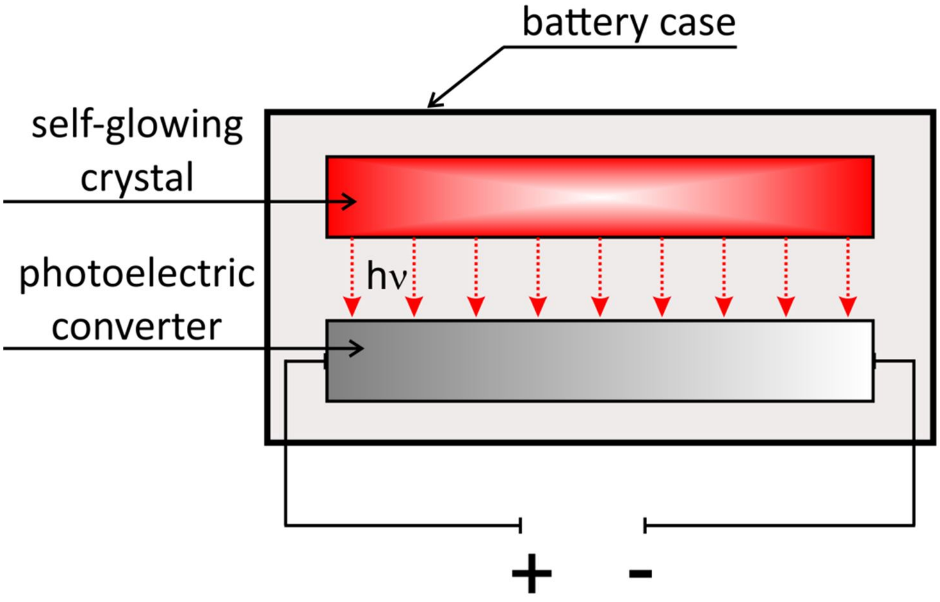


Fig.1 Nuclear electric batteries based on durable actinide-doped crystals

By now, there are number of supply sources based on radioactive elements, for example, thermoelectric and beta-voltaic. At the moment, commercially-available supplies are based on plutonium oxide. The electricity is obtained due to the heat released during radioactive decay. Also, supplies based on beta-radioactive isotopes of nickel Ni-63 and carbon C-14 (beta-voltaics) are well-known. These devices contain a very large amount of radionuclides. In this regard, they can be used only in special conditions. The main disadvantage of high power devices is the high content of radioactive isotopes, which leads to a very high cost and limited use. Radionuclides in such sources are in ecologically dangerous form (as a rule they are used in a form of powders-oxides) and are in quantities, that requires not only special control, but also particular working conditions and utilization after 5-15 years of exploitation. High concentration of radionuclides also leads to radiation damage of other structural elements that significantly limits the service life of such devices and makes their using is hazardous to the environment. The closest analogue of our development is the low-power battery based on tritium (half-life is 12 years). Radiation-stimulated luminescence of high-efficiency phosphors acts as an energy source in such supplies. Tritium and phosphors in the liquid phase are enclosed in an ampoule. The liquid phase complicates their utilization. In addition, their service time does not exceed four years.

To understand the principle of battery operation it is very important to understand the mechanism of transformation of the alpha particle energy into optical emission. The alpha particle with energy about six mega electron volts emitted by radionuclide undergoes collisions with the atoms of the matrix and loses energy as a result of elastic and inelastic collisions. When interacting with the matrix, part of the energy of the alpha particle is expended on the formation of radiation defects (displacement of the matrix atoms), part on the excitation of the electron system and heating (phonon formation). The distribution of the energy loss of alpha particles can be calculated in the STRIM program assuming that the particle irradiates the surface of the matrix. This slide shows the result of calculating the energy losses of the alpha particle during Xenotime irradiation. If the emitter of the alpha particle is inside the matrix, then for each particle the calculation remains correct. In this case, the formation of radiation defects, excitation of the electronic system and heating will be homogeneously distributed over the volume of the matrix.

The Tabl.1 shows the results of calculating the fraction of energy loss of the alpha particle upon irradiation of various materials: xenotime, zircon, and yttrium-aluminum garnet. As can be seen from the calculations, 99 per cent of the energy of the alpha particle is expended on the excitation of the electronic material system, about one percent is spent on the formation of radiation defects and two hundredths of a percent is spent on heating the matrix. It is important to note that the alpha particle path length in these materials is about fifteen microns.

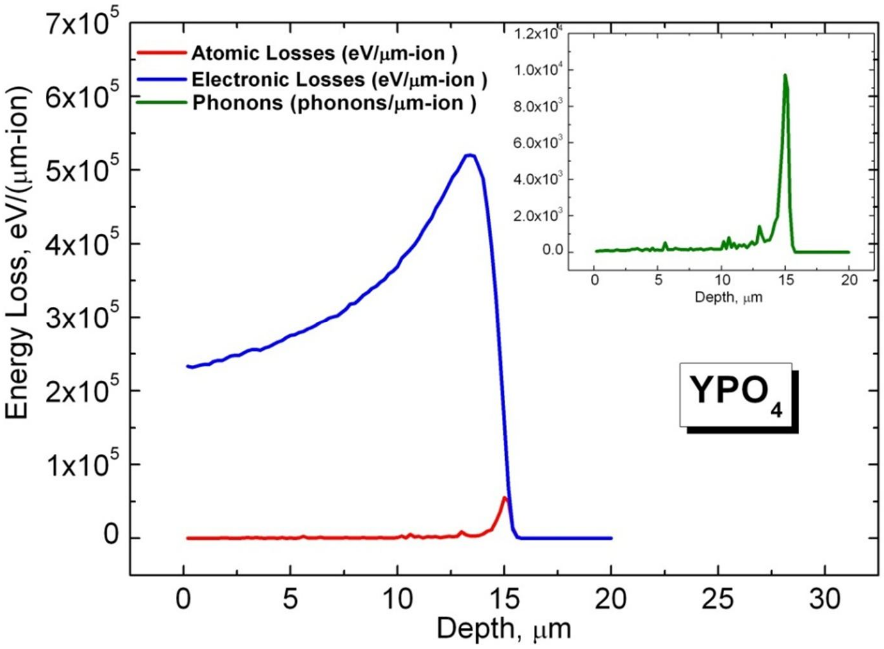


Fig.2 The distribution of the energy loss of alpha particles (6 MeV) in YPO_4

Tabl.1 The results of calculating the fraction of energy loss of the alpha particle upon irradiation of various materials: xenotime, zircon, and yttrium-aluminum garnet

The energy losses of the alpha particle:	$ZrSiO_4$	YPO_4	$Y_3Al_5O_{12}$
The excitation of the electronic subsystem, [eV · ion^{-1}]	$5*10^6$ **99.2%**	$5*10^6$ **98.7%**	$5*10^6$ **98.7%**
The displacement of atoms, [eV · ion^{-1}]	$0.4*10^5$ **0.8%**	$0.6*10^5$ **1.2%**	$0.6*10^5$ **1.2%**
The excitation of thermal oscillations, [the phonons · ion^{-1}]	10^4 **0.02%**	10^4 **0.02%**	$1.1*10^4$ **0.02%**
Number of vacancies created by one alpha particle, [ion^{-1}]	120	130	130
Travel of alpha particle, [μm]	15	16	15

Due to the fact that the alpha particle emitters are uniformly distributed inside the matric, only those particles that radiate radionuclides located at a depth of less than 15 microns can fly off.

The excitation of the electronic system is associated with the formation of secondary electrons and plasmons. We have carried out the calculations of the most probable losses of fast electrons energy during interaction with a solid. As calculations show, the probability of losing a certain fraction of the energy depends at first on the properties of the irradiated material, and not on the energy of the particle. This suggests that the probability of losing a certain fraction of the energy for a single collision for alpha particle will be the same as for a fast electron. The Fig.3 shows the results of calculation of the energy losses of a fast electron upon irradiation of silicon oxide. On the first image 3(a) it is the logarithmic scale, on the second 3(b) it is linear. On the graph, presented on a logarithmic scale in the first half, the energy losses of a particle spending phonons formation are shown. In the second half of the graph, energy losses on the excitation of the electronic system are presented. The graph presented on a linear scale shows that the real fraction of the particle energy expended on the production of phonons is very small. Basically, for a single collision, the more probable loses energy of the particle is in the range 10-50 electron volt.

