Temperature dependence of the luminescence of powder SrAl$_2$O$_4$:(Eu$^{2+}$,Dy$^{3+}$) phosphor excited by cw and pulsed laser radiation

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Abstract This paper presents the results of a study of the temperature dependence of the photoluminescence and phosphorescence of the mechanoluminophor powder SrAl$_2$O$_4$: (Eu$^{2+}$), SrAl$_2$O$_4$: (Eu$^{2+}$, Dy$^{3+}$), CaAl$_2$O$_4$: (Eu$^{2+}$, Dy$^{3+}$) which are promising materials for the creation of mecano-optical converters. The photoluminescence of the phosphors’ phosphorescence was excited by a set of cw lasers with different wavelengths. The temperature dependence of the kinetics of the photoluminescence and phosphorescence afterglow was studied. It is shown that with an increase in temperature to $T \approx 90 \, ^\circ\text{C}$, an increase in the intensity of the afterglow (phosphorescence) is observed in the initial period of time after switching off the exciting laser radiation.

1. Introduction

Interest in investigation of mechanoluminescent material has been gained in the recent years. In a number of works, promising forecasts for creation of new devices, in particularly, detectors for monitoring pressure and deformations which operation is based on the effect of mechanoluminescence [1–8]. The sensory element in such detectors is a mechanoluminescent material which converts mechanical impact into light signal. For that reason, one of the main requirements for these materials is a high coefficient of mecano-optical conversion.

A number of materials which can effectively convert mechanical impact into an optical signal have been obtained by now. Most of them are finely dispersed powders of dielectric or semiconductor materials doped with luminescent impurities, in which energy band structure and energy levels of impurities and defects are sensitive to material deformations, and can significantly shift due to deformation, which results in changes of optical and electrical properties of the material [9–13]. In most cases, such kind materials simultaneously show piezoelectric, phosphorescent and mechanoluminescent properties, and are able to effectively convert mechanical stresses (deformations) into optical radiation [14–21].

Rare-earth doped strontium (calcium) aluminates Sr(Ca)Al$_2$O$_4$:(Eu$^{2+}$,Dy$^{3+}$) are novel materials with high mechanoluminescence yield. These materials are fine powders that are obtained as a result of high-temperature sintering of Al$_2$O$_3$, Eu$_2$O$_3$, Dy$_2$O$_3$ and SrCO$_3$ components. Mechanoluminescence from SrAl$_2$O$_4$: (Eu$^{2+}$, Dy$^{3+}$) and CaAl$_2$O$_4$: (Eu$^{2+}$, Dy$^{3+}$) luminophores only appears after preliminary irradiation with the short-wave radiation ($\lambda \leq 480 \, \text{nm}$). As a result of irradiation, the traps are
populated with the carriers (accumulation of the light sum). After irradiation (charging) the luminophores can glow (phosphorescence) for a long time, as well as show pronounced mechanoluminescence that can be observed with the naked eye. Photoluminescence and mechanoluminescence spectra of these materials lie in the visible region, moreover, their maxima coincide. It was shown that the same radiative transitions between electronic levels of the europium ions are responsible for photoluminescence and mechanoluminescence, but the excitation mechanism for the photoluminescence differ from the one for mechanoluminescence. Photoluminescence is caused by excitation of the intracentral transitions of Eu\textsuperscript{2+} ions under laser irradiation. Mechanoluminescence is associated with the activation of the populated trap levels due to mechanical action and capturing the carriers on the upper electronic levels of the radiative transitions of the europium ions.

2. Materials and experimental setup
In current work luminescence decay kinetics and temperature dependences of the photoluminescence and phosphorescence spectra for fine powders of SrAl\textsubscript{2}O\textsubscript{4}: (Eu\textsuperscript{2+},Dy\textsuperscript{3+}) luminophores were investigated. X-ray structural analysis of the powder was conducted for clarifying crystal structure of the powder microparticles. It was found that the microparticles of the SrAl\textsubscript{2}O\textsubscript{4}: (Eu\textsuperscript{2+},Dy\textsuperscript{3+}) powder have monoclinic non-centrosymmetric crystal lattice with space group P2\textsubscript{1}(4). CW semiconductor lasers with wavelengths of 405 nm and 440 nm and pulsed YAG: Nd laser with a wavelength of 355 nm were used for phosphorescence excitation. Figure 1 shows the diagram of the experimental setup for investigating the luminescence of the SrAl\textsubscript{2}O\textsubscript{4}: (Eu\textsuperscript{2+},Dy\textsuperscript{3+}) powder under laser excitation. Spectra were recorded using a spectrometer. The luminescence kinetics was recorded using a monochromator tuned to the wavelength of 520 nm, which corresponds to the maximum spectrum intensity.

![Figure 1](image.png)

**Figure 1.** The scheme of the experimental setup: 1) – oven, 2) – luminophore, 3), 4), 5) – lasers, 5) – monochromator, 6) – spectrometer, 7) – PC.

3. Results and discussion
Temperature dependences of the luminescence of the SrAl\textsubscript{2}O\textsubscript{4}: (Eu\textsuperscript{2+},Dy\textsuperscript{3+}) luminophore are shown in the figure 2. It is known that the photoluminescence spectrum of the SrAl\textsubscript{2}O\textsubscript{4}: (Eu\textsuperscript{2+},Dy\textsuperscript{3+}) luminophore consists of a single wide inhomogeneously broadened spectral band with maximum at \(\lambda \approx 520\) nm. One can be seen from the figure that as the temperature rises, the luminescence intensity decreases, while the shape of the spectrum almost does not change.

