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Solid-state synthesis and luminescence study of Bi or Eu-doped $LiAlGeO_4$

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In this research pristine, Bi-doped and Eu-doped $LiAlGeO_4$ were prepared using a solid-state synthesis method. All samples were analysed by X-ray powder diffraction (XRD) and luminescence measurements. The highest Eu^{3+} concentration yielding monophasic samples in $LiAl_{1-x}GeO_4$: Eu_x was x = 0.08, while higher doping concentrations resulted in the formation of additional phases. The luminescence measurements revealed that the highest emission intensity was observed in the 16% Eu sample. Furthermore, the same sample demonstrated the highest quantum yield, while the longest luminescence decay was observed in the $LiAlGeO_4$:Eu 1% sample. The temperature-dependent luminescence measurements revealed that phosphor lost half of its efficiency at 323 K.

Keywords: luminescence, $LiAlGeO_4$, X-ray powder diffraction, solid-state synthesis

INTRODUCTION

Among all of the luminescent materials, rare-earth doped oxides have been in the center of attention for a very long time. Germanates, however, are not as popular as most other oxides. Most of the research done on germanate luminescence was on bismuth doped germanate based glasses. However, they have an outstanding advantage over the much researched silicate based glasses, because GeO_2 has more similar melting and boiling temperatures to those of Bi_2O_3 than SiO_2, which means that less Bi_2O_3 evaporates during synthesis. Germanates also have similar properties to those of silicates, since germanium is in the same element group as silicon [1]. There are a handful of different germanium based materials; however, there were barely any studies done on $LiYGeO_4$ and $LiAlGeO_4$. Luminescence studies on these materials include $LiYGeO_4$: Bi, $LiAlGeO_4$: Cr and $LiYGeO_4$: Eu. In this work, bismuth was chosen as an activator for $LiYGeO_4$ and $LiAlGeO_4$ so that their optical properties can be compared to one another as well as to those of $LiYGeO_4$ synthesised by J. Shi and the others [2]. Eu^{3+} was also chosen as an activator for $LiAlGeO_4$ to analyse optical properties of the material more thoroughly. Eu^{3+}-doped materials usually act as red phosphors and are suitable for various applications [3–6]. Therefore, $LiAlGeO_4$:Eu^{3+} samples were prepared by solid-state synthesis and luminescent properties were analysed. The obtained results are discussed in this paper.

EXPERIMENTAL

All samples were synthesised using a conventional solid-state synthesis method. Stoichiometric amounts of analytical grade starting materials (Li_2CO_3, GeO_2, Eu_2O_3, Al_2O_3, Y_2O_3 and Bi_2O_3) were mixed and ground in agate mortar. The obtained mixtures were transferred to a crucible and heated. $LiAlGeO_4$ was synthesised by heating samples the first time at 800°C for 6 h and afterwards at 1050°C for 6 h. The obtained products were reground in agate mortar and used for further analysis.

The purity of synthesised compounds was assessed by X-ray powder diffraction employing

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a MiniFlex II (Rigaku) diffractometer with Cu Kα radiation (λ = 1.5406 °A). Measurements were performed using a Bragg–Brentano geometry at a rate of 10 °/min. Excitation and emission spectra were recorded using an Edinburgh Instruments FLS980 spectrometer equipped with a 450 W Xe arc discharge lamp, a photomultiplier (Hamamatsu R928) and mirror optics for powder analysis. Excitation spectra were corrected with a reference detector.

RESULTS AND DISCUSSION

XRD analysis of $LiAlGeO_4$ samples

A series of $LiAlGeO_4$ samples was prepared and their structure and purity were recorded and evaluated using X-ray powder diffraction analysis. From Fig. 1 we can see that all samples except $LiAlGeO_4$:Eu 16% are monophasic and match the standard $LiAlGeO_4$ peaks (PDF#04-007-7636). The diffraction pattern of $LiAlGeO_4$:Eu 16% also mostly coincides with the standard; however, additional peaks at 31 and 34 degrees can be identified and the signal-to-noise ratio becomes much worse likely due to additional phases forming from excess europium.

