Structure, luminescence and mechano-optical properties of strontium aluminate doped with europium and dysprosium ions

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Abstract. Photoluminescence spectra and kinetics of mechanoluminescence of finely dispersed powder of SrAl₂O₄:(Eu²⁺, Dy³⁺) and Sr₄Al₁₁O₂₅:(Eu²⁺, Dy³⁺) phosphor was investigated. Photoluminescence was excited by nanosecond laser pulses with a wavelength of λ = 355 nm and by a group of cw lasers with different wavelengths (λ=355, 404, 440, 530 nm). Photoluminescence of the materials has been revealed in the long-wave (550 to 750 μm) spectral region, which is indicative of the existence of corresponding energy levels of Eu²⁺ions. It was shown that, at low power density, a single wide broadened line of photoluminescence was observed. As radiation power density is increased, additional photoluminescence lines begin to appear. The microstructure of the powders has been investigated with the scanning electron microscope. It has been found that the powder consists of microparticles (granules) of the sizes up to 100 μm. The microparticles show a granular structure, the grain size being as large as 25 μm. Mechanoluminescence was initiated by an acoustic wave generated by short laser pulses. A mechanism of mechanoluminescence excitation has been suggested. It has been concluded that mechanoluminescence of SrAl₂O₄:(Eu²⁺, Dy³⁺) is excited owing to activation of the traps during their interaction with the electric fields of moving grain boundary dislocations as the result of grain boundary sliding under deformation of microparticles on impact.

1. Introduction

The recent years show the increased interest in the investigation of mechanoluminescence (ML) of materials [1,2]. Mechanoluminescent materials are drawing the increasing attention of specialists engaged in both the fundamental investigations and applied research related to the properties of materials subjected to various force fields. This interest was stimulated, in particular, by the development of a new direction of research – straintronics, which studies the behavior of physical properties and effects in deformed materials. Mechanoluminescence (ML) is a capability of a material to luminesce (glow) as a result of deformation emerging under mechanical stresses. The mechanoluminescent materials are of interest as the basis for creating devices and elements for detecting, monitoring, imaging, and recording mechanical actions (impacts, vibrations, deformations, bending, compression, shock, and etc.) [3-6].

By now, a great quantity of materials is known which effectively transform mechanical actions to optical radiation, as well as to visible radiation. For example, the fine-dispersed powders of CaAl₂Si₂O₆:Eu²⁺ and SrMg₂(PO₄)₂:Eu²⁺ exhibit mechanoluminescence in the blue region [7, 8]; the powders of SrAl₂O₄:Eu²⁺ and BaSi₂O₅: Eu²⁺ reveal it in the green region [9-12], and ZnS:Mn²⁺, CaZnOS:Mn²⁺, Sr₂+Sn₃O₈₁⁺:Sm³⁺ – in the red region [13-16]. The work is being continued on the
synthesis of new mechanoluminescent materials with higher coefficients of mechanoluminescence efficiency and on studying the mechanisms of mechanoluminescence excitation. The search for new mechanoluminescent materials is continued, including those based on polymer and biopolymer.

The fine powder SrAl2O4:(Eu2+, Dy3+) 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. In work [18,19] it was established that strong ML of SrAl2O4:(Eu2+, Dy3+) is only observed in the piezoelectric phase with the twin structure. According to [20,21], the mechanoluminescence of SrAl2O4:(Eu2+, Dy3+) phosphor powder is attributed to the interaction of the impurity centers with the local piezoelectric fields emerging in the vicinity of the impurity centers under the material deformation. In papers [22-23] the mechanoluminescence of the SrAl2O4:(Eu2+, Dy3+) phosphor powder is explained by the interaction of the impurity centers with the grain boundary dislocations.

This paper presents the results of studies on photoluminescence spectra and photoluminescence decay kinetics for such luminescent substances as SrAl2O4:(Eu2+, Dy3+) and Sr4Al14O25:(Eu2+, Dy3+) excited by laser radiation with different wavelengths. The mechanoluminescence was excited by short acoustic pulses generated by laser pulses. The mechanoluminescence (sensor) layer sensitive to mechanical effects was formed directly in the surface layer of a polymer material transparent in the visible region—poly (methyl methacrylate) (substrate).