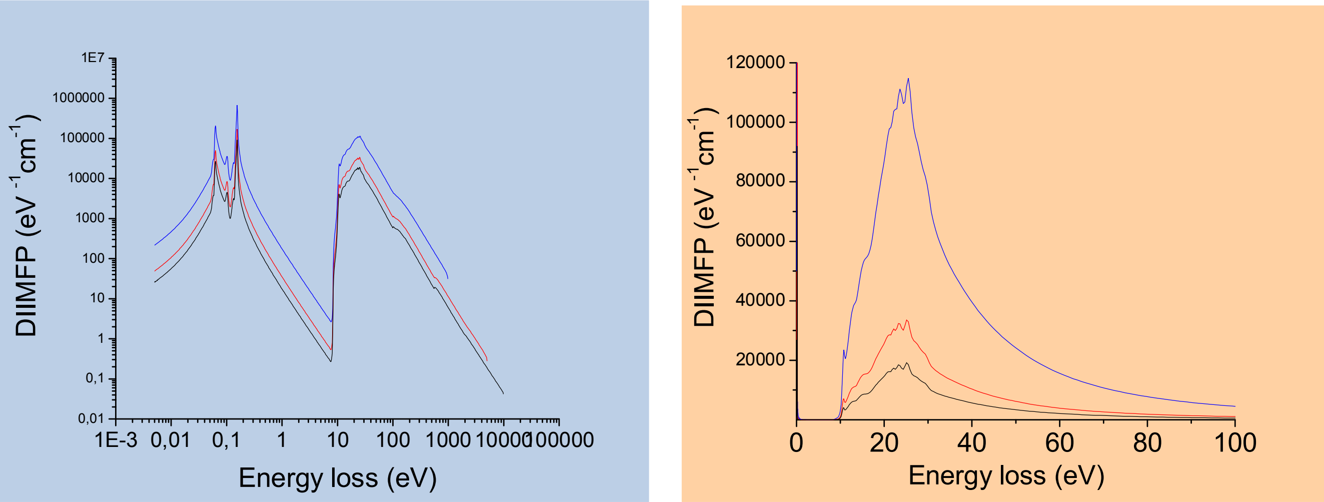


Fig.3 Calculation of the energy losses of a fast electron upon irradiation of silicon oxide (a) - logarithmic scale, (b) – linear scale.

The study of mechanisms of the transformation of the energy of 10-50 electron volts into optical excitation is associated with a number of experimental difficulties. In this case, it would be useful to investigate the luminescence excitation spectra in a wide energy range of 50 to 1 electron volts. At the moment we do not have such an opportunity. It is important to note that when a solid is irradiated by high-energy particles, the mechanism of excitation of luminescence is different than for photoluminescence. The efficiency of transfer of the excitation energy of the electronic matrix system to the luminescence centers is determined by very many factors: the relative location of the excited levels of the luminescence centers with respect to the conduction band, the presence of intrinsic defects and their energy levels, the channel of nonradiative deactivation of excitation, and others. This will be the subject of our further research.

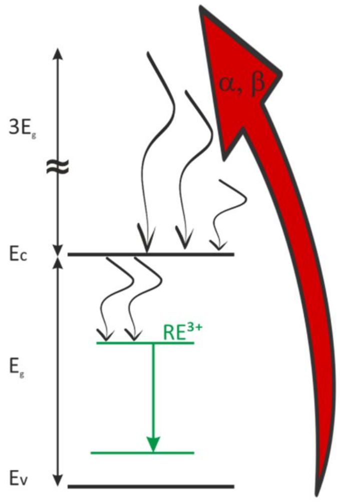


Fig.4 Excitation mechanism of the solid state electronic system by alpha- or beta - particles

In connection with the fact that the matrices we work are dielectric materials it is necessary to dwell on the nature of the luminescence of dielectrics. There are three basic mechanisms of luminescence in dielectrics. The first is self-trapped excitons. This luminescence can be observed only if the excitation energy is equal to or greater than the width of the band gap of the material. These emission bands have larger half-width. Despite the fact that to excite them it requires energy not less than the width of the band gap, the energy of their radiation can be noticeably less. The more perfect the crystal, the more intense this radiation band. It appears as a rule only at low temperatures. In connection with this fact for our problem they have no practical significance.

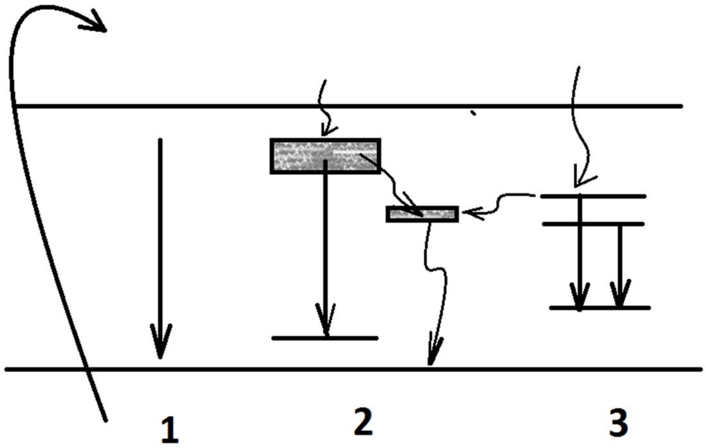


Fig.5 Three basic mechanisms of luminescence in dielectric, 1 - Self-trapped excitons, 2 - Point defects (vacancies, interstices, impurities), 3 - Intracenter transitions (transition metal ions or their complexes)

Also in many dielectrics, radiation bands associated with point defects (vacancies, interstices, impurities) are observed. To excite these bands, the energy required is less than the width of the forbidden band. However, the excitation of these luminescence bands can also occur from the conduction band, as was shown on the previous slide. To determine the nature of these bands, it is possible to conduct additional technological experiments (annealing, irradiation, etc.). These bands are observed at room temperature, usually characterized by the same large half-width. As a rule, in dielectrics these bands are manifested in the ultraviolet and blue spectral ranges. As an example, Fig. 6 shows the emission spectrum associated with intrinsic defects in the yttrium-aluminum garnet. As can be seen from the figure, the half-width of the emission band is more than one hundred nanometers. The spectral position of such bands and their intensity depend weakly on the temperature.