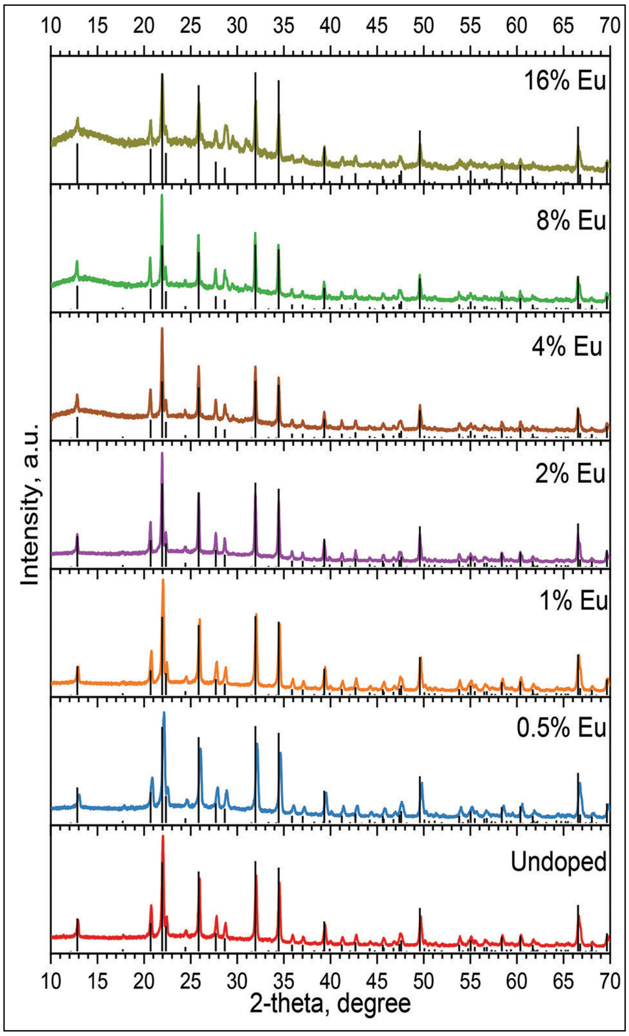

Fig. 1. XRD patterns of Eu-doped $LiAlGeO_4$ samples. Black bars represent standard diffraction peaks (PDF#04-007-7636)

Luminescence properties of the synthesised $LiAlGeO_4$:Eu powder

To determine optical properties of $LiAlGeO_4$:Eu samples, excitation and emission studies were performed, the results of which are shown in Fig. 2. As can be seen from the measurements presented below, the highest excitation and emission intensities were found to be in the $LiAlGeO_4$:Eu 16% sample.

The most intensive transition observed in the excitation (left) spectrum is $^5L_6 \leftarrow {}^7F_0$ (at 393 nm). Other excitation transitions with lower intensities are visible and marked in Fig. 2. A broad excitation peak around 250–300 nm is due to charge transfer (oxygen to europium). The emission spectra consist of four $^5D_0 \rightarrow {}^7F_{J=1,2,3,4}$ transitions. Emissions from $^5D_2$ and $^5D_1$ are quenched due to cross-relaxation. $^5D_0 \rightarrow {}^7F_1$ emission is observed due to magnetic dipole transitions and $^5D_0 \rightarrow {}^7F_{2,3,4}$ due to electric dipole transitions [7]. $^5D_0 \rightarrow {}^7F_3$ transition is forbidden thus of much weaker intensity. The strongest emission is at 702.5 nm ($^5D_0 \rightarrow {}^7F_4$ transition). Moreover, in the emission (Fig. 2, right) spectrum, the splitting of emission peaks is visible. The likely reason for these splittings is that the structure contains more than one crystallographic node that can be occupied by europium. Normally, the emission intensity should increase to a certain value and then decrease (due to concentration quenching), but in this case the mentioned decrease is not observed. During the preparation of the 32% Eu-doped sample, the desired phase could not be obtained, so we could not compare the emission.

