



## Excitation Luminescence of Microparticles $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$ in a Liquid at the Phase Transition Liquid – Crystal

A. A. Banishev<sup>1</sup> and A. F. Banishev<sup>1\*</sup>

<sup>1</sup>*Institute on Laser and Information Technologies RAS (ILIT RAS), Svyatoozerskaya Str. 1, 140700 Shatura, Moscow Region, Russia.*

### **Authors' contributions**

*This work was carried out in collaboration between both authors. Authors AAB and AFB made equally contribution to the work performance. Both authors read and approved the final manuscript.*

### **Article Information**

DOI: 10.9734/BJAST/2016/29871

#### Editor(s):

(1) Verlicchi Paola, Department of Engineering, University of Ferrara, Via Saragat 1, Ferrara, Italy.

#### Reviewers:

(1) Raunak Kumar Tamrakar, Bhilai Institute of Technology, India.

(2) Lung-Chien Chen, National Taipei University of Technology, Taiwan.

Complete Peer review History: <http://www.sciencedomain.org/review-history/16985>

**Original Research Article**

**Received 1<sup>st</sup> October 2016**  
**Accepted 9<sup>th</sup> November 2016**  
**Published 22<sup>nd</sup> November 2016**

### **ABSTRACT**

An investigation was conducted of mechanoluminescence of aqueous suspension of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  phosphor fine-disperse powder in the process of water crystallization (liquid-crystal phase transition) under fast cooling in liquid nitrogen. At the instant of water crystallization, the suspension revealed a glow which was associated with excitation of mechanoluminescence of the phosphor microparticles under mechanical stresses caused by crystallization of water. The phosphorescence and mechanoluminescence of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  phosphor microparticles were studied in the photopolymer matrix with temperature variation from the room to liquid nitrogen temperature. The phosphor mechanoluminescence was shown to weakly change on temperature lowering, while the photoluminescence decayed fast.

**Keywords:** *Phosphorescence; mechanoluminescence;  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  fine-disperse powder; polymer; composite material; low temperatures; crystallization.*

\*Corresponding author: E-mail: [banishev@mail.ru](mailto:banishev@mail.ru);

## 1. INTRODUCTION

Mechanoluminescence (ML) is the ability of materials to luminescence (glow) under mechanical stresses (bending, compression, shock, vibration, etc.). By now, a great number of materials are known to exhibit the mechanoluminescence property [1]. The mechanoluminescence intensity of different materials can differ by orders. Some materials offer high luminescence efficiency, for example, the ZnS:X phosphor (where X=Mn, Cu, Al). Lively interest has currently been shown to the research of mechanoluminescence of alkali-earth aluminates doped with rare-earth components, for example, strontium (calcium) aluminates  $\text{Sr}(\text{Ca})\text{Al}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  [2-9]. These aluminates (phosphors of long afterglow) present a significant class of phosphorescent materials which show high quantum efficiency and fluorescence persistence in the visible spectrum and possess a pronounced mechanoluminescence property.

Thus, the new possibilities for practical use of these materials as sensing elements for mechanical actions, in particular, have been defined [10,11]. In [12], it is suggested that the mechanoluminescent properties of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  microparticles be used to activate photocatalytic processes in the regions of material inaccessible for radiation delivery.

Despite the practical interest to these materials, their physical properties call for further study. There is no consensus to date on the mechanism of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  mechanoluminescence excitation. There are no convincing facts regarding the location of the energy levels of  $\text{Eu}^{2+}$  activator ions and traps in the forbidden zone; the type of traps (electron or hole) has not been ascertained.

## 2. EXPERIMENTAL SETUP

This paper reports on the results of research on low-temperature phosphorescence (PS) and mechanoluminescence (ML) of fine-disperse powder of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  phosphor in the polymer matrix.

The polycrystalline fine-dispersed powder of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  phosphor was prepared in the course of high-temperature solid state reaction of the mixture of components  $\text{SrCO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Dy}_2\text{O}_3$  having stoichiometric

composition. The dimensions of phosphor microcrystals were  $0.5 \div 30 \mu\text{m}$ .

Mechanoluminescence of the phosphor microparticles in the liquid was investigated in the process of liquid crystallization (liquid-crystal phase transition). The mechanisms of PS and ML excitation in the materials are discussed.

The investigation of photo- and mechanoluminescence of the phosphor microparticles in the photopolymer matrix involved the use of a suspension of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  phosphor powder and photopolymerizing resin in a 1:3 weight ratio.