The decay kinetics of the luminescence at 520 nm is presented in the figure 3. The luminescence was excited by the CW laser with the wavelength of 404 nm. After turning off the laser irradiation (closing the shutter), there is a rapid drop in the intensity glow (luminescence) of the powder during the time \(\Delta t \approx 1\) ms, which is typical for the photoluminescence arising from intracentral transitions of the Eu\textsuperscript{2+} ions.
Figure 2. Photographs of spectral curves of the SrAl₂O₄:Œu²⁺,Dy³⁺) luminophore. 1) T = 20 °C; 2) T = 90 °C; 3) T = 120 °C; 4) T = 200 °C.

Figure 3. Temperature dependence of the photoluminescence and phosphorescence kinetics. Further, the time dependence of the glow becomes smoother, and a long afterglow of the powder can be observed. Such behavior of the glow is typical for phosphorescence which duration is determined by the rate of thermal activation of the traps. It is known that the temperature rise leads to thermal quenching of the luminescence, i.e. to decrease in luminescence intensity. On the other hand, increase in temperature leads to increase in thermal activation of the traps. Therefore, luminescence intensity drop due to temperature quenching is compensated by thermal activation of the traps. This is probably why photoluminescence intensity weakly depends on the temperature below T ≤ 80 °C.

With a further increase in temperature, the photoluminescence intensity begins to drop rapidly. However, as one can see from the figure 3, phosphorescence at T = 90 °C is slightly higher compare with the one at T = 20 °C, which indicates a higher rate of thermal activation of the traps at T = 90 °C than at T ≈ 20 °C. Further increase in temperature T > 90 °C leads to a rapid decrease in both photoluminescence and phosphorescence.

Figure 4a,b shows the temperature dependences of the photoluminescence at a wavelength of 520 nm for powders of SrAl₂O₄:Œu²⁺) and SrAl₂O₄:(Eu²⁺,Dy³⁺) phosphor excited by pulsed radiation of a YAG: Nd³⁺ laser (λ = 355 nm, τ ≈ 7 ns).
4. Conclusion
In current research the temperature dependences of photoluminescence and phosphorescence from mechanoluminophore of the SrAl$_2$O$_4$: (Eu$^{2+}$,Dy$^{3+}$) powder, which is a promising material for the fabrication of mechano-optical converters, were investigated. Photoluminescence and phosphorescence were excited by the set of lasers with different wavelengths. It is shown that as the temperature rises to $T \approx 90 \degree C$, increase in intensity of the afterglow (phosphorescence) is observed in the initial period of time after switching off the exciting laser radiation. It is shown that increase in temperature above $T \approx 90 \degree C$ leads to rapid thermal quenching of photoluminescence, as well as to rapid thermal activation of the traps and emission of the stored light sum.

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References
[1] Terasaki N, Yamada H and Xu C N 2013 Catalysis Today 201 203–8
[2] Chandra B P, Chandra V K, Mahobia S K et al. 2012 Sensors and actuators A: Physics 173 9–16
[3] Wang C, Dong L, Peng D et al. 2019 Advanced Intelligent Systems 1900090
[4] Qian X, Cai Z, Su M et al. 2018 Adv Mater 30 1800291
[5] Banishev A A, Lotin A A and Banishev A F 2014 Int. J. Modern Phys. B 28 13450154
[6] Banishev A F and Banishev A A 2011 Phys. Lett. A 375 2767-9
[7] Banishev A F and Banishev A A 2019 Inorganic Materials: Applied Research 10 3 646–50
[8] Banishev A F and Banishev A A 2019 Technical Physics Letters 45 5 475–7
[9] Banishev A F, Banishev A A and Lotin A A 2012 Fizika I khimiya obrabotki Materialov [Physics and Chemistry of Materials Treatment] 5 89–92 (in Russian)
[10] Leeelachao S, Muraishi S, Sannomiya T, Shi J and Namamura Y 2015 Optics Letters 40 19 4468–71
[11] Feng A and Smet P F 2018 Materials 11 484
[12] Zhang H, Peng D, Wang W et al. 2015 J. Phys. Chem. C 119 28136
[13] Wang X, Peng D, Huang B, Pan C and Wang Z L 2019 Nano Energy 55 389–400
[14] Zhang J-C, Wang X, Marriott G and Xu C-N 2019 Progress in Materials Science 103 678–742
[15] Banishev A F, Banishev A A, Bolshukhin V A, Syrov Yu V and Khort A M 2010 Fizika I khimiya obrabotki materialov [Physics and Chemistry of Materials Treatment] 2 60–5 (in Russian)
[16] Rahimi M R, Yun G J, Doll G L and Choi J S 2013 Optics Letters 38 4134–7
[17] Timilsina S, Lee K H, Jang I Y and Kim J S 2013 Acta Mater 61 7197–206
[18] Banishev A A and Banishev A F 2018 Inorganic Materials: Applied Research 9 3 484–9
[19] Botterman J, van den Eeckhout K, de Baere I, Poelman D and Smet P F 2012 Acta Mater 60 5494–500
[20] Zhang J C, Xu C N, Kamimura S, Terasawa Y, Yamada H et al. 2013 Opt Express 21 12976–86
[21] Kamimura S, Yamada H and Xu C N 2012 Appl. Phys. Lett. 101 9 091113–8