

## Deformation Stimulated Luminescence of Nano-micro-parcticles $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$ in a Matrix of Photopolymer and Creation of Sensor Elements of Mechanical Stresses

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The work deals with low-temperature photoluminescence and deformation luminescence (mechanoluminescence) of a composite material based on fine disperse powder of phosphor  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  and photopolymerizing resin that is transparent in the visible region. It has been shown that at the low temperature ( $T=15\div 200$  K) the photoluminescence spectrum of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  displays two wide, partially overlapping bands with the maxima at  $\lambda_{1\text{max}}\approx 517$  nm and  $\lambda_{2\text{max}}\approx 446$  nm. The short-wave luminescence band ( $\lambda_{2\text{max}}\approx 446$  nm) has been found to undergo temperature quenching and to completely decay at  $T\geq 200$  K. A mechanism of mechanoluminescence excitation has been suggested. It has been shown that the composite material exhibits high sensitivity to mechanical action.

**Keywords:** Photoluminescence, Mechanoluminescence, Phosphor, Composite Material, Low Temperature

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The fine powder  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  attracts attention as a phosphor that is capable of accumulating large light energy and possessing the property of long afterglow. Besides, this material offers the pronounced mechanoluminescence property. Mechanoluminescence (ML) is a capability of a material to luminesce (glow) as a result of plastic deformation emerging under mechanical stresses (bending, compression, shock, vibration, etc.) [1-4].

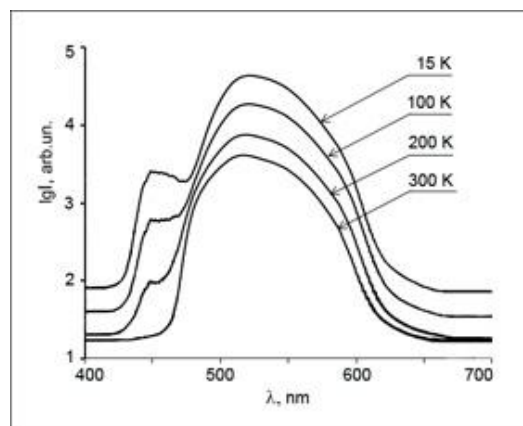
Photoluminescence of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  was studied in the temperature range  $T=15\div 300$  K. A HeCd laser ( $\lambda=325$  nm) was used to excite photoluminescence. The photoluminescence spectra were recorded with a CCD-matrix polychromator.

Mechanoluminescence was excited by pulsed mechanical stresses. The stresses were produced by a mechanical spring striker with a tapered tip, installed on the substrate side. The ML signal was recorded with a visible-spectrum photomultiplier.

In the investigation, the composite materials were employed which were based on the fine disperse polycrystalline powder  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  ( $\text{Eu}^{2+}\approx 2\%$ ,  $\text{Dy}^{3+}\approx 3.5\%$ , the sizes of particles from 0.5 to 30  $\mu\text{m}$ ) and the photopolymerizing resin that is transparent in the visible region. The weight relation of the powder and the resin in the produced suspension was 1:4. A thin layer of the liquid suspension was applied to the metallic substrate of  $d\approx 3$  cm diameter and  $h\approx 100=200$   $\mu\text{m}$  thickness. The suspension was covered at the top with a quartz plate having the diameter  $d\approx 3$  cm and thickness  $h\approx 1$  mm. To specify the required thickness of the suspension layer, an intermediate ring of the thickness of  $h\approx 200-300$   $\mu\text{m}$  was placed between the metallic substrate and the quartz plate. Then, the substrate with the liquid suspension (a sample) was exposed to UV radiation of the mercury lamp for the time  $t\approx 10$  min. A solid layer of the composite material 200-300  $\mu\text{m}$  in thickness formed on the substrate surface as the result of photopolymerization of the suspension.