From emission spectra CIE 1931 colour coordinates were calculated and are depicted in Fig. 3. We can see that the $LiAlGeO_4$:Eu samples are orange-red in colour and the emission colour coordinates vary only slightly with the Eu concentration in the compound. However, the colour coordinates shift slightly to the red side (to

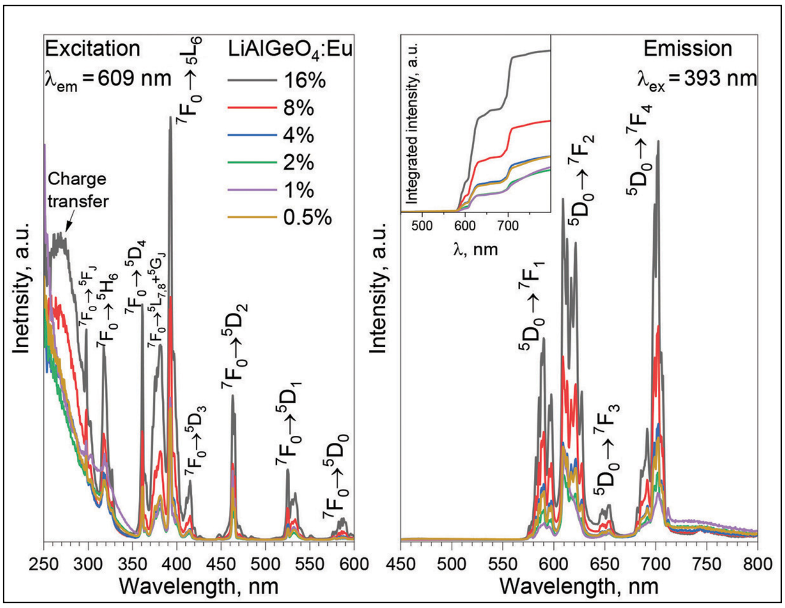

Fig. 2. On the left: excitation (λ_{em} = 609 nm) spectra of $LiAlGeO_4$:Eu samples; on the right: emission (λ_{ex} = 393 nm) spectra of $LiAlGeO_4$:Eu samples. Inset: integrated emission intensity spectra

the right) with the increase of Eu concentration in the sample.

Luminescence kinetics were evaluated as well. As can be seen from Fig. 4, the longest luminescence lifetime is observed in the $LiAlGeO_4$: Eu 1% sample. To determine these figures more accurately, the luminescence lifetimes were fitted using the bicomponent exponential decay function and their average values (combined from t_1 and t_2) were calculated.

The calculated $LiAlGeO_4$:Eu luminescence lifetime values show the same results as in Fig. 4 – the longest luminescence is observed in $LiAlGeO_4$: Eu 1%, and the shortest by $LiAlGeO_4$:Eu 4% sample.

Studies of the luminescence quantum yields of the samples were carried out, the results of which

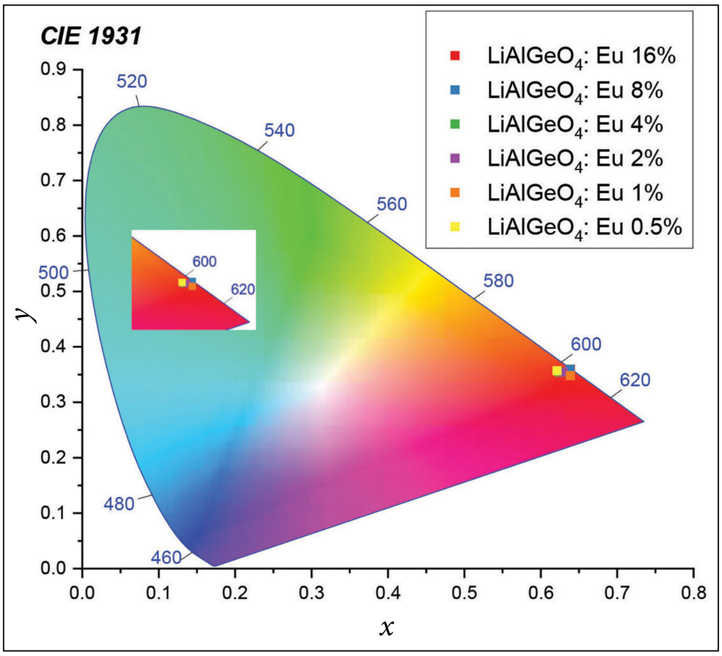

Fig. 3. CIE 1931 chromaticity diagram of the $LiAlGeO_4$:Eu samples with the magnified part of the diagram

