Structure and luminescence properties of SiO₂ sol-gel glass doped with Eu³⁺

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Abstract. In this work, SiO₂ sol-gel glass doped with Eu³⁺ was investigated its structural and luminescence properties. It was shown that a area containing crystallites of cristobalite with a size of about 45 nm is formed on the glass surface. The Eu³⁺ spectrum in surface area was obtained. It was demonstrated that the main part of the sample is X-ray amorphous; however, the Eu³⁺ spectrum in it demonstrates the presence of short-range order.

1. Introduction
Rare-earth ion (RE) doped oxide dielectric materials are promising radiation-resistant scintillators [1]. In this regard, one of the most relevant areas is the development of methods for the synthesis of optically homogeneous glass-crystalline materials based on rare-earth doped oxides. Such hybrid materials combine the properties of glasses and crystals. Their synthesis and subsequent processing is similar to the synthesis and processing of one of glass. Silicon oxide matrices have high chemical and thermal stability, which is important when interacting with high-energy ionizing radiation. Therefore, a silica sol-gel matrix impregnated with salts of Y, Eu, and Nb was chosen as the matrix for the low-temperature synthesis of oxide glass ceramics doped with RE. It was assumed that YNbO₄ crystallizes in sol-gel glass matrix. This matrix is characterized by a relatively low synthesis temperature (up to 1200 °C). It was assumed that upon sintering and subsequent slow cooling, crystallites doped with europium ion are formed in a sol-gel silicon matrix.

The objective of this work is to study the elemental composition, structure and cathodoluminescence of the sol-gel glass doped with Eu³⁺.

2. Samples synthesis
Silica sol-gel glass was chosen as a matrix for low-temperature synthesis of oxide glass ceramics with yttrium niobate inclusions doped with Eu³⁺. Compounds of yttrium, niobium and europium were added to the matrix in such a ratio that the following molar ratios were satisfied in the synthesized material: Eu₂O₃: Y₂O₃ ≤ 0.2 and (Eu₂O₃ + Y₂O₃): Nb₂O₅ ~ 1.

The first ratio follows from the optimal concentration of activator - Eu in yttrium niobate [2]. The second ratio is chosen so that YNbO₄ is formed in the matrix [3]. Reagents with a purity of at least 99% were used as starting components for glass melting.

Glass ceramics based on silica sol-gel glass were synthesized by preparing a xerogel based on SiO₂, which was impregnated in a solution of Eu, Y, and Nb salts and heat treated in a muffle furnace for 4 hours at 1200 °C in air. After completion of the heat treatment, the samples were gradually cooled to room temperature over 4 hours.
After synthesis, the samples were ground and polished. Investigated samples were coated with a thin carbon film using a universal vacuum station JEE-4C (JEOL, Japan).

### 3. Experimental methods

To determine the elemental composition of the samples, the electron probe microanalysis (EPMA) method was used. Luminescent properties were studied by local cathodoluminescence (CL) methods. The presence of the crystalline phase in the samples was determined by X-ray diffraction phase analysis (XRD) and by spectroscopic characteristics of Eu$^{3+}$ in the material. The CL and EPMA studies were performed on electron probe microanalyzer (Cameca, France) combined with an CL station. XRD analysis was performed on a D2 Phaser X-ray diffractometer (Bruker, Germany).

The local CL method allows to obtain CL spectra with a lateral resolution of 1 micron, which allows one to study the homogeneity of the luminescent properties of the samples. The method also allows one to obtain CL images of samples in a defocused electron beam. This makes it possible to evaluate the CL homogeneity and the size of inclusions from ~ 1 to ~ 200 μm. CL spectra were obtained at an electron beam diameter of 4 microns, an electron beam energy 20 keV, and an absorbed current of 20 nA. CL images were obtained with an electron beam diameter of 200 microns, an electron beam energy 20 keV, and an absorbed current of 100 nA.

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The locality of the EPMA and CL methods depends on the diameter of the electron beam, which varies in the range from 1 to 200 microns. The composition of the samples was measured at an electron beam energy 20 keV and an absorbed current of 15 nA, an electron beam diameter of 4 microns. EuPO$_4$, SiO$_2$, Nb, and Y$_3$Al$_5$O$_{12}$ were used as standards. The oxygen content was calculated by stoichiometry. At least five analyzes of the composition of the matrix in random areas were performed for each sample. This made it possible to obtain an averaged elemental composition and evaluate the uniformity of the distribution of elements in the samples.

Since CL and EPMA studies are performed on the same instrument, it is possible to analyze the composition and record CL spectra in the same region of the sample. This allows us to unambiguously interpret the contrast of the CL image and the heterogeneity of the sample in composition.