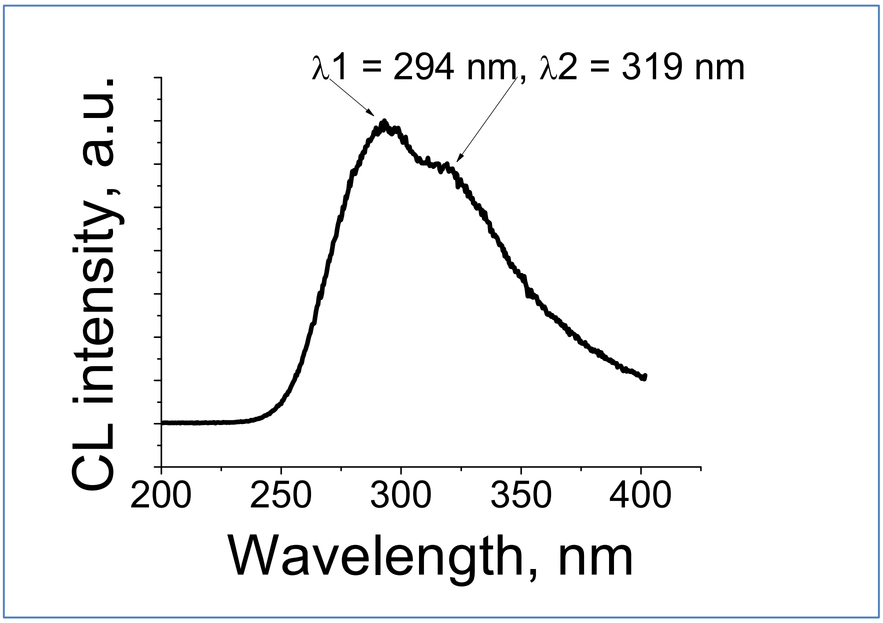


Fig. 6 Luminescence of points defects in $Y_3Al_5O_{12}$

The third, very important luminescence mechanism is associated with intracenter transitions. They occur in luminescence centers - transition metal ions or their complexes. In most phosphors, solid-state laser crystals, scintillators, rare-earth ions in tri- and divalent state are used as luminescence centers. The luminescent properties of trivalent ions of rare-earth elements in connection with their wide application have been studied in detail. They have properties that distinguish them from other transition ions - luminescence centers. The luminescence features of these ions are determined by their electronic structure. These elements have an incomplete 4f electronic shell, which is shielded by “higher" shells. Optical spectra of rare-earth ions are determined by the energy transitions of f-electrons, which are relatively well screened by 5s2 5p6 electron shell. Due to the screening of the 4f-shell from the influence of an external crystal field, the luminescence spectra are characterized by a set of narrow bands. The spectral position of the emission bands of rare-earth ions depends weakly on the matrix. However, depending on the local environment of the ion, the structure of the bands and their relative intensity can change. In connection with the fact that the spectral position of the luminescent bands of trivalent rare-earth ions depends weakly on the matrix, the possible excited states for these ions were calculated. The results of these calculations are presented on the Fig. 7. On the basis of these theoretical calculations and a huge number of published experimental data, one can choose an activator emitting in the required region.

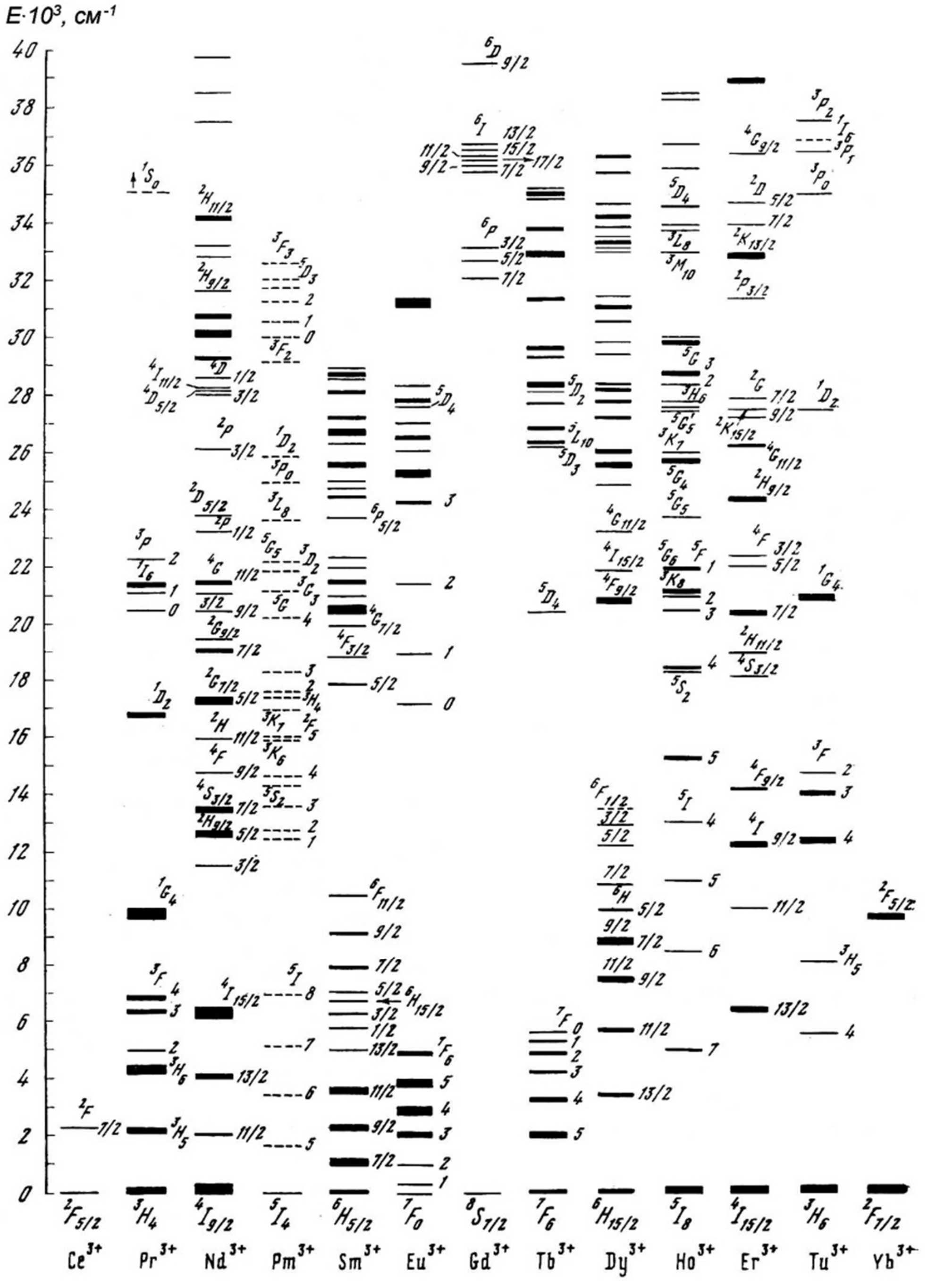


Fig. 7. Diagram of energy levels

For example, Fig. 8 represents the scheme of electronic transitions and the corresponding luminescence bands for two rare-earth ions: Eu^{3+} and Tb^{3+}. As seen on the slide, the terbium ion emits predominantly in the green region of the spectrum, and europium emits in the red.

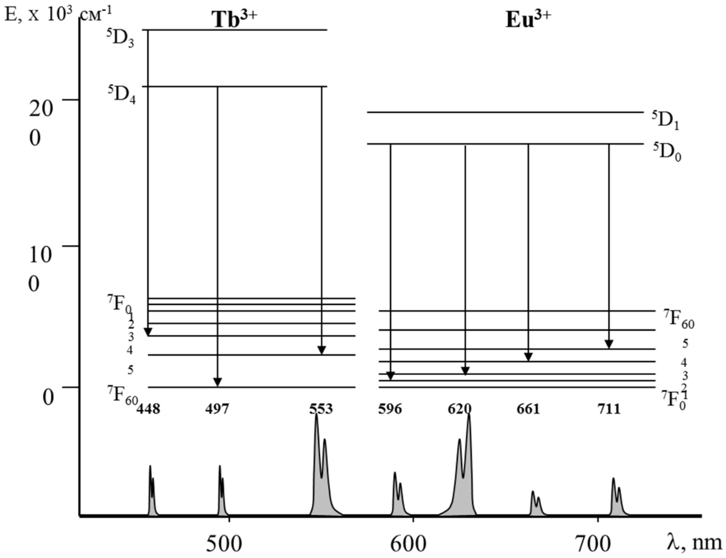


Fig. 8 the scheme of electronic transitions and the corresponding luminescence bands for two rare-earth ions: Eu^{3+} and Tb^{3+}

In addition, in crystals, as a rule, there are electronic states, which are not the cause of luminescence, but decrease the radiation intensity. These states form channels of nonradiative relaxation (Fig.9). The nature of these conditions, as a rule, is very difficult to determine. However, the more defects in a crystal, the greater the probability of formation of such states. One of the consequences of the presence of such states is the concentration quenching of luminescence centers

