

PHOTOLUMINESCENCE OF Eu AND Ce ACTIVATED  
OXYFLUORIDE GLASS AND GLASS CERAMICS

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The photoluminescence of  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-LiO}_2\text{-LaF}_3$  oxyfluoride glass and glass ceramic samples doped with  $\text{Ce}^{3+}$ ,  $\text{Eu}^{2+}$  and  $\text{Ce}^{3+} / \text{Eu}^{2+}$  is investigated, and the spectra and fluorescence intensities are compared. The luminescence of samples activated by Eu ions is found to be more intensive than of the samples doped with Ce or Ce/Eu. The luminescence of glass ceramics is higher than that of the corresponding glass, which indicates that a proportion of the activator ions are embedded in the fluoride crystallites.

**Key words:** *photoluminescence, oxyfluoride glass, glass ceramics,  $\text{Ce}^{3+}$ ,  $\text{Eu}^{2+}$  ions, luminescence intensities, spectra.*

## 1. INTRODUCTION

Oxyfluorides are interesting compounds because it is possible to synthesise a wide variety of materials by choosing different oxides, fluorides as well as their compositions. These materials have many applications – as infrared sensors to visualise the IR light using the up-conversion process [1], scintillators [2] and visible light phosphors. It is possible to compare various properties of oxyfluorides using not only different components but also glasses and glass ceramics with the same base components or varying the rare-earth activators. Spectral properties of an activator in the material depend on the structure forming atoms. The light emitting diodes (LED) are more energy efficient as compared with conventional light bulbs. Phosphors used for LED lamps should not only have high fluorescent emission intensity, but also should emit wide enough spectra of visible light. The  $\text{Ce}^{3+}$  and  $\text{Eu}^{2+}$  ions are usually chosen as activators for the visible light phosphors owing to the intensity and wide band of the emitted luminescence spectra. Active research aimed at finding new visible light phosphors is now in progress [3, 4].

In our work, the luminescence of Eu and Ce ions as well as their emitted spectra in oxyfluoride glass and glass-ceramics is discussed, and the luminescence intensities are compared with those of commercial LED phosphors.

## 2. SAMPLES AND LUMINESCENCE MEASUREMENTS

First, the respective proportions of oxide and fluoride powders were chosen (Table 1) and thoroughly mixed to provide the homogeneity of sample composition. The mixture was then heated for 1h at the temperature of 800 °C, which

was followed by melting the sample at 1400 °C for an hour. The liquid sample was poured on the metal surface and rapidly cooled to achieve transparency of the oxyfluoride glass. To produce glass ceramics, the glass sample obtained was heated at the appropriate temperature (usually in the range 700–800 °C depending on the resultant luminescence intensity) for one hour and then slowly cooled down.

A deuterium lamp was used as the light source to compare the intensities of the integral luminescence through YΦC5 filter (transparent for the ultraviolet-violet light, 200–420 nm). Then the luminescence of the sample was recorded with an FEP 106 photomultiplier through ЖC11 filter (transparent for the light in the visible range from 400 nm).

Table 1

The composition and abbreviations of the studied samples

Phase	Composition	Abbreviation
<i>glass</i>	50SiO <sub>2</sub> –6Al <sub>2</sub> O <sub>3</sub> –24Li <sub>2</sub> O–20LaF <sub>3</sub> –2CeO <sub>2</sub>	<b>SALL:Ce</b>
<i>ceramics</i>	<b>SALL:Ce</b> heated 750°C	<b>SALL:Ce 750</b>
<i>ceramics</i>	45SiO <sub>2</sub> –7Y <sub>2</sub> O <sub>3</sub> –22Li <sub>2</sub> O–21LaF <sub>3</sub> –5CeO <sub>2</sub>	<b>SYLL:Ce</b>
<i>glass</i>	59SiO <sub>2</sub> –10Y <sub>2</sub> O <sub>3</sub> –24LaF <sub>3</sub> –7CeO <sub>2</sub>	<b>SYL:Ce</b>
<i>glass</i>	<b>SYL:Ce</b> heated 800°C	<b>SYL:Ce 800</b>
<i>glass</i>	50SiO <sub>2</sub> –6Al <sub>2</sub> O <sub>3</sub> –24Li <sub>2</sub> O–20LaF <sub>3</sub> –2EuF <sub>2</sub>	<b>SALL:Eu</b>
<i>ceramics</i>	<b>SALL:Eu</b> heated 750°C	<b>SALL:Eu 750</b>
<i>glass</i>	50SiO <sub>2</sub> –6Al <sub>2</sub> O <sub>3</sub> –24Li <sub>2</sub> O–20LaF <sub>3</sub> –CeO <sub>2</sub> –EuF <sub>2</sub>	<b>SALL:Ce,Eu</b>

The luminescence spectra of the sample were measured using a solid-state pulsed laser NT342/3UV with variable wavelength from 210 to 2300 nm, the pulse length 4ns, and the pulse frequency 10 Hz. The spectra were taken using 340 nm, 324 nm, and 315 nm laser beams. An *Andor* SR-303i-B monochromator was used to obtain the spectra; the measurements were taken at room temperature with an *Andor* D4-401-BV CCD camera. Additionally, in order to prevent the second order of laser diffraction spectrum, BC8 filter was used. The spectra were taken 20 times, and the intensities were summed.

