Stimuli-Responsive Mechanoluminescence in Different Matrices

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ABSTRACT: Here, for the first time, we investigated the effects of matrices with different nature on the stimuli-responsive mechanoluminescence (ML) of incorporated nanoparticles. It turned out that the contraction forces initiated by polymerization process can have compressive effects that differ by orders. This effect was achieved owing to the introduction of ML crystals in an alumina sol–gel system, which has large surface of coagulation contact. As one particle of boehmite results in a tension of 10^{-17}−10^{-16} N per one particle of matrix, compared to 10^{-19} N of PDMS matrix, the threshold of mechanoluminescence was reached at 0.04 Pa, whereas the most active materials to date did not exceed this value. Thus, this material can be a perspective for the production of impact detectors, photonic displays of the next generation, and other advanced devices.

INTRODUCTION

Nowadays, the steady trend to transition from electronic elemental base and electric systems to photonic ones is seen. The new direction of research—photronics—has a huge amount of achievements, which are used increasingly during the development of information-measuring systems of new generation, so the interest in sensor elements or photon-induced materials based on ML properties increases. Because the feature of as-mentioned sensor elements is a direct transformation of mechanical action into an optical signal, these can be integrated in fiber-optic information-measuring systems and networks. Sensor elements may be applied in common with devices of integral and fiber optics, impact detectors, registration and monitoring systems of impulse mechanical loads and vibrations, and production of sensor photonic displays of new generation. Furthermore, application of these elements in optical memory cells is highly perspective. Mechatronic networks based on mechanoluminescent sensor elements and fiber-optic data transmission lines are insensitive to external electromagnetic interference, which provides automatically galvanic isolation. The use of amplitude–time parameters of optical signal, its spatial modulation, spectrum (color), and polarization state raises the informativity of transmitted signal. In this case, both investigation of known ML materials, which are rather effective in the transformation of mechanical action into optical signal, and the search for new ones become especially actual. A large number of chemical compounds are famous for their mechanoluminescence (ML). Despite the common name, ML mechanism varies in different groups of composites, which is important for further mechanoluminophore application in device engineering. At the moment, mechanisms of several groups of compounds, such as metals and quartz, semiconductors doped with d metals in the form A(II)B(VI), and composites MAl2O4 (M = Sr or Ba) doped with rare-earth elements, are relatively well studied. The recent reviews reported and summarized the information about ML materials and described further applications of composites (bioapplications are also present) and some perspectives of this field of science.

However, it is now hard to achieve light emission because strong mechanical action is required for an ML effect. In this work, we examine the influence of an alumina sol–gel matrix on mechanoluminescence and compare its effect with an Si-organic matrix. The investigation was carried out with use of SrAl2O4:(Eu²⁺,Dy³⁺) nanocrystals.

ML process in a group of chemical composites MAl2O4 (M = Sr or Ba) doped with rare-earth elements (i.e., europium and dysprosium) is the result of a multistage mechanism, as seen in Figure 1a and shown as the original mechanism by Dorenbos et al.20 In this case, electrons that are excited from Eu²⁺ are released to the 5d level. Next, these are caught by Dy²⁺ ions. Then, when strong mechanical action is required for an ML effect, these are released to the conduction band, which is situated close to the 5d level. Next, these are caught by Dy²⁺ ions. Then, when pressure is applied, recombination takes place, which results in light emission (Figure 1b).

Organic (PVC) or inorganic (silica) substrates may be used as matrices of mechanoluminescent crystals. The highest emission was reached owing to polydimethylsiloxane (PDMS) matrices. However, a soft PDMS matrix absorbs the basic load and transmits enough amount of energy to tribocrystals only under conditions of significantly high tension. The general

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advantage of alumina matrix is its ability to demonstrate contraction. While the gel is desiccated, recombination of matrix particles happens, which results in its compression. This provides an additional load to ML crystals, which are included in the matrix, so the required value of force for the activation of ML effect decreases.

It is known that the state of the luminescent material and its photon emission can be significantly influenced by the matrix, which contains a luminescent substance, or by a solvent with this material. The purpose of the study is to investigate the influence of different transparent matrices on ML properties of Sr0.95Eu0.02Dy0.03Al2O4 nanoparticles, followed by the possibility of coating creation, which is able to induce photon emission in the visible spectral region under an action of extremely low loads.