2. Materials, experimental procedure and results

In the present work, consideration was given to photo- and mechanoluminescence of the fine-dispersed powders of the SrAl2O4:(Eu2+, Dy3+) and Sr4Al14O25:(Eu2+, Dy3+) phosphors. In particular was studied the spectra and kinetics of photoluminescence of fine-dispersed powders of phosphors SrAl2O4:(Eu2+, Dy3+) and Sr4Al14O25:(Eu2+, Dy3+). For the excitation of photoluminescence in the samples, were used a set of lasers with different values of radiation wavelength—the third harmonic of a pulsed solid-state YAG:Nd3+ laser with \( \lambda = 355 \) nm (\( \tau = 7 \) ns, \( W = 10 \) mJ) and semiconductor continuous radiation lasers with \( \lambda \approx 405 \) nm, (I = 70 mW).

Figure 1 shows a schematic diagram of the experimental setup. A Clacier-X spectrometer was used to register and analyze the photoluminescence spectra. The photoluminescence signal through an optical fiber was fed to the spectrometer and, with the help of a second optical fiber, was supplied to the input of a monochromator for studying the kinetics of photoluminescence decay.

Figure 2 depicts the photoluminescence spectra of the resulting powders at room temperature. The photoluminescence was excited by the continuous-wave laser with the wavelength \( \lambda = 405 \) nm. The photoluminescence of the powders is seen to be a single wide line occupying a large part of the visible spectrum. The wavelengths \( \lambda = 497 \) nm and \( \lambda = 520 \) nm correspond to the photoluminescence maxima of the Sr4Al14O25:(Eu2+, Dy3+) and SrAl2O4:(Eu2+, Dy3+) powders, respectively.

Figure 1. Schematic diagram of experimental setup: (1) luminophore under investigation; (2–5) lasers; (6) spectrophotometer; (7) monochromator; (8) computer.
Figure 2. The photoluminescence spectra of the powders under excitation by a laser with \( \lambda = 405 \) nm: 1. The radiation of the excitation laser, 2. The photoluminescence spectrum of \( \text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+} \), 3. The photoluminescence spectrum of \( \text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+}) \).

It is known, that the photoluminescence spectrum of \( \text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+}) \) is determined by the electron transitions of \( \text{Eu}^{2+} \) ion. The phosphorescence and mechanoluminescence spectra are also governed by the transitions of \( \text{Eu}^{2+} \) ion, but the intensity and duration of phosphorescence and mechanoluminescence depend to a large extent on the processes of carrier trapping and trap activation.

To the traps belong impurities and (or) defects whose energies \( E_{n,p} \) are, as a rule, in the forbidden zone near the conduction band bottom or near the valence band top. It may be believe, that \( \text{Dy}^{3+} \) impurities in the \( \text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+}) \) phosphor form the electron traps.

Figure 3 illustrates the spectra of the \( \text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+}) \) powder photoluminescence excited by the pulses of the laser with \( \lambda = 355 \) nm wavelength having various radiation power densities. At low power density, a single wide inhomogeneously broadened line with a maximum at \( \lambda = 525 \) nm is observed. As radiation power density is increased, additional photoluminescence lines begin to appear.

Figure 3. The photoluminescence spectra of the fine-dispersed powder \( \text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+}) \). The laser pulse power density: a) \( I = 5 \times 10^6 \) W/cm\(^2\); b) \( I = 7 \times 10^6 \) W/cm\(^2\)

Figure 4. The photoluminescence spectra of the powders under excitation by a laser with \( \lambda = 355 \) nm: 1) \( \text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+} \); 2) \( \text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+}) \)
Figure 4 shows the photoluminescence spectra of the produced powders under excitation by a laser with the wavelength \( \lambda = 355 \) nm and the power density \( I = 7 \times 10^6 \) W/cm\(^2\). The appearance of the new lines in the photoluminescence spectrum with an increase in the power density testifies that there exist the electron levels and corresponding radiative transitions which have not been registered under the action of laser radiation with low power density.

Figure 5 displays the photos of the microparticles of the \( \text{SrAl}_2\text{O}_4: (\text{Eu}^{2+}, \text{Dy}^{3+}) \) and \( \text{Sr}_4\text{Al}_{14}\text{O}_{25}(\text{Eu}^{2+}, \text{Dy}^{3+}) \) powders obtained with the scanning electron microscope. The microparticles are seen to consist of a large number of grains with the distinguished boundaries; the grains are closely adjacent to each other with no pores and microcavities commonly encountered in conglomerates.