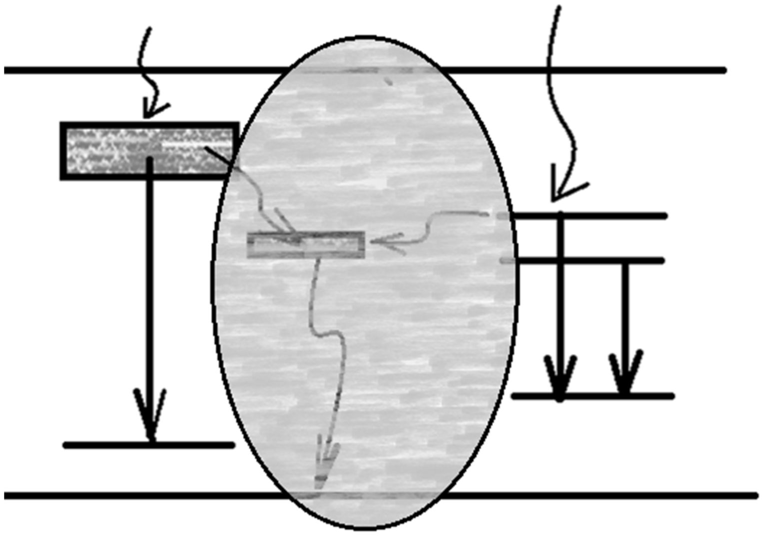


Fig.9 Diagram of channels of nonradiative relaxation

As a result,, the concentration dependence of the luminescence intensity is not linear. This is due to the fact that as the content of the luminescence centers increases, the actual distance between them decreases. As a result, there is a probability of a resonant transfer of excitation energy from one center to the other. This increases the probability of meeting with the energy level leading to nonradiative relaxation. A typical example of the concentration dependence of the intensity is presented on the Fig. 10. The position of the maximum of this dependence is determined by the mechanism of interaction between the luminescence centers and the number of defects in the crystal that promote nonradiative relaxation. Thus, the choice of the rare-earth ion-luminescence center is determined by the spectral ranges in which it is planned to observe the luminescence. The content of ions-luminescence centers depends on the type of ion and the quality of the matrix. It is usually selected experimentally.

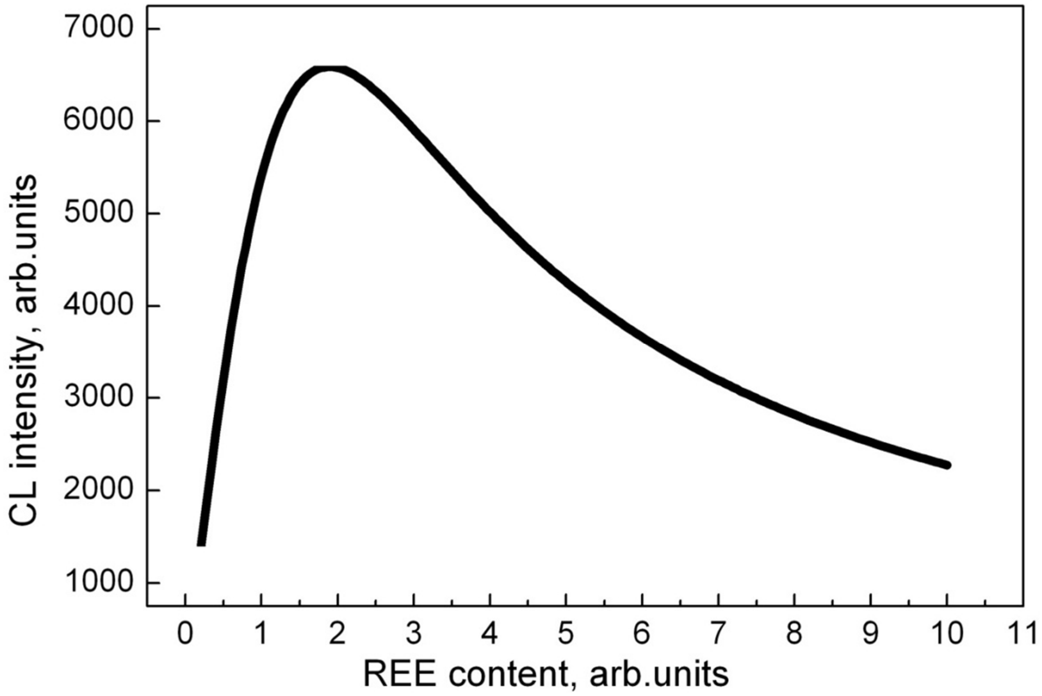


Fig. 10Ttypical example of the concentration dependence of the luminescent intensity

In this way for realize our idea, it is necessary to carry out research in several directions: to choose a crystalline matrix, to determine the optimum radionuclides and luminescence centers, to develop methods of synthesis.

1. **Optimal radionuclide determination**. Luminescence can be excited by alpha, beta and gamma irradiation, but in this case it is better to use alpha irradiation. At first, it is related with ecological safety. The mean free path of the alpha particle in solid materials is not more than tens of microns. Any protection cover with a thickness of a hundred microns will absorb all the alpha particles. In this case the device comprising self-glowing element can be safe for other

elements of device and for human. On the other hand, all the energy of emitting alpha particle is rest in self-glowing material. In this work we deal with two alpha isotopes: ^{238}Pu and ^{241}Am. There isotopes are alpha emitters. The main difference of these isotopes is their half-life. It is eighty seven and four hundred thirty years respectively.

We calculated the possible efficiency of such battery with the self-glowing crystal. We did several calculation approaches: the content of alpha-isotope in the active element does not exceed 0.1% weight; the conversion efficiency of alpha-decay energy into optical radiation is not worse than 10%;the efficiency of the photocell is 50%. In this case, the conversion efficiency of the radionuclide energy into an electric current may be 5%. The results of our calculations are shown in the table 2. The calculations were done for self-glowing crystal with the size of 1cm^3. Obviously, it may be only the low-power battery. It is possible to increase the power only by increasing the size of self-lowing crystal.

Table 2. Results of battery efficiency calculations

Alpha isotope	**Pu^{238}**	**Am^{241}**
The half-life of the isotope	87 years	432 years
The power drop time of alpha radiation on 20%	28 years	139 years
The activity of one gram of the isotope (1Bq - 1 decay per second)	633 GBk	127GBk
The calculated power of the battery with a crystal size of 1 cm^3	0.1 mW	0.02 mW
Voltage	1.5 V	1.5 V
Maximum load current	60 mkA	12 mkA
The energy released over 28 (139) years	22 W*hour	4.4 W*hour
The stored energy of a lithium AAA battery	1.1 W*hour	

3. **Choosing of luminescent centers**. In our initial experiments, we chose trivalent europium and terbium ions characterized by red and green luminescence. We have grown the crystals, activated by plutonium europium and terbium. To obtain blue self-glowing zircon was activated with plutonium without rare-earth ions. In this case, the luminescentet centers of the

luminescence were point defects of the crystals. To increase the number of point defects zircon was activated by indium.

2. **Choosing of crystalline matrix for a self-glowing crystal**. When choosing a matrix for a self-glowing crystal, the following requirements must be satisfied. It must be non hygroscopic, mechanically and chemically strong, radiation-resistant, should be able to form solid solutions with radionuclides, have good scintillation properties. To date, a number of materials with high efficiency of the alpha-particle converting energy into optical radiation are well known. Such substances are called scintillators. The most widely known alpha- particle scintillators produced on an industrial scale are $CaF_2:Eu^{2+}$, $Cs_2LiLaBr_6:Ce^{3+}$, organic solids. None of these substances have the above properties. A common drawback of these materials is the hygroscopicity, low radiation resistance.

That is why the first step was the search for analogs of minerals with radiation-resistant properties which form solid solutions with radionuclides (Pu and Am). Such types of minerals confirm their mechanically and radiation-resistant properties during several millions of years. At this point, we begin with Zircon, Hafnon, Baddeleyite (monoclinic zirconia), Tajeranite (cubic zirconia), Xenotime, Monazite, Garnet, Perovskite. Such types of minerals confirm their mechanically and radiation-resistant properties during several millions of years.

3. **Methods of synthesis.** When choosing methods for the synthesis of self-glowing crystals, activated simultaneously by luminescence centers and radioactive isotopes, an important criterion was the minimization of possible contamination of a growth setup by radioactive isotope. We used two technologies. One of them- growth from solution in melt, or pulling from flux. This method will make it possible to obtain structurally perfect crystals with a minimum content of intrinsic defects, uncontrolled impurities, without phase boundaries. The crystal of Zircon and Xenotim doped with Pu and luminescent active centers were successfully grown by this method. The second method is the cold molding followed by sintering, which gives the possibility to obtain the ceramics based on Tajeranite (cubic zirconia).

The both growing methods were developed in Khlopin Institute in laboratory of matrix materials. Though self-growing crystals and ceramics are ecologically safe, the growing possess is rather dangerous. For this it is necessary to use special room, box and other special equipment. Really only in several laboratories in the world it is possible to do such growing process. In Khlopin Institute the synthesis of Zircon and Xenotim doped with Pu was worked out.