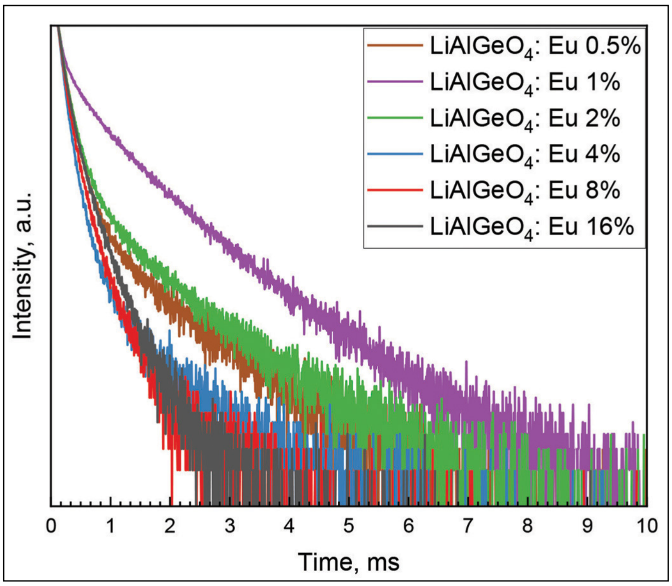

Fig. 4. Luminescence lifetimes of $LiAlGeO_4$:Eu samples

are presented in Table 2. Measurements of quantum yields were performed using the integrated sphere method.

Table 1. **Calculated LiAlGeO4:Eu luminescence lifetimes**

Eu concentration in the compound	Luminescence lifetime
0.5%	317.57 µs
1%	763.88 µs
2%	414.04 µs
4%	168.14 µs
8%	175.52 µs
16%	209.91 µs

Table 2. **Calculated LiAlGeO4:Eu quantum efficiencies**

Eu concentration in the compound	Quantum efficiency
0.5%	N/A
1%	5.60%
2%	4.62%
4%	3.56%
8%	4.50%
16%	6.31%

These measurements reveal which concentration of Eu the $LiAlGeO_4$:Eu compound has the highest rate of emitted electrons to absorbed photons, which basically shows the luminescence efficiency of the compound. $LiAlGeO_4$:Eu has the highest quantum efficiency at 16% and the lowest at 4%. The emission intensity of the sample doped with 0.5% Eu was too low, so the quantum yield could not be determined.

Investigation of the thermal quenching properties of the synthesised $LiAlGeO_4$:Eu 1% powder

For phosphors actual application, the temperature stability is also one of the most important parameters because it greatly affects the output of the light and CRI in LEDs [8]. Figure 5 shows the temperature-dependent PL spectra. The highest emission peak of $LiAlGeO_4$:Eu 1% sample is due to the $^5D_0 \rightarrow {}^7F_3$ transition at 610.5 nm. The highest luminescence excitation intensity is observed at room temperature, but the highest emission intensity at 77 K temperature. The likely reason for this is photoionization.

In Fig. 6 we can see that colour coordinates also vary very slightly with changes in temperature. As the temperature increases, the colour coordinates shift slightly to the left side of the spectrum.

As can be seen in Fig. 7, change in temperature also has an effect on the luminescence lifetime of a sample. As the temperature increases, luminescence lifetimes decrease.

Normalised total emission intensities were calculated ant plotted in Fig. 8. In order to calculate $TQ_{1/2}$ (temperature at which emission loses half of its intensity) the exponential decay fit was performed to the data. The obtained results revealed