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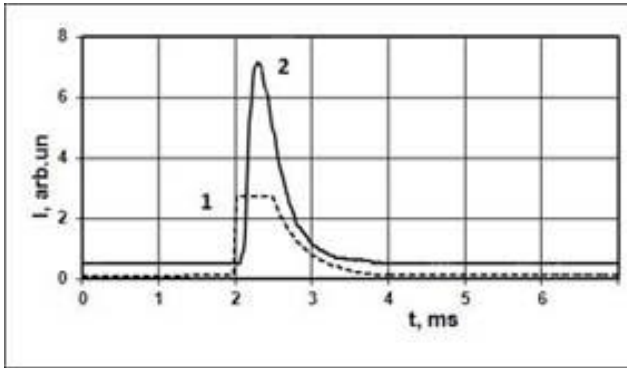
Fig.1 illustrates the variations in the photoluminescence spectrum of the compressed powder  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  on cooling the sample in the temperature range  $T=15\div 300$  K. As evident from the figure, the photoluminescence spectrum (at  $T=200-300$  K) presents a wide non-uniformly broadened band with a maximum at  $\lambda_{1\text{max}}\approx 517$  nm. As the temperature is reduced ( $T\leq 200$  K), the second wide luminescence band starts to appear that has a maximum at  $\lambda_{2\text{max}}\approx 446$  nm and is partially overlapped with the first one. The second band intensity is increased as the temperature drops up to  $T=15$  K, though it remains considerably lower than the intensity of the first band with  $\lambda_{1\text{max}}$ . As the temperature is raised again, the intensity of the band with  $\lambda_{2\text{max}}$  declines and the band totally disappears at  $T\approx 200$  K.



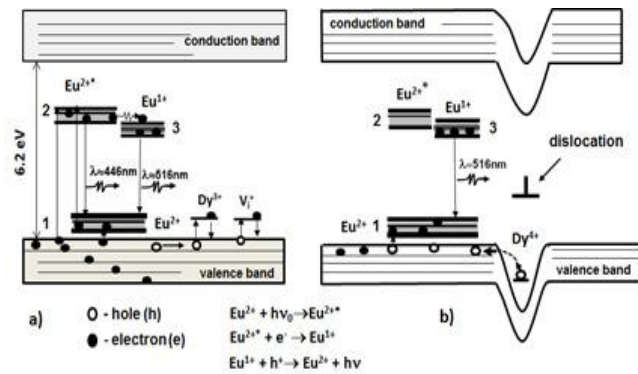
**Fig. 1** – The low-temperature photoluminescence spectra of the compressed  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  powder

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Relying on the available results, the following mechanism for stimulation of photo- and mechanoluminescence of the investigated materials can be suggested.



**Fig. 2** – Mechanoluminescence of the composite material:  
 1 – the shape of mechanical impact  
 2 – the mechanoluminescent signal form the composite material



**Fig. 3** – The structure of energy levels of the luminescent center ( $\text{Eu}^{2+}$ ) and the traps ( $\text{V}^{1-}$ ,  $\text{V}^{1+}$ ,  $\text{V}^{2+}$ ,  $\text{Dy}^{3+}$ ) in the fine disperse powder of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  and the mechanism of photo- and mechanoluminescence excitation:  
 - away from the dislocation;  
 - in the vicinity of the dislocation

On exposure to short-wavelength laser radiation, the ions of  $\text{Eu}^{2+}$  are excited and recharged. Two channels of excitation and recharging are possible. In the first case, radiation quanta are directly absorbed by  $\text{Eu}^{2+}$  ions and transit to the excited state  $\text{Eu}^{2+*}$  (transition 1→2). Owing to close location of bands 2 and 3, the nonradiative relaxation transition (at the cost of electron-phonon interaction) of electrons from levels 2 to levels 3 occurs quickly. There are practically no electrons at levels 2 at room temperature. The vacant lower levels of  $\text{Eu}^{2+}$  ions are set closely to the valence band, so they are populated by electrons from the valence band due to thermal activation. As a result, metastable  $\text{Eu}^{1+}$  ions are formed. In the second case, metastable  $\text{Eu}^{1+}$  ions can emerge from absorption of radiation by the electrons of the valence band and their transition to the upper levels of  $\text{Eu}^{2+}$  ions ( $\text{Eu}^{2+} + e^- \rightarrow \text{Eu}^{1+}$ ). In either case metastable  $\text{Eu}^{1+}$  ions and free holes arise in the valence band and can be captured by traps ( $\text{Dy}^{3+}$  ions or intrinsic defects  $\text{V}_i^+$ ) whose levels