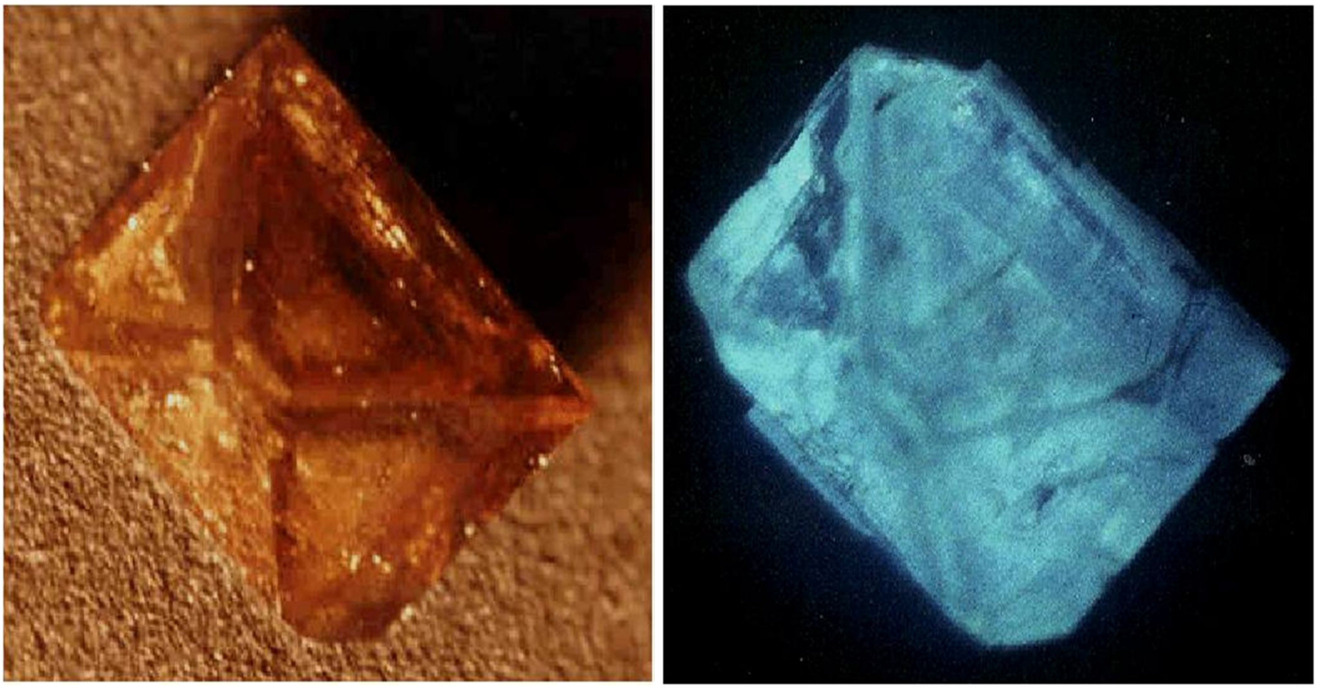
Experimental result

The table 3 shows the main crystals grown by us, in which self-glowing was observed. It could be observed in the dark. In the last line of the table, the composition is not a single crystal, but ceramics based on zirconium oxide.

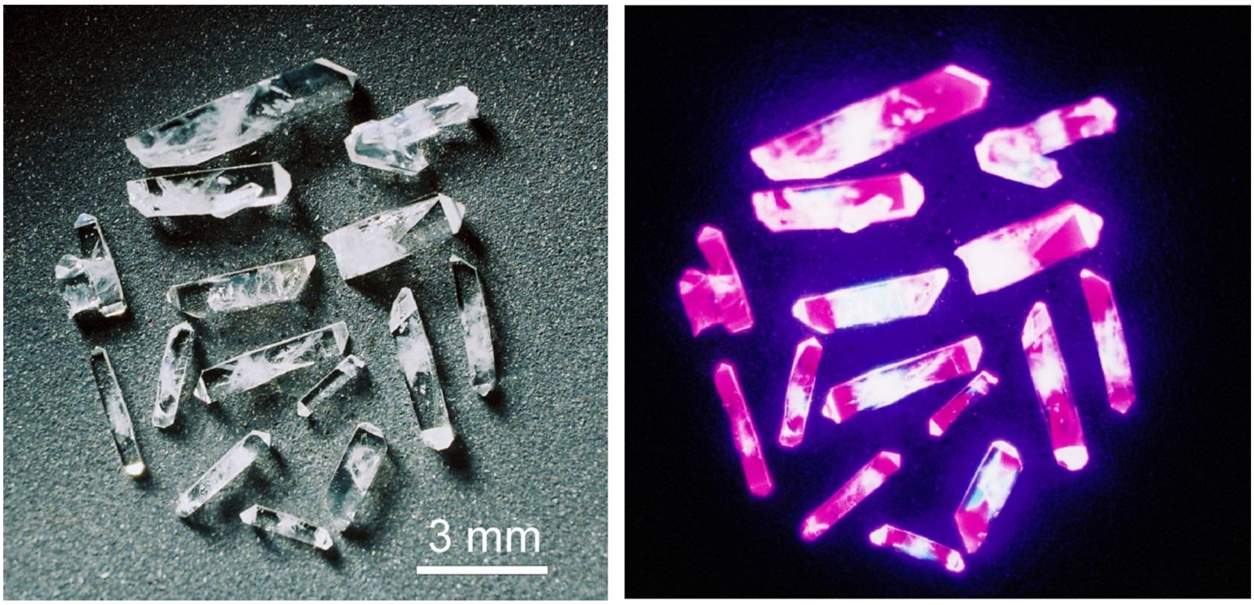
Table 3 The main crystals, in which self-glowing was observed

Crystal	Luminescence ion	Actinide content (in wt.%)	Relative intensity of self-glowing
Zircon $(Zr, \ldots)SiO_4$	none	2.4-2.7 ^{238}Pu	weak
	Eu^{3+}	0.007 ^{238}Pu	weak
	In	0.02 ^{238}Pu	weak
	In, Tb^{3+}	0.01 ^{238}Pu	high
Xenotime $(Y, \ldots)PO_4$	Eu^{3+}	0.002 ^{238}Pu	weak
	Eu^{3+} (optimal content from CL study)	0.1 ^{238}Pu	high
Monazite $(Eu, \ldots)PO_4$	Eu^{3+}	4.9 ^{238}Pu	very weak
		0.04 ^{241}Am	high
ZrO_2	Eu + Tb	0.1 ^{238}Pu	high