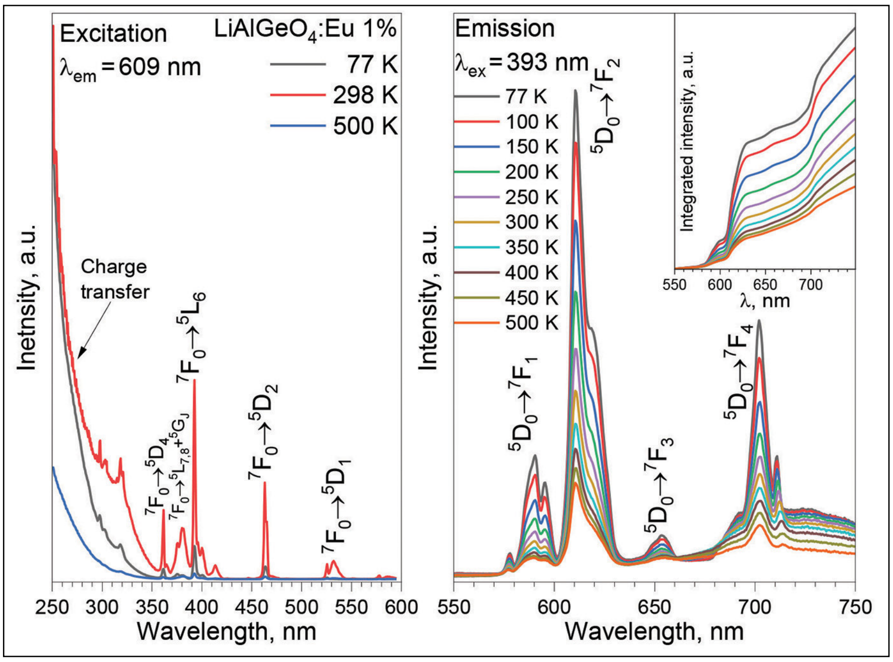

Fig. 5. On the left: excitation (λ_{em} = 609 nm) spectra of the $LiAlGeO_4$:Eu 1% sample at different temperatures; on the right: emission (λ_{ex} = 393 nm) spectra of the $LiAlGeO_4$:Eu 1% sample at different temperatures. Inset: integrated emission intensity spectra

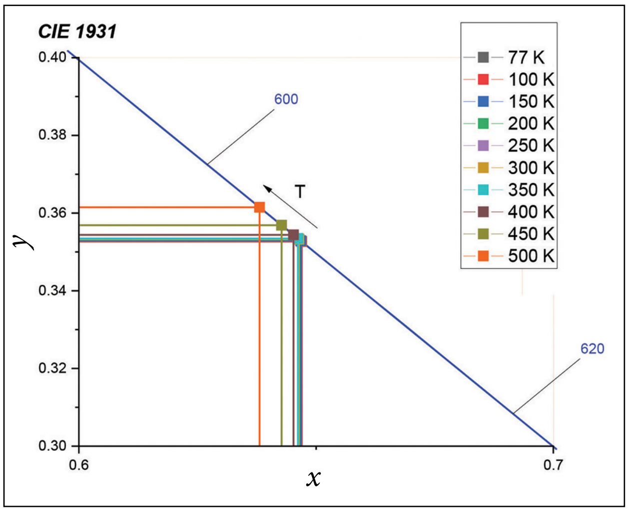

Fig. 6. CIE 1931 chromaticity diagram (magnified part) of the $LiAlGeO_4$:Eu 1% sample at different temperatures

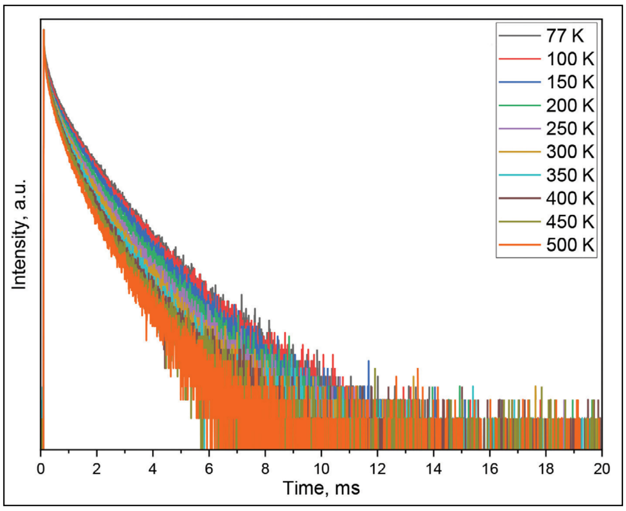

Fig. 7. $LiAlGeO_4$:Eu 1% luminescence decay lifetimes at different temperatures

that the emission reached half of its maximum value at 323 K.

Investigation of the luminescence properties of the synthesised $LiYGeO_4$:Bi and $LiAlGeO_4$:Bi powders

Luminescence excitation and emission studies of the samples were conducted, the results of which are shown in Fig. 9. As can be seen from Fig. 9, the $LiYGeO_4$:Bi samples have a much higher intensity excitation and emission spectrum compared to those of $LiAlGeO_4$:Bi. One of the possible reasons for this is the fact that Bi^{3+} is of a more similar size to Y^{3+} than it is to Al^{3+}.

