Mechanoluminescence of a composite based on polymethylmethacrylate and fine-disperse powder of SrAl$_2$O$_4$: (Eu$^{2+}$, Dy$^{3+}$) phosphor

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Abstract. The paper deals with photoluminescence and deformation luminescence (mechanoluminescence) of a composite material based on fine-disperse powder of phosphor SrAl$_2$O$_4$: (Eu$^{2+}$, Dy$^{3+}$) and polymethylmethacrylate that is transparent in the visible region. The luminescent (sensory) layer responsive to mechanical action was formed in the surface layer of the polymethylmethacrylate. To excite of photoluminescence the short pulses of a nanosecond laser were used. Mechanoluminescence was excited by the short acoustic impulses generated by a nanosecond laser. New information about the energy levels of impurities was obtained.

1. Introduction

In recent years, the research of mechanoluminescent properties of various materials has aroused considerable interest. The increased attention is, in particular, given to the investigation of mechanoluminescence of the alkaline-earth aluminates with admixture of rare-earth elements, for example, strontium (calcium) aluminate Sr(Ca)AlO$_4$: (Eu$^{2+}$, Dy$^{3+}$). These aluminates (long-persistence phosphors) present a significant class of phosphorescent materials exhibiting high quantum efficiency and glow persistence in the visible spectrum, good stability and resistance [1, 2]. The mechanoluminescent properties of these materials have caused the growth of interest in them with the aim of employing them as sensing elements in production of control devices and mechanisms. The works have recently appeared which suggest that the ML nanoparticles of SrAlO$_4$: (Eu$^{2+}$, Dy$^{3+}$) introduced into the material should be used as catalysts in initiating photocatalytic processes in the regions of the material where photoinitiating radiation (light) cannot be delivered. For ML excitation, ultrasound is used [3, 4].

Nevertheless, there is so far no consensus on the mechanism of SrAl$_2$O$_4$: (Eu$^{2+}$, Dy$^{3+}$) mechanoluminescence excitation. There is no convincing data on the location of the energy levels of activator ions Eu$^{2+}$ and traps in the forbidden zone, and the type of traps (electron or hole) has not been ascertained.

In this work, the mechanoluminescent layer sensitive to mechanical action (a sensory layer) is formed directly in the surface layer of the polymer material polymethylmethacrylate (the substrate) that is transparent in the visible region. The kinetics of glow and the mechanoluminescence and the photoluminescence spectra of the SrAl$_2$O$_4$: (Eu$^{2+}$, Dy$^{3+}$) phosphor microparticles in the
polymethylmethacrylate matrix excited by the action of short laser pulses and the mechanical hammer have been studied.

2. Materials and experimental procedure
In the samples prepared for the investigation the surface layer of the substrate material was a mechanoluminescent layer. Polymethylmethacrylate transparent in the visible region was chosen to be the substrate material. The mechanoluminescent layer was formed in the surface layer of the polymethylmethacrylate. The plate surface was preliminarily covered with a layer of dichloroethane (Δh2 ≈ 1-2 mm thickness). As the result of dissolution of the polymethylmethacrylate surface layer in dichloroethane, a liquid layer of polymethylmethacrylate solution was formed in 10-15 min on the surface of the solid polymethylmethacrylate plate. Then, the surface of the liquid layer of polymethylmethacrylate solution was covered with a thin layer (100-150 μm) of mechanoluminescent fine-dispersed powder of SrAl2O4:(Eu2+, Dy3+) phosphor with the grain size of 0.5-30 μm. A flat and smooth metal plate of stainless steel (or another metal plate) h = 100 μm thick was placed on the powder layer. The diffusion of the phosphor particles into the solution and its solidification in the surface layer of the transparent substrate resulted in the formation of a responsive to mechanical action mechanoluminescent composite layer of 150-200 μm thickness based on the polymethylmethacrylate and the mechanoluminescent powder of SrAl2O4:(Eu2+, Dy3+) phosphor. As the substrate is transparent, the glow (mechanoluminescence) emerging under the action of laser pulses and the mechanical hammer on the mechanoluminescent layer from the side of the metallic plate can be registered from the substrate side.

Figure 1 presents the experimental setup for investigation of the kinetics of mechanoluminescence excited by the action of mechanical hammer and short laser pulses. The mechanical hammer was a metal rod of l = 3 cm length and d0 = 0.3 cm diameter, one of its ends being cone-shaped with the vertex radius r ≈ 0.5 mm. The rod was inserted into the pipe containing a spring. Pulling the spring off made it possible to shoot the hammer from the pipe in the direction of the sample under study. To excite mechanoluminescence by short acoustic pulses, a laser with short pulses was used. The laser pulse was focused on the surface of the stainless-steel plate to a spot of dlas = 0.5±2.0 mm diameter. At the cost of material evaporation and emergence of vapor pressure impulse, the laser pulse gave birth to an acoustic pulse. Propagating through the metal plate, the acoustic pulse reaches the mechanoluminescent layer contacting with the metal plate and excites the mechanoluminescence signal.