are above the valence band top. Thus, irradiation of the sample  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  is accompanied by formation of both excited  $\text{Eu}^{2+*}$  ions and metastable and, as the rule, long-lived  $\text{Eu}^{1+}$  ions.

The radiative transitions from levels 3 to levels 1 generate a wide luminescence band with a maximum at  $\lambda_{1\text{max}} \approx 517$  nm. As the temperature falls, a probability of electron-phonon interaction and nonradiative relaxation transitions 2→3 is decreased. This permits the life time of electrons at levels 2 to be extended and the probability of radiative transitions 2→1 to be increased, so at the temperature  $T \leq 200$  K the second (low-temperature) luminescence band with the maximum at  $\lambda_{2\text{max}} \approx 446$  nm starts to emerge, its intensity enhancing with the temperature fall. The absence of the maximum  $\lambda_{2\text{max}} \approx 446$  nm under laser irradiation at the wavelength of  $\lambda_{\text{ex}} > 370$  nm at  $T \leq 200$  K is likely to be due to the lack of radiation quantum energy for transporting of electrons to excited levels 2 (transitions 1→2), though the transitions of electrons to lower excited levels 3 (1→3) are possible, so only one luminescence band with the maximum  $\lambda_{1\text{max}} \approx 517$  nm is observed.

Long luminescence (phosphorescence) at room temperature is generated from the decay of metastable  $\text{Eu}^{1+}$  ions which are controlled by the velocity of thermal activation of the traps (thermal release of holes from traps) and by a probability of interaction between the free holes and the  $\text{Eu}^{1+}$  ions. The interaction between the free holes and the  $\text{Eu}^{1+}$  ions leads to a transition of electrons from the lower levels 1 to the valence band and to recombination with the holes. The resulting excited  $\text{Eu}^{2+*}$  ions accomplish a radiative transition to the ground state of  $\text{Eu}^{2+}$  (transitions 3→1). Thus, the duration of afterglow (phosphorescence) is defined by a probability of thermal activation of the traps (mainly  $\text{Dy}^{3+}$ ) and by a probability of interaction between the free holes and the  $\text{Eu}^{1+}$  ions.

Fig.2 displays a mechanoluminescence signal excited by the mechanical impact on the metallic substrate coated with a film from the composite material by the described above procedure. The impact force value approximates that of the metallic ball weighing 0.13 g which falls on the same sample from the height of 20 cm.

The mechanoluminescent properties of the materials are governed by the peculiarities of location of the energy levels of the activator ( $\text{Eu}^{2+}$ ), co-activator ( $\text{Dy}^{3+}$ ) and intrinsic defects. The features of mechanoluminescence behavior observed in the experiments agree well with the dislocation mechanism that associates its appearance with curving of the energy bands and levels in the vicinity of dislocations [5]. Under plastic deformation of the material subjected to, for example, a mechanical impact, the motion of dislocations is activated and if a trap (in this case a dysprosium ion with a captured hole, i.e. the  $\text{Dy}^{4+}$  ion or an intrinsic defect) turns out to be near the moving dislocation, the energy level of the trap may prove to be lower than the valence band top, that may result in a transition of the captured hole from the trapping level to the valence band

(see Fig.3). The free holes moving through the crystal collide and interact with the metastable  $\text{Eu}^{1+}$  ions which then undergo a radiative decay thus giving rise to a mechanoluminescence signal.

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