Afterglow times were measured by monitoring emission at 375 nm and exciting with 254 or 295 nm light. After 60 s, the excitement source was shut and the emission intensity was continued to measure, as can be seen in Fig. 10. The luminescence lifetime of $LiAlGeO_4$:Bi was not measured

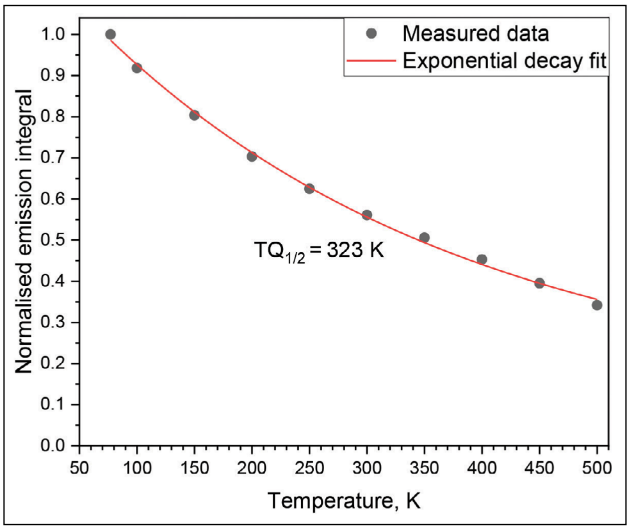

Fig. 8. Normalised emission intensities of the $LiAlGeO_4$:Eu 1% sample at different temperatures

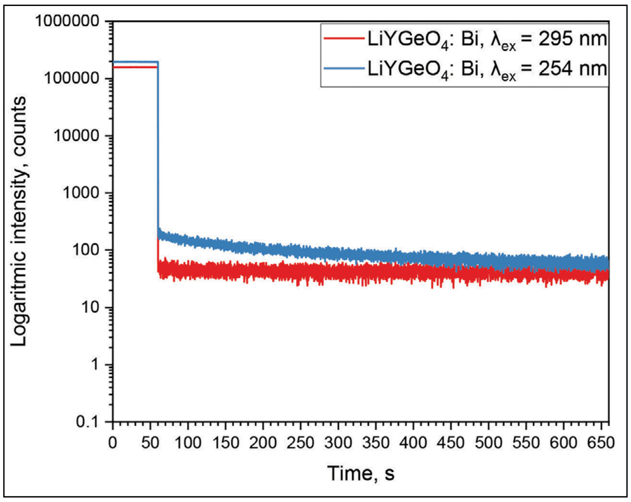

Fig. 10. Measurements of $LiYGeO_4$:Bi luminescence lifetimes at different excitation wavelengths

because compared to $LiYGeO_4$:Bi the emission was much weaker, thus reliable data could not be obtained. $LiAlGeO_4$:Bi and LiYGeO4:Bi were prepared because the previously published research [2] stated that $LiYGeO_4$:Bi has a very long luminescence lifetime. The source states that the luminescence of this compound is still bright after 72 h and is still observed 300 h after excitation has passed. Our results showed that $LiAlGeO_4$ is much less suitable host for bismuth doping compared to $LiYGeO_4$. On the other hand, our $LiYGeO_4$:Bi sample showed afterglow lasting for a few minutes – no way near super-long persistent luminescence reported by Shi et al. One of possible explanations of such discrepancy might be use of different synthesis and measurement approaches.