One of the approaches to studying the structural properties of materials is the use of luminescent centers as a luminescent probe. Typically, with this approach, the material is activated by rare earth ions (RE), for example, Eu$^{3+}$. This approach allows us to study the structure of the alloyed material, including the short-range order of amorphous materials [4,5,6]. The luminescence spectrum of europium is determined by transitions inside the f shell and is a set of narrow bands that are associated with transitions between the $^5D_0$ and $^7F_J$ ion levels. The intensity of the $^5D_0$ - $^7F_2$ electric dipole transition is extremely sensitive to the local symmetry of the ion, in contrast to the most intense $^5D_0$ - $^7F_2$ magnetic dipole transition. The band position, the ratio of the band intensities, and the number of components in the europium spectra depend on the local symmetry of the ion in the material. This allows us to draw conclusions about a change in the local symmetry of the ion in the material with a change in the ratio of intensities and the number of splitting of Eu$^{3+}$ bands in the spectrum.

### 4. Results and discussion

#### 4.1. EPMA studies

Optical microscopy showed that the grown sample consists of two parts that differ in composition and structure. The surface area is 200 microns thick. The main part of the sample has a size a few millimeters. Table 1 presents the measured composition of both the surface area and the main part of the Si-Sol sample.
Measurements show that small fractions of other oxides enter the sol-gel silica matrix. Niobium content is at the limit of detection. A significantly larger number of rare-earth elements were found in the surface area than in the main part of the sample. This may be due to the shrinkage of the sol during sintering in the furnace.

4.2. XRD analysis
The results of XRD analysis of Si-Sol samples are presented in Figure 1. The narrow diffraction maxima in Figure 1 refer to polycrystalline cristobalite. The content of cristobalite in the sample volume is (3.6 ± 0.2)%(). The crystallite size is (45 ± 5) nm. A wide "galo" in the range of 2theta angles of 17-25 degrees indicates the presence of X-ray amorphous SiO₂ having a structural motive of cristobalite. Thus, the sample is an X-ray amorphous material with cristobalite crystallites.

| Table 1. Sample compositions Si-Sol |
|-------------------------------------|
| components                          | SiO₂   | Nb₂O₅ | Y₂O₃   | Eu₂O₃ |
| surface area (mol%)                 | 99.8±0.1 | 0.005±0.005 | 0.08±0.03 | 0.03±0.01 |
| main part of the sample (mol%)      | 99.7±0.1 | 0.006±0.005 | 0.18±0.04 | 0.13±0.04 |

4.3. CL studies
To assess the homogeneity of the samples, CL images were obtained in a defocused electron beam (Figure 2 right inset). In the CL image of the Si-Sol sample, luminescence contrast is observed only near the surface of the sample (Figure 2 (right inset)).

The CL shape of the Eu³⁺ spectrum varies significantly depending on the local position of the rare-earth ion in the material. It is known that in amorphous oxide materials based on SiO₂ and B₂O₃, rare-earth trivalent ions including Eu³⁺ occupy local positions close to C₂ᵥ [7,8]. In this case, the luminescence spectrum of Eu³⁺ in such materials has a characteristic shape, which was studied in detail in [7, 8, 9], including in silicon sol – gel glasses [9]. The significant difference can be explained by the presence of Y and Nb coactivators [10], as well as possible clustering processes in glass [11]. It should be noted that similar spectra are found in works with site-selective spectroscopy [10,12].

The CL shape of the Eu³⁺ spectrum for the surface region (Figure 2 (a)) significantly differs from the spectrum of the rest of the sample Figure 2 (b)). Given the XRD data, it can be assumed that the surface region consists of cristobalite polycrystals. Thus, in the surface area, the clustering processes were significantly different. It can be assumed that these processes significantly affected the structure of the local environment of Eu. To establish in which specific matrix Eu is located in the surface region, additional studies are needed.

Figure 1. XRD analysis of sample Si-Sol.
5. Summary
It was shown that only hundredths of the oxides Y, Eu, and Nb dissolve in the sol–gel silicon matrix. This is not enough for the crystallization of rare earth niobate in an amount sufficient for registration. It was found that a surface area with a thickness of 200 μm was formed in the sample. This area is significantly different in composition and luminescent properties from the main part of the sample. The combination of methods used allows us to state that polycrystalline cristobalite is formed in the surface area under synthesis conditions. Most of the sample consists of an X-ray amorphous substance, which is different from an amorphous material.

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Figure 2. CL image of the surface area of the sample (right inset (a)) and CL spectra of the surface area (a) and CL image of the rest of the Si-Sol sample (right inset (b)) and CL spectra of the rest of the Si-Sol sample (b). The left inset shows an enlarged image of the spectra in the 580-640 nm region. In inset (c) is a diagram of the energy levels of Eu$^{3+}$.
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