Figure 1. The scheme of the installation for studying the kinetics of mechanoluminescence excited by the action of short laser pulses and a hammering device: 1. Laser pulse, 2. Plate of stainless steel, 3. Mechanoluminescent layer, 4. Substrate of polymethylmethacrylate, 5. Photomultiplier.

3. Results and discussion
Figure 2 displays the photoluminescence spectra of the SrAl2O4:(Eu2+, Dy3+) phosphor microparticles and of the phosphor microparticles in the polymethylmethacrylate matrix at room temperature under the action of YAG:Nd³⁺ laser pulses τp pulse ≈ 7 ns, λ = 355 nm at the power density of I₁ ≈ 5×10⁶ W/cm² and I₂ ≈ 7×10⁶ W/cm².
Figure 2. The photoluminescence spectrum of SrAl$_2$O$_4$:(Eu$^{2+}$, Dy$^{3+}$) phosphor powder excited by the laser pulse of $\lambda = 355$ nm: a) $I_1 = 5 \times 10^6$ W/cm$^2$, b) $I_2 = 7 \times 10^6$ W/cm$^2$.

It is seen that increasing the laser pulse power density results in the appearance of new photoluminescence bands of longer waves at $\lambda \approx 573$ nm, 693 nm, 755 nm (shown by the arrows in the figure), which is indicative of a complex structure of the electron levels of europium, dysprosium and other various defects in this material. The above-mentioned transitions were not observed under the action of laser radiation of low power density.

It is known that photoluminescence and mechanoluminescence of SrAl$_2$O$_4$:(Eu$^{2+}$, Dy$^{3+}$) are due to the same electron transitions of europium ions. Long afterglow (phosphorescence) is related to thermal activation of the traps populated because of carrier trapping in the course of exciting irradiation of the samples. The intensity and duration of SrAl$_2$O$_4$:Eu$^{2+}$ phosphorescence are known to be considerably increased on adding the admixture of dysprosium Dy$^{3+}$. The ions of Dy$^{3+}$ are the traps which accumulate the luminous energy.

Figure 3 illustrates the mechanoluminescence signals produced by a laser pulse with $W_{\text{pulse}} \approx 10$ mJ, $\tau_{\text{pulse}} \approx 7$ ns, $\lambda = 355$ nm. The effect of a short laser pulse on the surface of the metal plate (figure 1) can result in the excitation of “acoustic” pulses (at the cost of the impulse of vapor pressure). Next, the acoustic pulse propagates through the metal plate and excites the mechanoluminescence of the mechanoluminescent layer.
Figure 4 present possible electron transitions corresponded to this lines. Photoluminescence occurs on transitions of $3 \rightarrow 1$ ions Eu$^{2+}$. Electrons radiatively transit from level 3 to level 1 ($\lambda = 525$ nm) and nonradiatively relax to level 4. The probability of transition $w_{31}$ is more larger than the probability $w_{32}$ ($w_{31} >> w_{34}$).

![Figure 4](image)

**Figure 4.** The proposed scheme of electronic levels and transitions in Eu$^{2+}$ located in SrAl$_2$O$_4$:(Eu$^{2+}$, Dy$^{3+}$).

At a low intensity of the exciting radiation, the level 4 is practically empty, since $w_{31} >> w_{34}$, so only the $3 \rightarrow 1$ transitions are observed (figure 2). As the power of the exciting radiation increases, the level 4 begins to populate. Then the radiative transitions $4 \rightarrow 1$ lead to the appearance of lines $\lambda \approx 573$ nm, 693 nm.

![Figure 5](image)

**Figure 5.** The scheme of the mechanoluminescence recording device: 1 – substrate of polymethylmethacrylate; 2 – sensor layer; 3 – CCD matrix; 4 – computer.

Figure 5 shows the scheme of the experimental setup used for visualization of the mechanical actions. The mechanoluminescent layer (containing no stainless-steel plate) prepared using the procedure described above is a sensing cell. By way of illustration, figure 6 demonstrates the trajectory (track) of the stylus-like object moved by hand over the surface of the mechanoluminescent layer. The mechanoluminescent signal was registered from the back side of the substrate.

![Figure 6](image)

**Figure 6.** The trajectory of stylus sliding over the surface of the mechanoluminescent (sensory) layer, obtained from the back side of the substrate.

4. **Conclusions**

A method of formation of the mechanoluminescent composite layer based on the polymethylmethacrylate and the SrAl$_2$O$_4$:(Eu$^{2+}$, Dy$^{3+}$) phosphor powder in the surface layer of the polymethylmethacrylate transparent in the visible region is suggested. To excite of
mechanoluminescence, short acoustic impulses generated by a nanosecond laser were used. It is shown that the produced mechanoluminescent layer is highly sensitive to short acoustic and mechanical shock (normal and tangential) actions and can be used in registration and visualization of mechanical actions.

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