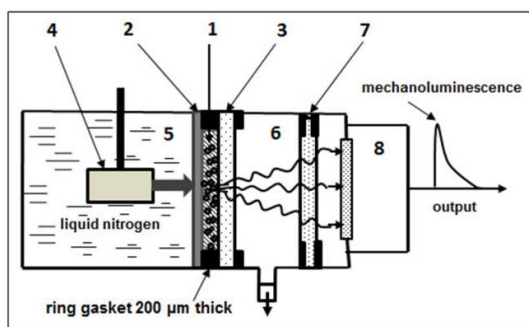
To study the phosphor microparticles mechanoluminescence in water (liquid-crystal phase transition), a suspension was made of fine-disperse powder of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  phosphor and water in a 1:1 weight ratio. The effect of hydrolysis of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  during the measurement (about 10 minutes) can be neglected. A thin layer of liquid suspension 1 (Fig. 1) was applied to the metal substrate 2 with the diameter of  $d \approx 3 \text{ cm}$  and the thickness of  $h \approx 100\text{-}200 \mu\text{m}$ . The liquid suspension was covered and squeezed with a quartz plate 3 with the diameter of  $d \approx 3 \text{ cm}$  and the thickness of  $h \approx 1 \text{ mm}$ . For specifying the certain thickness of the suspension layer, a ring gasket 200-300  $\mu\text{m}$  thick was placed beforehand between the metal substrate and the glass plate. Thus, the thickness of suspension made 200-300  $\mu\text{m}$ .

Then the samples were put into the light-tight camera, so that the suspension was inside the camera, i.e. shielded from light, but the metal substrate on the outside of the camera faced the cuvette. It was possible to fill the cuvette with liquid nitrogen and cool the suspension fast to the temperature of liquid nitrogen. Fig. 1 shows the scheme of the experimental setup.

The suspension and photopolymer were exposed in advance for  $t \approx 10 \text{ min.}$  to UV radiation of the mercury-vapor lamp for suspension hardening. This resulted in formation of a solid film of composite material on the substrate surface.

Phosphorescence and mechanoluminescence of the resulting composite material were studied at

the room temperature ( $T \approx 293\text{K}$ ) and at the temperature of liquid nitrogen ( $T \approx 77\text{K}$ ). Phosphorescence was excited by helium-cadmium laser radiation ( $\lambda = 327\text{ nm}$ ). Excitation of ML was attained by the action of pulsed impact mechanical stresses. The spring-loaded hammering device with tapered tip, used for this purpose, was installed on the substrate side in the cuvette containing liquid nitrogen. The phosphorescence and mechanoluminescence signals were recorded by a visible-spectrum photomultiplier placed on the film side at the distance  $l \approx 5\text{-}6\text{ cm}$ .



**Fig. 1. The scheme of the experimental setup:**  
 1 – mechanoluminescent suspension;  
 2 – metal substrate; 3 – glass plate; 4 – hammering device; 5 – cuvette with liquid nitrogen; 6 – light-tight vacuum camera; 7 – output window; 8 – photomultiplier

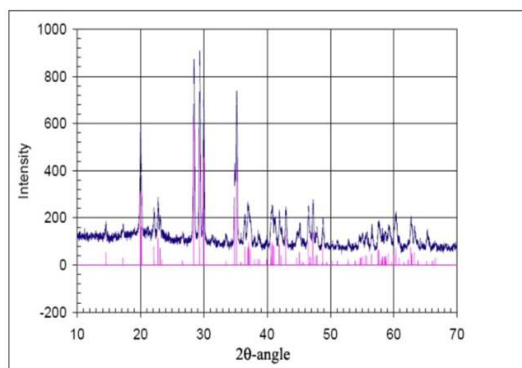
### 3. RESULTS AND DISCUSSION

Fig. 2 presents an X-ray diffraction pattern of the fine-dispersed powder of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  phosphor. The diffraction peaks of the powder are seen to correspond to the crystalline structure of  $\text{SrAl}_2\text{O}_4$  (the symmetry group  $P2/m$ ). The scanning electron microscopy (SEM) images of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  phosphor powder are shown in Fig. 3. It is seen that the powder consists of the coarse granules as large as  $200\mu\text{m}$ . The granules are formed from a set of smaller grains of the sizes from  $0.5\mu\text{m}$  to  $30\mu\text{m}$ .