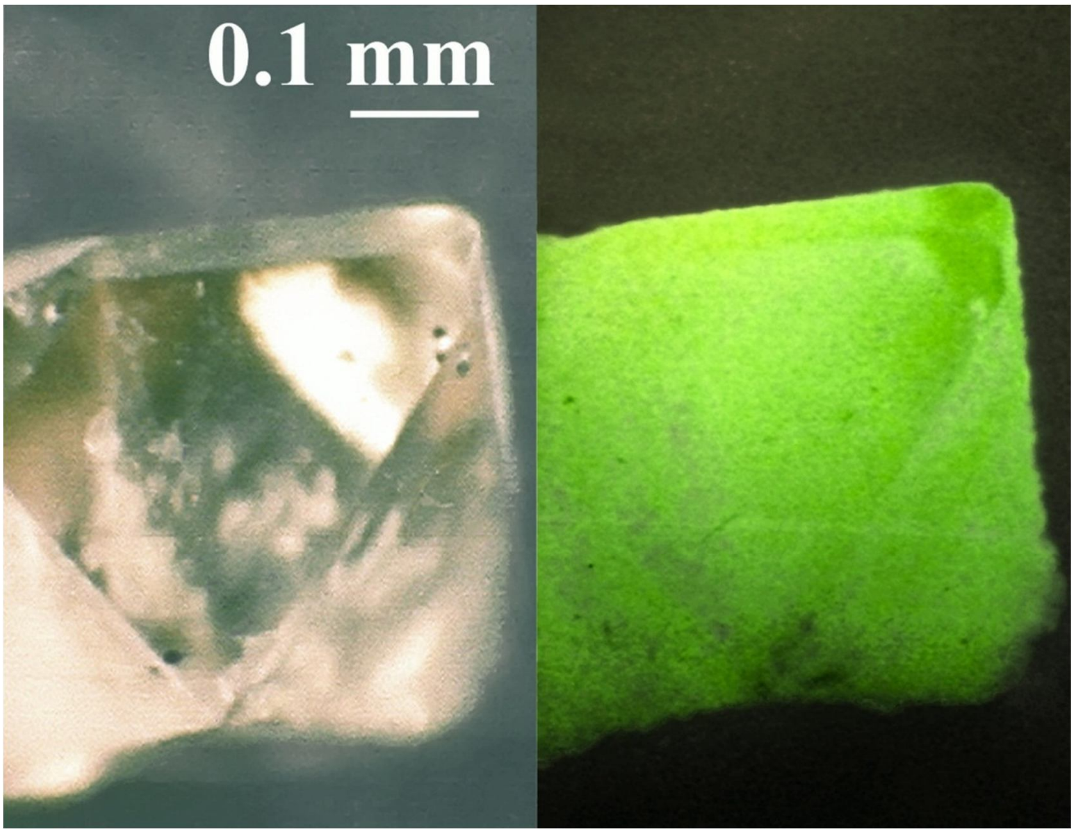
The following pictures (11-14) show the topographies of the most bright self-glowing crystals. Left – image of crystals was obtaind in a day light; right – self-glowing of crystals in dark. Fig. 11 shows the photographs of zircon crystals not activated by rare-earth ions. In this case, the levels associated with intrinsic defects in zircon emit.



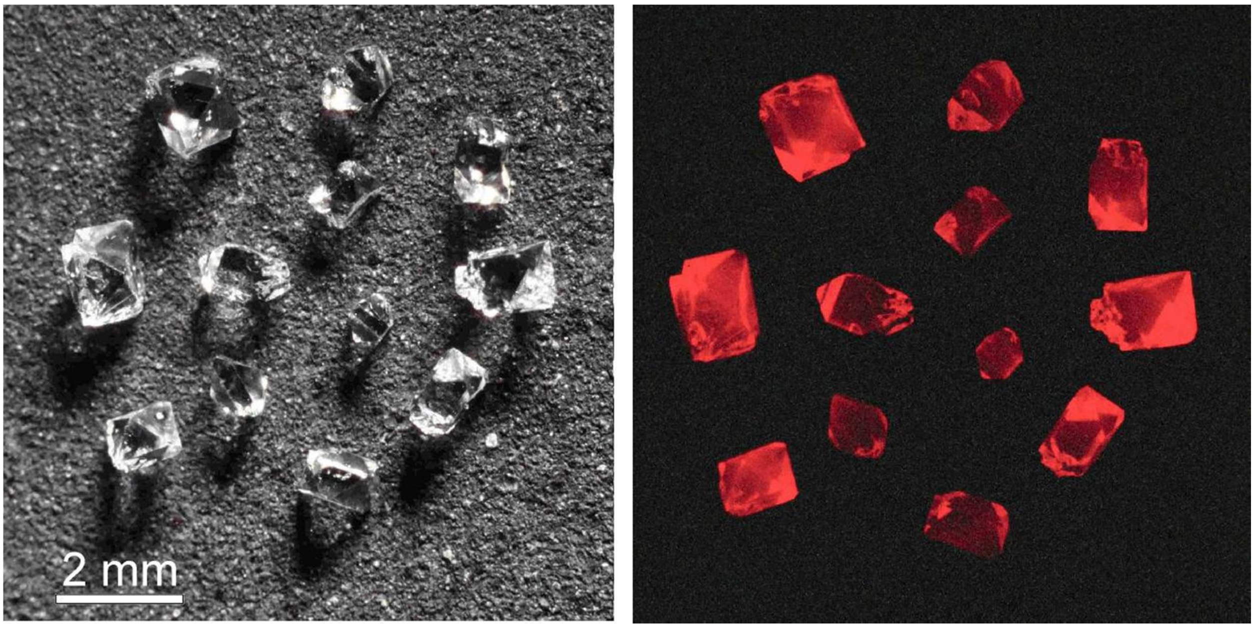
. Fig. 11 The photographs of zircon crystals ($ZrSiO_4$:Pu) not activated by rare-earth ions.



. Fig. 12 The photographs of zircon crystals ($ZrSiO_4$:Pu, In) not activated by rare-earth ions



. Fig. 13The photographs of zircon crystals ($ZrSiO_4$:Pu, Tb^{3+})



. Fig. 14 The photographs of xenotim crystals (YPO_4:Pu, Eu^{3+})

Spectra of self-glowing of crystals (Fig.15) were obtained at a special stand. Unfortunately, due to the small amount of material, we were not able to obtain a good spectral resolution.

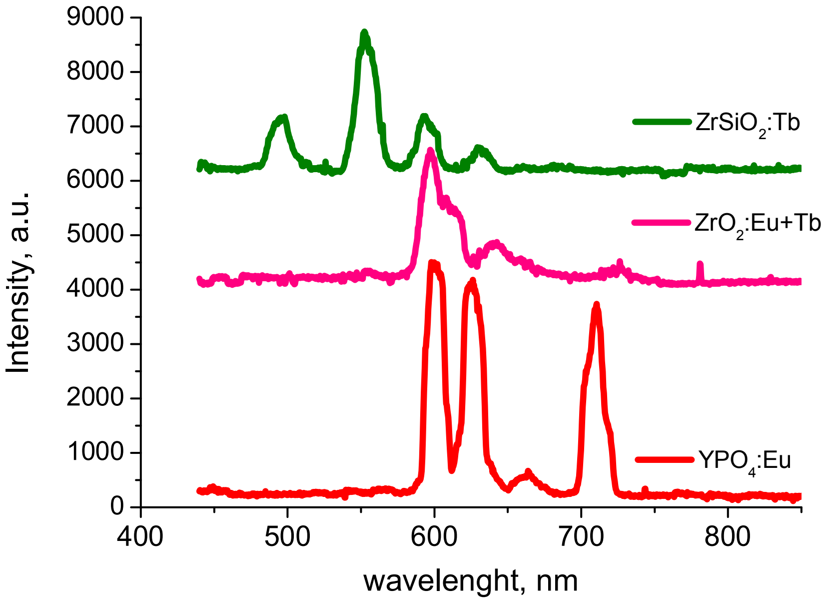


Fig.15 Spectra of self-glowing of crystals

Investigation of composition, homogeneities and cathodoluminescent properties of self-glowing crystals

The composition of crystals and ceramics, their homogeneity, were studied by microprobe analysis and local cathodoluminescence.

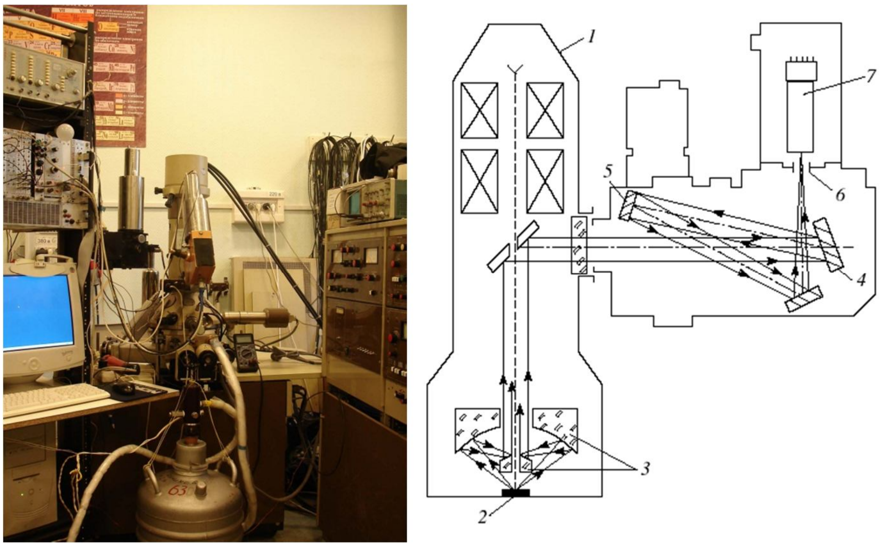


Fig.16 Picture of cathodoluminescent station and its optical scheme. 1- Column of microanalyzer, 2 – Sample, 3 -. Optical objective, 4 - Diffraction grate, 5- Concave mirror, 6 – Slit, 7 - Detector

This cathodoluminescence system makes it possible to obtain cathodoluminescent images of a sample in a defocused electron beam to estimate its homogeneity. By focusing the electron beam, it is possible to detect the emission spectra of the cathodoluminescence of a microvolume and to study the element composition of the same microvolume by the method of electron probe microanalysis. Self-glowing crystals and ceramics were investigated by these local methods.

