Development and synthesis of orthophosphate single crystals of YPO$_4$ and LuPO$_4$ activated with Er$^{3+}$

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Abstract. Crystals of xenotime-structured phosphates doped with erbium had been grown from molybdate flux at a temperature 1220 °C followed by slow cooling. The crystals synthesized had been studied using X-ray diffraction and electron probe microanalysis in combination with optical microscopy and luminescence studies.

1. Introduction

Microprocessors and memory modules require low-current power supplies to ensure that data is retained in device memory when the main power supply fails. One of the solutions to solve such a problem is a development of a low-power power source based on the energy of radioactive decay. An admixture of alpha-emitting radionuclides in some solids (for example, crystals and ceramics) can cause scintillation of these matrices (or so-called «self-glowing»). This intense glow can be converted into an electrical current. However, for industrial applications, an important requirement for such scintillators is the combination of intense luminescence and the lowest possible content of radionuclides in their matrix. Besides, the working time of such sources of electric current depends on radionuclide half-life and it can be lasted from tens to thousands of years.

The core of such a power source should be based on a chemically and mechanically durable and radiation-resistant matrix, which is characterized with good scintillation properties but reasonable small content of radioisotope. The radioactive core should be combined with optical energy-to-electric current converter. Some promising materials suitable for this purpose are rare earth orthophosphates activated with trivalent rare earth ions, which are responsible for luminescence centers.

Xenotime-structured orthophosphate with simplified formula MePO$_4$ (Me – Y and lanthanides of the Tb-Lu series) is a well-known crystalline material. Natural species of this mineral usually contain significant admixtures of radioactive actinides (U and Th). A study of natural xenotime demonstrates damage of its crystalline structure under self-irradiation over a very long time (millions of years) however it is possible to conclude that this mineral is relatively resistant to natural radiation. In addition, yttrium and lutetium orthophosphates activated with trivalent REE ions exhibit bright luminescence in the visible range of the spectrum.

The target of this paper was to clarify xenotime as promising matrix for development of low-power electric sources to be used over a long time (hundreds and thousands of years).

For this, it’s necessary to investigate the optimal synthesis conditions and the proper content of the luminescence. Current work was dedicated to the study of Lu- and Y-xenotime doped with Er$^{3+}$. Single crystals with different content of Er$^{3+}$ had been synthesized by flux method and studied using X-ray
diffraction and electron probe microanalysis in combination with optical microscopy and luminescence spectroscopy.

2. Experimental

All crystals had been grown in the flux melt of the following initial composition:

90 wt. % MoO₃ + 10 wt. % (3.5 wt. % Li₂MoO₄ + 6.5 wt. % Li₂CO₃).

Li₂MoO₄ was obtained by the reaction in Pt-bowl at temperature 800 °C for 20 minutes:

\[ \text{MoO}_3 + \text{Li}_2\text{CO}_3 \rightarrow \text{Li}_2\text{MoO}_4 + \text{CO}_2 \uparrow. \]

Li-molybdate obtained was mixed with MoO₃, ground in agate mortar and heated at 810 °C for 30 minutes. Then it was thoroughly ground again in agate mortar and Li₂CO₃ was added.

The compositions of starting blends before synthesis were:

a) Y-xenotime: 90 wt. % flux, 3 wt. % (YPO₄ + ErPO₄), content of ErPO₄ was calculated as 3 wt. % of YPO₄.
b) Lu-xenotime: 90 wt % flux, 3 wt % (LuPO₄ + ErPO₄), content of ErPO₄ was calculated as 3 wt. % of LuPO₄.

Precursors for xenotime synthesis were placed into platinum crucibles of 15 ml volume. The crucibles were installed into quartz ampoule and heated in a vertical tube-type furnace. The temperature was controlled by a VARTA TP 403. The temperature achieved 1220 °C for 4 h, and then it was fixed for 3 h and slowly decreased to 850 °C at a rate of 6 °C/h. Finally, furnace was turned off and cooled to room temperature without control. The crystals obtained were extracted from the rest of the flux by washing crucibles in 25 % ammonia hydroxide aqueous solution during 24 h. These synthesis conditions made it possible to obtain crystals of a much larger size than under other conditions.