Fig. 4 illustrates the variations in glow phosphorescence intensity (i.e. in the afterglow intensity) of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  phosphor microparticles in the photopolymer matrix in the process of cooling in liquid nitrogen. The dotted line denotes the moment of submersion into the liquid nitrogen.

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 kind of the spectrum is temperature dependent, which is generally associated with temperature quenching of the photoluminescence peak at the wavelength of  $450\text{ nm}$  [9,13-14]. 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. We suppose that thermal activation of the shallow traps with the depth of  $\Delta E \approx kT(300\text{K})$  mainly contributes to phosphorescence. With the temperature lowering, the probability of trap thermal activation as well as the phosphorescence intensity are expected to decrease, which is consistent with the results obtained in [13] and with Fig. 4 of our work.



**Fig. 2. X-ray diffraction (XRD) pattern of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$**

This phosphorescence behavior is in whole consistent with the conventional mechanism of phosphor long afterglow. According to this mechanism, phosphors contain the traps (of electrons or holes) which are capable of accumulating light energy, i.e. capturing the charge carriers generated as the result of photoexcitation of the phosphor luminescence centers. 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 (electron traps,  $E_n$  is measured from the bottom of conduction band) or near the valence band top (hole traps,  $E_p$  is measured from the valence band top). We believe, as it is reported in paper [9], that  $\text{Dy}^{3+}$  impurities and structural defects in the  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  phosphor form the hole traps, and the intensity and duration of phosphorescence are governed by thermal activation of the hole traps  $E_p \approx kT(300\text{K})$ .

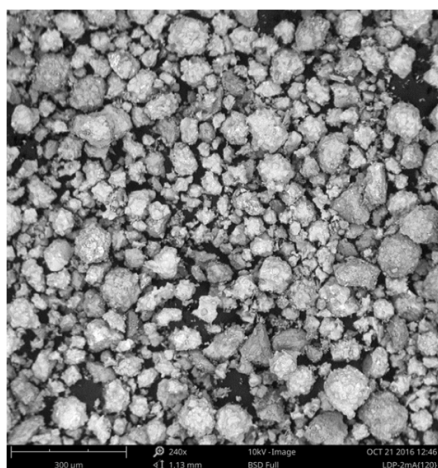


Fig. 3a

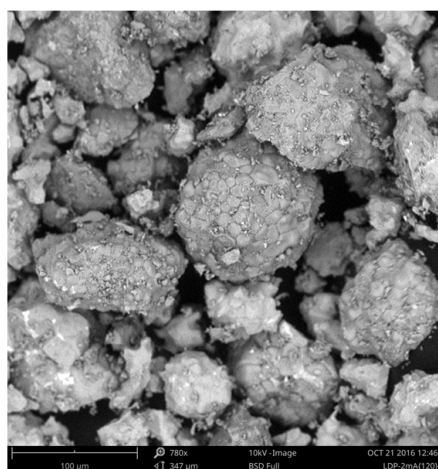


Fig. 3b



Fig. 3c

Figs. 3a-c. Scanning electron microscopy images (SEM) of  $\text{SrAl}_2\text{O}_4:\text{Dy}^{3+}$  phosphor

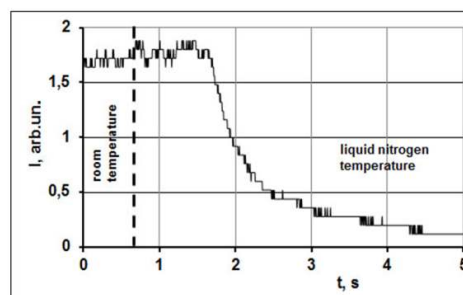


Fig. 4. Temperature dependence of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  phosphorescence

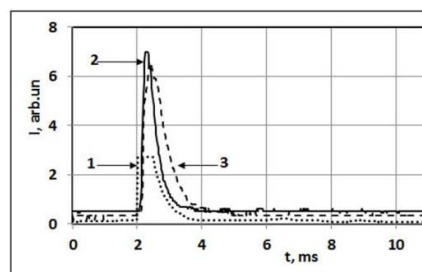
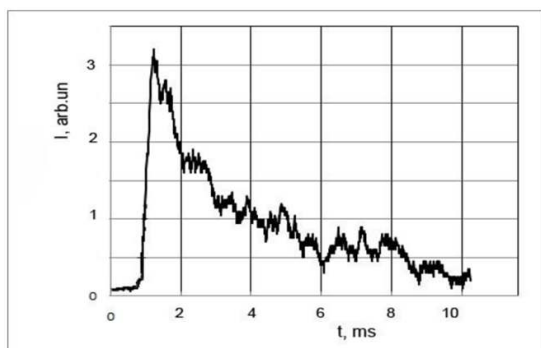