### 3. RESULTS AND DISCUSSION

The integral fluorescence intensity of the investigated oxyfluoride samples is shown in Fig. 1.

As a rule, our Ce-doped samples have a luminescence in the blue-violet spectral range, the samples doped with Eu – in the orange spectral range, and those containing both Ce and Eu glow red.

The most intensive luminescence glow of all our glass and glass-ceramic samples is observed for the samples doped with Eu. The fluorescence intensity of these samples is comparable with that of commercial phosphors already used in white LEDs. As compared with the luminescence intensities of glass **SALL:Ce**

and glass-ceramic **SALL:Ce 750** samples (the latter obtained after heating of **SALL:Ce**), the luminescence intensity of the glass-ceramic sample is higher. The **SALL:Ce** samples glow brighter if  $\text{Al}_2\text{O}_3$  in their composition is replaced by  $\text{Y}_2\text{O}_3$ . However, it was observed that **SYLL:Ce** samples are inhomogeneous – there are areas where the intensity of luminescence is much weaker. It was visually detectable that the sample consists of both glass and glass-ceramic parts.

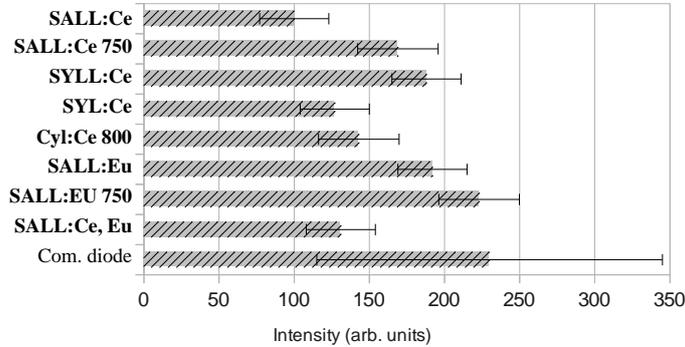


Fig. 1. Integrated fluorescence intensity of the samples.

Commercial diode – phosphor, which is separated from a commercially produced white LED.

To find the cause of **SYLL:Ce** inhomogeneities, the chemical composition of brightly glowing and poorly glowing areas were investigated using an X-ray fluorescence (XRF) spectrometer. With the available equipment it was impossible to detect light elements (Li, F and O) in the sample. No significant differences in the composition between the areas were detected; therefore, the sample could be considered homogeneous. The luminescence intensity of the sample being non-uniform is likely due to one of the elements that could not be detected. Probably, lithium which can form complex compounds such as  $\text{LiLaSiO}_4$  was responsible for that. To prove this hypothesis, a **SYL:Ce** sample containing no Li was prepared, and in this case no inhomogeneity or non-uniform luminescence was observed. Heating this sample did not lead to the formation of glass-ceramics, so the structure of the sample remained the same, with no nano-crystallites formed.

Luminescence spectra of the **SALL:Ce** glass excited with a 340 nm laser beam consist of a wide  $\text{Ce}^{3+}$  luminescence band, with its half-width being  $\sim 90$  nm and the maximum at 410 nm (Fig. 2). For the **SALL:Ce 750** glass-ceramics the luminescence band maximum is shifted to the long wavelengths by  $\sim 11$  nm. This shift could be explained by structural changes, e.g. the formation of crystallites in the glass matrix containing the activator ions. Similarly, for the **SYLL:Ce** sample the wide luminescence band shifts to the long-wave side when Al is replaced with Y.

As shown in Fig. 3, the spectra of **SALL:Eu** glass sample contain a wide  $\text{Eu}^{2+}$  luminescence band with the half-width of  $\sim 105$  nm and the maximum at 435 nm as well as narrow and intensive  $\text{Eu}^{3+}$  luminescence bands, the most intensive one has a half-width of 17 nm and a maximum of 615 nm. The narrow  $\text{Eu}^{3+}$  luminescence band is more intensive than the wide luminescence band of  $\text{Eu}^{2+}$ . Besides, if the sample is excited by a 324 nm instead of a 340 nm laser beam, the luminescence intensity of the narrow band increases more than one order of magnitude, while the luminescence intensity of the wide band does not change

significantly. The spectra of **SALL:Eu 750** glass-ceramic sample mainly have the  $\text{Eu}^{3+}$  luminescence lines, whereas the luminescence of  $\text{Eu}^{2+}$  is very weak. However, a shift of the fluorescence maximum to the long-wave side has been observed.