Figure 1 shows 3D images of xenotime crystals obtained.

![Figure 1](image1.png)

3. Results and discussion

All crystals had been studied using the cathodoluminescence method (CL), electron-probe microanalysis (EPMA) and 3D optical microscope. The content of Er was determined using EPMA (Table 1).

Xenotime crystals shaped as bipyramids in combination with prism faces were transparent and characterized with yellow-brown colour. They demonstrated intensive yellow-green UV in the dark.
Crystal chemical composition is relatively uniform (Table 1) and admixture of Er incorporated into their crystalline structures corresponds to calculated content of Er loaded into precursor (approximately 3 wt. %).

Table 1. Chemical composition of xenotime crystals (from EMPA in at. %).

| Crystal No. | Er  | Y   | Lu | P  | O  |
|-------------|-----|-----|----|----|----|
| 1           | 0.60| 14.80| -  | 17.6| 67.0|
| 2           | 0.60| 14.90| -  | 17.5| 67.0|
| 3           | 0.62| 14.78| -  | 17.6| 67.0|
| average     | 0.61| 14.80| -  | 17.5| 67.0|
| 4           | 0.80| -    | 15.9| 16.7| 66.7|
| 5           | 0.71| -    | 16.2| 16.5| 66.7|
| centre      | 0.73| -    | 16.2| 16.5| 66.6|
| 6           | 0.84| -    | 16.1| 16.5| 66.6|
| edge        | 0.84| -    | 16.1| 16.5| 66.6|
| average     | 0.78| -    | 16.2| 16.5| 66.6|
| average     | 0.77| -    | 16.1| 16.5| 66.6|

Some differences in content of Er in crystal matrix had been observed (Crystal № 6, Table 1) that is typical for crystal growth from the flux: higher concentration is favorite for the crystal edge zones.

Figure 2 shows clearly crystal zoning under electron beam. We assume that these zoning is associated with intrinsic defects of the crystals. The use of alpha-emitting $^{238}$Pu in combination with non-radioactive Er$^{3+}$ incorporated into xenotime structure will allow in the future obtaining crystals with strong radioluminescence.

Figure 2. Photomicrographs of the samples under an electron beam: a) LuPO$_4$ + ErPO$_4$ b) YPO$_4$ + ErPO$_4$.

It’s known that intense luminescence is observed in area 520-560 nm (transitions $^2$H$_{11/2}$ $\rightarrow$ $^4$I$_{15/2}$ and $^4$S$_{3/2}$ $\rightarrow$ $^4$I$_{15/2}$). In addition, two groups of bands are observed in the emission spectrum of Er$^{3+}$ in range 405-420 nm (transitions $^4$H$_{9/2}$ $\rightarrow$ $^4$I$_{15/2}$) and 650-670 nm (transitions $^4$F$_{9/2}$ $\rightarrow$ $^4$I$_{15/2}$). All these transitions are clearly visible in the presented spectrum (Figure 3). The CL spectra of Y-xenotime and Lu-xenotime are similar.
4. Conclusions
The following conclusions had been made:

1. Xenotime single crystals up to 3 mm in size have been successfully synthesized by the flux method at temperature 1220 °C for 4 h followed by slow cooling to 850 °C.
2. Cathodoluminescence and EPMA analyses confirmed relatively uniform chemical composition of xenotime crystal matrices.
3. A light green glow in the dark was recorded under the influence of UV excitation. Lu-xenotime and Y-xenotime demonstrate comparable CL intensity.

Experiments on the synthesis of self-glowing crystals doped with $^{238}$Pu and non-radioactive Er$^{3+}$ is the subject of our future research.

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