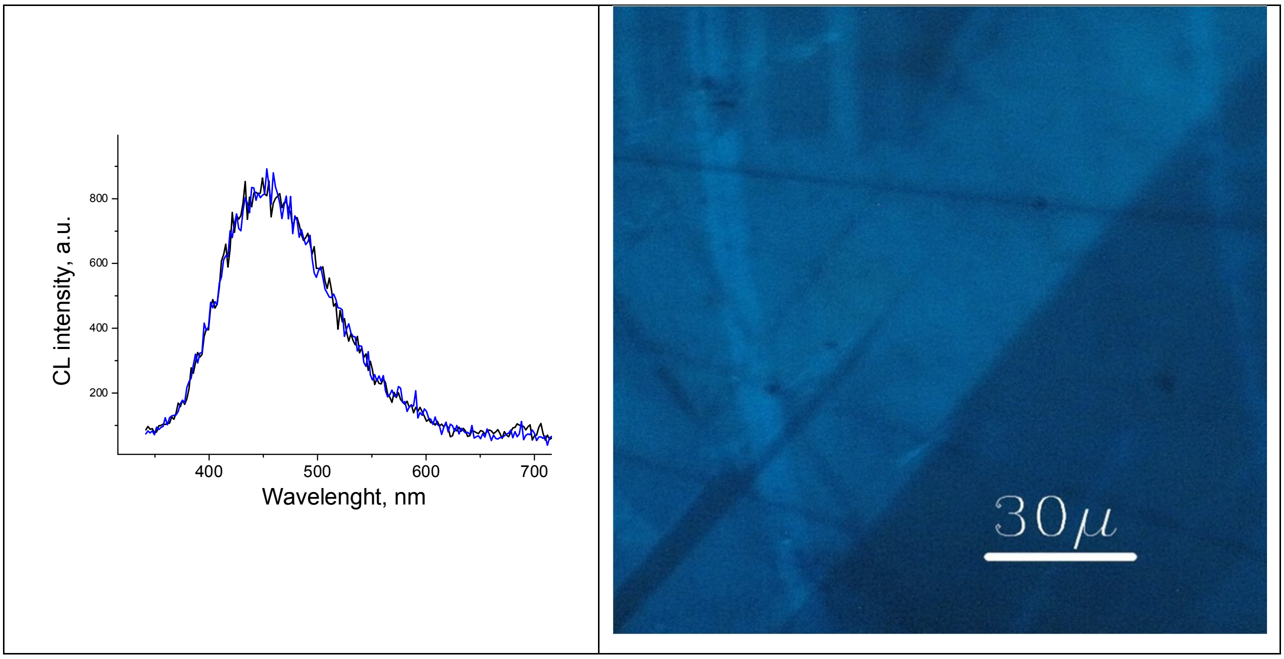


Fig. 17 Cathodoluminescence spectrum and cathodoluminescence image of of zircon crystals ($ZrSiO_4$:Pu) not activated by rare-earth ions

Fig. 17 shows the cathodoluminescence image of a zircon crystal and its cathodoluminescence spectrum. In this case, the radiation was additionally excited upon irradiation of the crystal by a focused beam of electrons with an energy of 10 keV. The cathodoluminescent image shows that the distribution of defects in the crystal is inhomogeneous. At this stage of the work, we did not investigate the nature of these inhomogeneities.

Similar studies were carried out for other crystals and ceramics. Fig. 18 shows a cathodoluminescent image of zircon activated by terbium. The cathodoluminescence spectra demonstrate the emission of terbium ions and a broad band with a radiation maximum of 400 nm. The inhomogeneity of the crystal is also associated with the brightness of this band, which is also responsible for the intrinsic defects in the crystal.

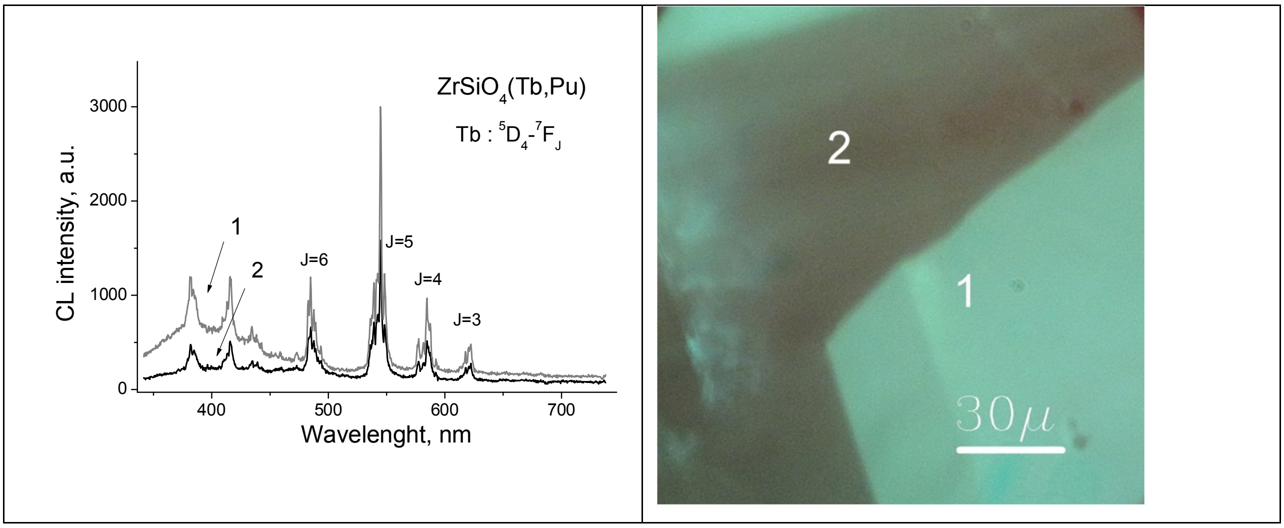


Fig. 18 *Cathodoluminescence spectrum and cathodoluminescence image of of zircon crystals ($ZrSiO_4$:Pu, Tb^{3+}).*

The xenotime crystal is characterized by better homogeneity. The contrast of the cathodoluminescence image is most likely related to the surface relief. The cathodoluminescence spectra are analogous to the emission spectra of the europium ion in yttrium phosphate (Fig.19)