Fig. 5. 1 - The curve illustrates the duration of mechanical impact on the sample;  
2 - mechanoluminescence of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  at room temperature;  
3 - mechanoluminescence of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  at liquid nitrogen temperature

Fig. 5 above depicts a ML signal at the room temperature and at the temperature of liquid nitrogen. The investigation of mechanoluminescence was pursued on the samples that had been kept at room temperature in darkness for a long time (more than 24 hours) till total attenuation of phosphorescence. The samples were then cooled to the liquid nitrogen temperature; mechanoluminescence was also studied under the same mechanical action. The intensities of mechanoluminescence at room temperature and at the liquid nitrogen temperature were only slightly different. Hence, we suppose that a considerable contribution to mechanoluminescence intensity is made by the deep traps of  $\Delta E > kT(300\text{K})$  depth. Thermal activation of these traps at low temperatures is unlikely, but their activation is possible under a mechanical action.

Fig. 6 displays mechanoluminescence that emerges on cooling of the aqueous suspension of the fine-disperse powder phosphor  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$ . The investigation of mechanoluminescence was pursued on the samples that had been kept at room temperature in darkness more than 24 hours till total

attenuation of phosphorescence. Since the suspension is contained in a tightly closed volume and occupies the whole volume (as shown in Fig. 1), water crystallization causes a pressure jump (it is known that water expands upon crystallization). If under the same conditions water is cooled, no glow pulse is observed. But since the suspension cooling gives rise to a glow pulse, we relate this phenomenon to mechanoluminescence of the phosphor particles during water crystallization. As shown in the figure, the shape of the ML signal differs from the shape formed by a shock.



**Fig. 6. Mechanoluminescence at crystallization of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  powder aqueous suspension**

It has been revealed in [8] that strong mechanoluminescence of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  is only observed in the piezoelectric phase  $\alpha$ - $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  with the twin structure.

In recent years in a number of studies, for example, [10,11,15], the excitation of mechanoluminescence has been explained by the interaction of traps with piezoelectric fields arising during the deformation of the material.

The authors of [16-19] suppose that excitation of ML occurs in the process of crack formation in the material under the impact. The electric field emerging between the crack walls causes a reduction of the depth of traps that increases the probability of their activation.

In our work, mechanoluminescence takes place under uniform compression of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  microparticles during the liquid suspension crystallization (phase transition), when their polarization is insignificant. We cannot advocate that in this case crack formation happens in the granules under compression. Deformation of the granules resulting in a displacement (sliding) of the grains relative to each other seems more

probable. A change in the energy of interaction of the grain surface layers in sliding can bring about a decrease of the depth of traps in the surface layer and their activation.

#### 4. CONCLUSION

The low-temperature investigations of phosphorescence and mechanoluminescence of the composite based on the  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  phosphor fine-disperse powder in the photopolymer and the phosphor powder suspension in water have been conducted. It has been found that the intensities of phosphorescence of the composite are fast decreased as the temperature lowers from the room value to the liquid nitrogen temperature, whereas the intensity of mechanoluminescence does not practically change on cooling. This implies the existence of the shallow traps ( $E_p \approx kT(300\text{K})$ ) with high probability of thermal activation, and the deep traps whose thermal activation is highly improbable. The intensity and duration of phosphorescence are controlled by thermal activation of the shallow traps. The intensity and duration of mechanoluminescence largely depend on activation of the deep traps in the process of mechanical action.

Mechanoluminescence of the suspension of  $\text{SrAl}_2\text{O}_4:(\text{Eu}^{2+}, \text{Dy}^{3+})$  phosphor fine-disperse powder in a liquid (water) was investigated in the process of liquid crystallization (liquid-crystal phase transition) on fast cooling in liquid nitrogen. At the instant of water crystallization the suspension revealed a glow which was associated with excitation of mechanoluminescence of the phosphor microparticles under the action of a jump of compressive mechanical stresses arising in the volume at the liquid-crystal phase transition. The shape of mechanoluminescence signal differs essentially from that of ML signal observed under mechanical shock.

The work has been supported by the Russian Foundation for Basic Research (Grant № 16-29-14003).

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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