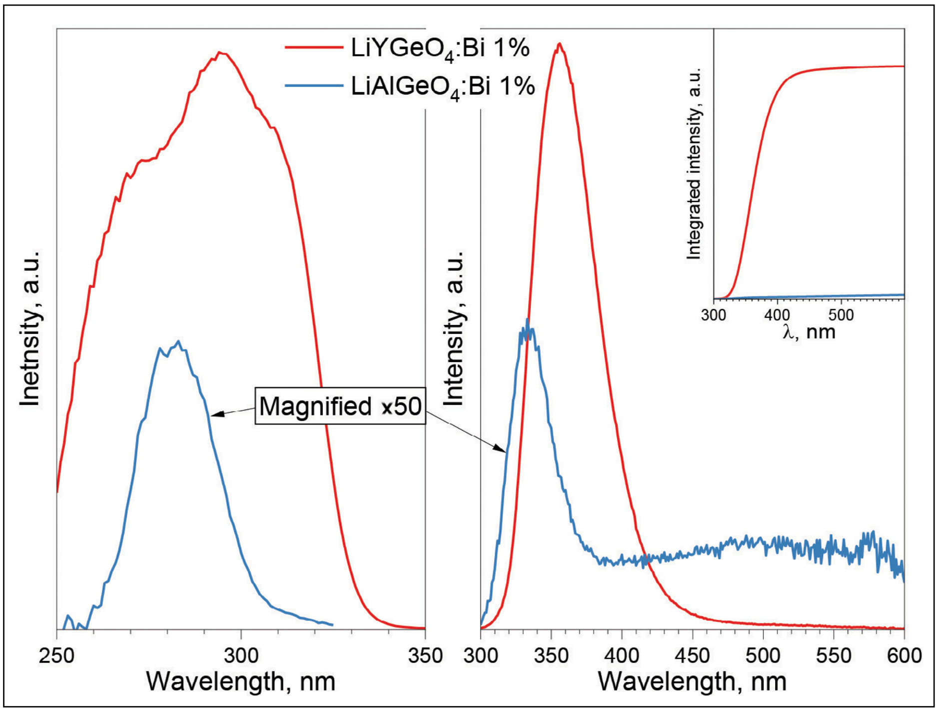

Fig. 9. On the left: excitation (λ_{em} = 340 nm ($LiAlGeO_4$:Bi), λ_{em} = 375 nm ($LiYGeO_4$:Bi)) spectrum; on the right: emission (λ_{ex} = 280 nm ($LiAlGeO_4$:Bi), λ_{ex} = 290 nm ($LiYGeO_4$:Bi)) spectrum. The integrated emission intensity spectrum can be seen in an inset at the top-right corner

CONCLUSIONS

In summary, $LiAlGeO_4$: Eu phosphors were synthesised using the solid state synthesis method with 1% Bi and 0.5, 1, 2, 4, 8 as well as 16% Eu, and their phase purity was confirmed by X-ray diffraction analysis. After studying the luminescence of bismuth in $LiYGeO_4$ and $LiAlGeO_4$ compounds, it was found that $LiYGeO_4$:Bi exhibits a significantly more intensive emission. In addition, this compound was characterised by emission afterglow measurement; however, the obtained afterglow times were much shorter than reported in other studies. The comparison of emission intensities of different $LiAlGeO_4$:Eu samples revealed that $LiAlGeO_4$:Eu 16% has the highest excitation and emission intensity. After performing studies on the luminescence kinetics of $LiAlGeO_4$:Eu, it was found that the $LiAlGeO_4$:Eu 1% sample has the longest emission decay times (τ = 1047.66 μs), while increasing the europium concentration decreases the quenching times. The highest quantum yield was found in the $LiAlGeO_4$:Eu 16% sample and reached 6.31%. Thermal quenching studies were also carried out on the $LiAlGeO_4$:Eu 1% sample. The highest excitation intensity was observed at room temperature, on the other hand, the highest emission intensity was determined at 77 K. The increase in temperature also reduces the luminescence afterglow time, with the longest one observed at 77 K. The calculated temperature at which phosphor loses half of its maximum emission was 323 K.

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Bi ARBA Eu LEGIRUOTO $LiAlGeO_4$ SINTEZĖ KIETAFAZIŲ REAKCIJŲ METODU BEI LIUMINESCENCIJOS TYRIMAI

Santrauka

Šio tyrimo metu, panaudojus kietafazių reakcijų sintezės metodą, buvo paruošti gryni, bismutu arba europiu legiruoti $LiAlGeO_4$ mėginiai. Visi mėginiai ištirti rentgeno difrakcijos bei liuminescencinės spektroskopijos tyrimų metodais. Didžiausia Eu^{3+} koncentracija, kai gaunami vienfaziai $LiAl_{1-x}GeO_4:Eu_x$ mėginiai, buvo x = 0,08, o didesnės legiravimo koncentracijos lėmė papildomų fazių formavimąsi. Liuminescencijos tyrimai atskleidė, kad didžiausiu emisijos intensyvumu pasižymėjo 16 % Eu legiruotas mėginys. Be to, pastarasis mėginys išsiskyrė didžiausia emisijos kvantine išeiga, tačiau liuminescencijos gesimo trukmė ilgiausia užfiksuota $LiAlGeO_4$:Eu 1 % mėginyje. Emisijos priklausomybės nuo temperatūros matavimai atskleidė, kad šio fosforo emisijos efektyvumas sumažėja pusiau pasiekus 323 K temperatūrą.