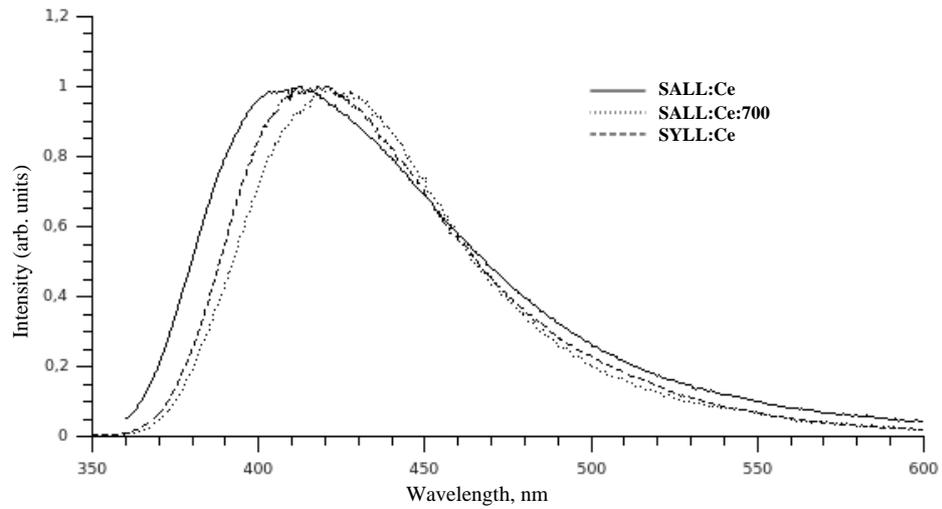


Fig. 2. Normalized luminescence spectra of the **SALL:Ce**, **SALL:Ce 750** and **SYLL:Ce** samples excited with a 340 nm laser beam.

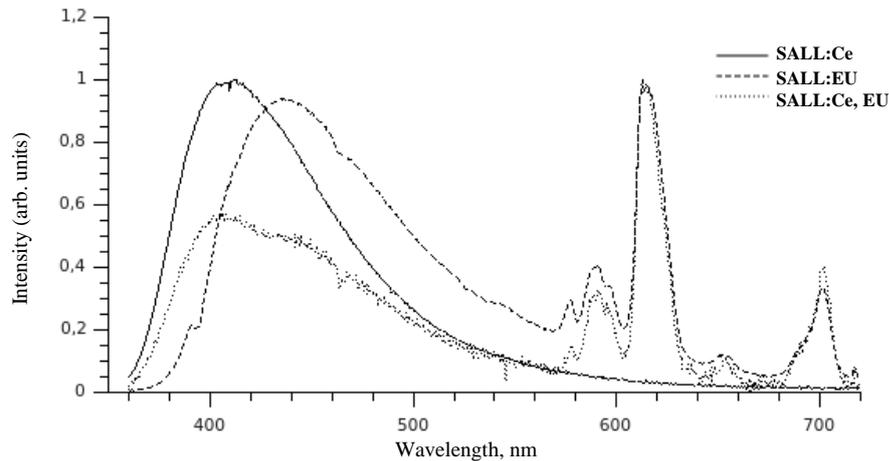


Fig. 3. Normalized luminescence spectra of the **SALL:Ce**, **SALL:Eu** and **SALL:Ce, Eu** samples excited with a 340 nm laser beam.

The spectra of the **SALL:Ce, Eu** glass contain a wide luminescence band of the  $\text{Ce}^{3+}$  and luminescence lines of the  $\text{Eu}^{3+}$  ions. However, the luminescence is considerably less intensive than in the samples containing only Ce or Eu ions when excited by the same laser wavelength.

#### 4. CONCLUSIONS

The most intensive luminescence of **SALL** glass and glass-ceramic samples has been obtained for the samples doped with Eu. A glass-ceramics sample was produced by heating the glass sample, and this treatment was found to increase the

luminescence intensity, since a proportion of the activator ions are embedded in the crystallites.

Although the luminescence intensity of the doped oxyfluoride sample is comparable with that of commercially used phosphors, the emitted spectral range of the investigated compositions is not optimal for the visible light phosphors used for white LEDs. The compositions of samples could be varied without losing the intensity of luminescence to shift the wide luminescence band to the long-wave side. An attempt to move luminescence bands through replacing  $\text{Al}_2\text{O}_3$  by  $\text{Y}_2\text{O}_3$  was unsuccessful owing to inhomogeneity of the sample obtained.

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#### Eu UN Ce JONU LUMINISCENCE OKSIFLUORĪDU STIKLOS UN STIKLA KERAMIKĀ

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#### Kopsavikums

Darbā pētīta ar  $\text{Ce}^{3+}$ ,  $\text{Eu}^{2+}$ , kā arī  $\text{Ce}^{3+}/\text{Eu}^{2+}$  aktivētu oksifluorīdu stiklu un stikla keramiku luminescence  $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--LiO}_2\text{--LaF}_3$  oksifluorīdu matricās, iegūtas paraugu luminescences intensitātes un spektri un tie salīdzināti. Ar Eu aktivētu paraugu luminescence ir intensīvāka par Ce aktivēto paraugu vai arī paraugu, kurā ir abi aktivatori, luminescenci. Ar Eu aktivētās stikla keramikas luminescence ir augstāka par atbilstošo stiklu luminescenci, kas liecina par aktivatoru iebūvēšanos fluorīdu kristalītos.

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