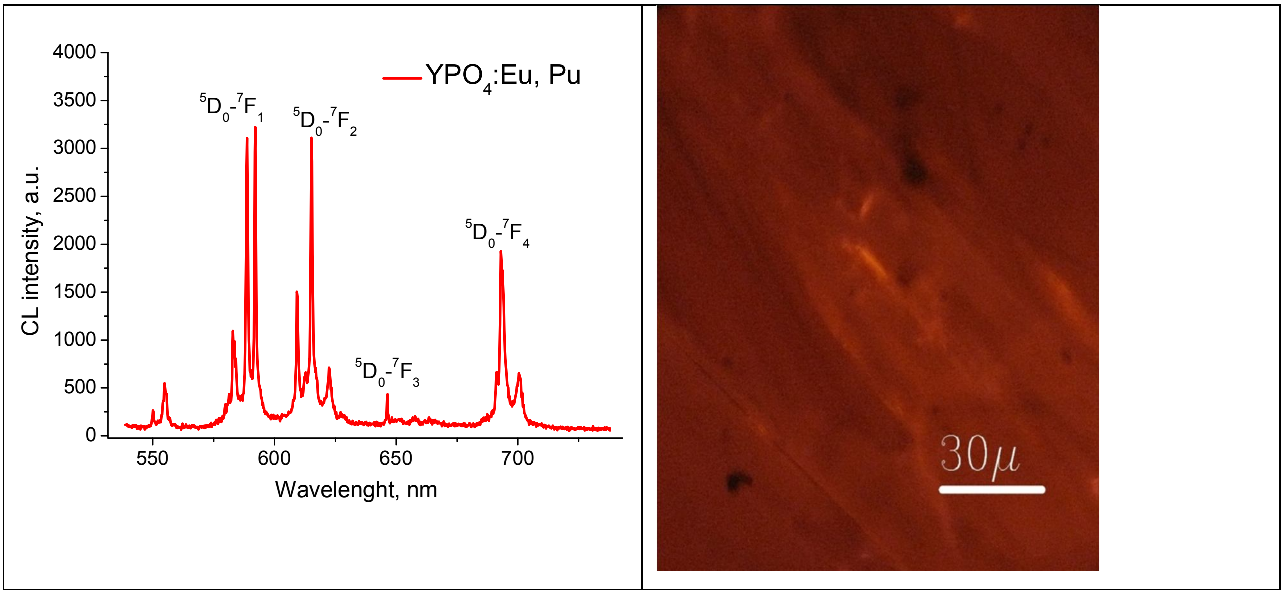


Fig. 19 *Cathodoluminescence spectrum and cathodoluminescence image of xenotime crystals ($YPiO_4$:Pu, Eu^{3+}).*

Fig 20 shows the results of a study of ceramics based on zirconium oxide, activated by terbium and europium. The ceramics are fairly homogeneous.

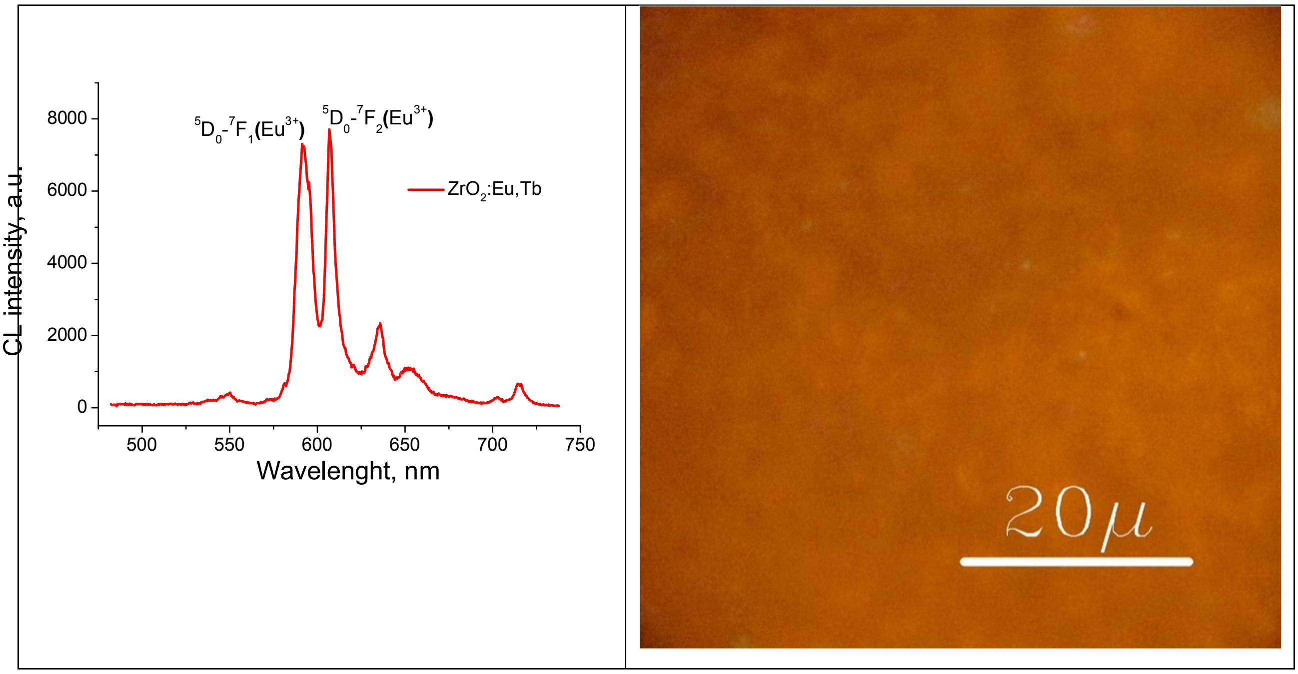


Fig. 20 *Cathodoluminescence spectrum and cathodoluminescence image of ZrO2 ceramic (ZrO_2:Pu, Eu^{3+},Tb^{3+}).*

For the most bright self-glowing xenotime crystal, a series of samples with different contents of plutonium was obtained. The optimal content of europium was determined on the basis of a concentration series not activated by plutonium. Based on these results, the most intensive luminescence show crystals with 1.7% content of Eu and 0.1% of Pu (Fig. 21).

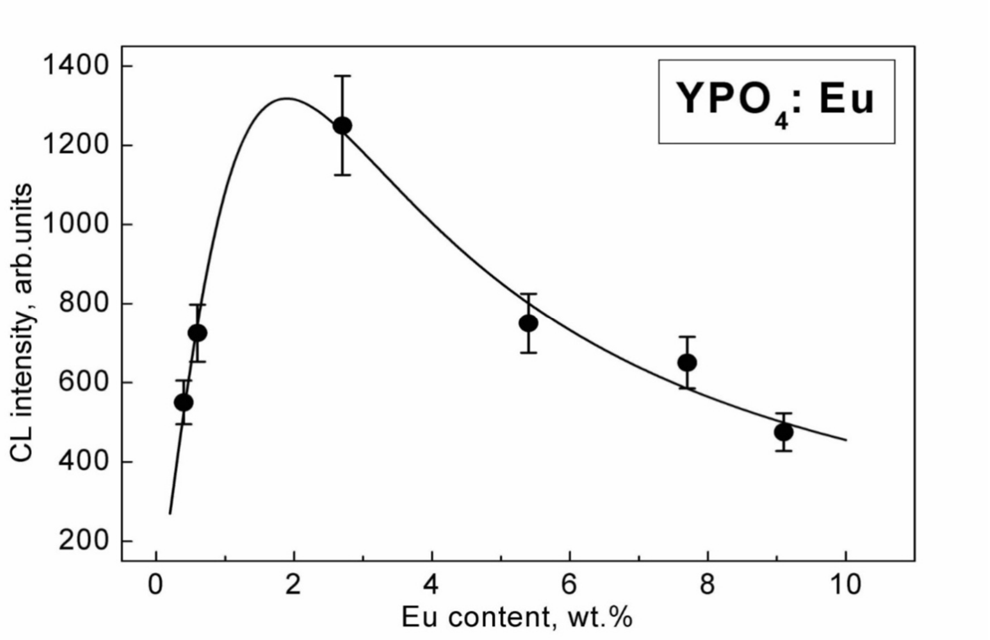


Fig. 21 Concentration dependence of Cathodoluminescence intensity of Eu^{3+} in YPO_4

For $YPO_4:Eu^{3+}$ crystal synthesized in 2006 with a volume of 0.02 cm^3 with a Pu-238 content of 0.1% by weight and a silicon detector, an electric power output of 0.1 μW was recorded. This confirms the prospects of this research area

Possible areas of application of self-glowing low-radioactive crystals with high chemical, mechanical and radiation resistance are: main elements of a battery in combination with a converter of optical energy into electric current; elements of an optoelectronic pair in robotics; etc. The long life and reliability of the proposed sources of optical radiation make it possible to use these elements in conditions where regular monitoring of the serviceability of the source is impossible (conditions of the Far North, space, expeditions, etc.)

Conclusions. The first self-glowing crystals and ceramic based on $ZrSiO_4$, YPO_4, ZrO were synthesized. On YPO_4: Eu^{3+}, ^{238}Pu crystal an electric power output of 0.1 μW was recorded. To increase the self-glowing of crystals, it is necessary to continue the search of radiation-resistant matrices with better scintillation properties (ex. garnet or perovskite based on Al-Y-O)