In appearance, the microparticles have a polycrystalline structure. The structure of the microparticles and the shape of the grains in \( \text{Sr}_4\text{Al}_{14}\text{O}_{25}: (\text{Eu}^{2+}, \text{Dy}^{3+}) \) differ essentially from those of \( \text{SrAl}_2\text{O}_4: (\text{Eu}^{2+}, \text{Dy}^{3+}) \). The grain boundaries are also different in their shape.

![Figure 5](image_url)

**Figure 5.** The photographs obtained with the scanning electron microscope: a) A microparticle of the phosphor powder \( \text{SrAl}_2\text{O}_4: (\text{Eu}^{2+}, \text{Dy}^{3+}) \); b) A microparticle of the phosphor powder \( \text{Sr}_4\text{Al}_{14}\text{O}_{25}: (\text{Eu}^{2+}, \text{Dy}^{3+}) \).

The paper presents the results of investigation mechanoluminescence of the composite materials produced from the photopolymerizing resin (photopolymer) and the fine disperse powder \( \text{SrAl}_2\text{O}_4: (\text{Eu}^{2+}, \text{Dy}^{3+}) \). A thin layer (300 μm) of the composite formed on a metal substrate, see figure 6.

Mechanoluminescence was excited by the acoustic pulses emerging under the action of short laser pulses upon the metal plate surface. The laser pulse (\( \lambda = 355 \) nm, \( \tau = 7 \) ns, \( W = 10 \) mJ) was focused to a spot of the diameter \( d \approx 1 \) mm (see Figure 6). As the result, a pulse of vapor pressure and acoustic pulse in metal substrate is produced [24].

Figure 7 presents the mechanoluminescence signal of the \( \text{SrAl}_2\text{O}_4: (\text{Eu}^{2+}, \text{Dy}^{3+}) \) powder, excited by an acoustic pulse arising from the action of a short laser pulse. The action of an acoustic pulse brings about the deformation of the polycrystalline microparticles of the phosphor.

![Figure 6](image_url)

**Figure 6.** 1)-Substrate (metal plate, \( h = 100 \) μm), 2)-Suspension of photopolymer and powder \( \text{SrAl}_2\text{O}_4: (\text{Eu}^{2+}, \text{Dy}^{3+}) \), \( h = 300 \) μm, 3)-Laser pulse, 4). Photomultiplier
In the polycrystalline materials the deformation mainly results from intergranular sliding at the cost of motion of the grain boundary dislocations. It is known, see [25], that there exist rather strong mechanical stresses in the neighborhood of the dislocations, which can cause curving (displacement) of the bands and the levels of impurities and defects. In the stress field of the dislocation, the energy level of a trap is shifted in the direction of the conduction zone. As the result, the energy separation $\Delta E$ between the levels of traps and the bottom of the conduction zone is reduced. At the same time, the probability of tunnel transitions of the electrons from the filled trapping levels to the conduction zone is dramatically increased. Then, the nonradiative capture of the electrons from the conduction zone by the $\text{Eu}^{2+}$ ions proceeds, leading in appearance of the excited ions $\text{Eu}^{2+*}$. The mechanoluminescence is due to the radiative transitions of $\text{Eu}^{2+*}$ ions. It should be noted that $\text{Sr}_{4}\text{Al}_{14}\text{O}_{25}:(\text{Eu}^{2+}, \text{Dy}^{3+})$ powder under the same loads does not exhibit any mechanoluminescent properties. The features of mechanoluminescence behavior observed in the experiments agree well with the dislocation mechanism [1, 17] that associates its appearance with curving of the energy bands and levels in the vicinity of dislocations.

3. Conclusion
The paper deals with the mechanism of excitation of the photoluminescence and mechanoluminescence of the cited above powders. It has been shown that the nonuniformly broadened band of photoluminescence of the $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$ microparticles with the maximum $\lambda=525$ nm is divided into several spectral bands (573 nm, 693 nm and 755 nm) with an increase in the exciting radiation power. A mechanism of mechanoluminescence excitation is suggested. It is anticipated that mechanoluminescence is excited due to activation of the traps when they interact with the moving grain boundary dislocations at the moment of exposure to the acoustic pulse.

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