## RESULTS AND DISCUSSION

Contraction Phenomenon in the Composites. The effect of contraction forces, which emerges during condensation of colloidal inorganic systems, is found to exert a favorable action on mechanoluminescence. The most interesting example of this effect is the observed consequence of transition of the crust from the liquid to the solid state, which is supported by the generation of a developed rough surface that is mountains (Figure 2d). Tangential forces of compression originating from these formations are highly valuable, because crustal folding, oscillatory motion, magma rising, and discontinuous dislocations are produced. The translation of analogous processes to micro- and nanoscale processes leads to the same effects. For instance, drying of hydrogels, regardless of their characteristics, is connected to a drop in surface tension of intermicellar liquid. It is obvious that if the surface tension of intermicellar liquid falls, then capillary contraction forces, which thicken a structure of a solid body, will decrease. Sol–gel transition, such as the formation of a hard xerogel with inorganic network compaction, depicts the most successful example of this phenomenon. At the same time, the instances of liquid-phase hardening, when a compressing action on damped objects is absent, are known. One example of these is the production of amber, which is a high-molecular-weight compound of organic acids (Figure 2b). Consequently, it is possible to assume that the mechanisms of contraction force action in organic and inorganic polymers are principally different. According to the SEM data in Figure 2a,c, the same effects are observed at the studied systems. Namely, Figure 2c demonstrates strontium aluminate formations, which stand out on the surface of boehmite xerogel. These were obtained during the polycondensation process and drying of the xerogel. On the other hand, the organosilicon matrix does not show the effect that is identical to the classical behavior of organic polymers (Figure 2a). The comparison involved allows the determination of the influence of matrices on the processes of quenching and amplification of mechanoluminescence of encapsulated objects.

### XRD Data.

The XRD pattern of Sr0.95Eu0.02Dy0.03Al2O4 phosphor samples is depicted in Figure 3 as the gray graph. It is shown that the diffraction peaks match well with the 90 JCPDS card no. 74-0794, indicating that the pure monoclinic crystal structure with space group P2 is obtained. Co-doping with Eu2+ and Dy3+ does not cause any significant change in the host structure. Diffractograms of composite materials based on alumina and PDMS matrices, which were obtained in the presence of Sr0.95Eu0.02Dy0.03Al2O4 nanoparticles, prove the preservation of strontium aluminate structures (characteristic peaks of strontium aluminate present on both composites). Moreover, the structure of matrices also persists in composites. The only difference is the appearance of a wide peak in the alumina composite (left graph, wide peak at 20°) due to the presence of polyvinyl alcohol as a stabilizer in this system.

### Influence of Solvent on Phosphorescence.

As MO: xAl2O3 doped with rare-earth elements are usually produced by the ceramic method, it was comfortable to employ the ball mill to obtain the acceptable fine powder of strontium aluminate doped with Eu and Dy. This methodology partially destroys the crystal structure of powders and increases their reactivity. As soon as the ground powder is in contact with water, the hydrolysis reaction looks like

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**Figure 1.** (a) Mechanism of mechanoluminescence in SrAl2O4(Eu2+,Dy3+) crystals by Matsuzawa et al., where 1 is Eu2+, 2 is Eu+, 3 is the dot, 4 is Dy4+, 5 is Dy3+, and 6 is the quantum of light. (b) Band model of recombination processes in a crystal of SrAl2O4(Eu2+,Dy3+) by Dorenbos et al.

**Figure 2.** Different examples of the presence or absence of contraction. (a–d) SEM images of (a) Sr0.95Eu0.02Dy0.03Al2O4@PDMS, (b) hardening of amber without compressing tension, (c) Sr0.95Eu0.02Dy0.03Al2O4@alumina, and (d) mountain formation provided by tangential forces of compression during hardening of the crust.
\[
\text{SrAl}_2\text{O}_4 + 4\text{H}_2\text{O} \rightarrow \text{Sr}^{2+} + 2\text{OH}^- + 2\text{Al(OH)}_2^+ + 2\text{O}_2
\]

Hydrolysis products include aluminum hydroxide and are soluble in water strontium hydroxide, which lowers the pH of the medium after dissolution of the powder. During hydrolysis, phosphorescence of the powder is assumed to degenerate, whereas the crystal structure of luminophores decays. Polyvinyl alcohol played the role of a modifying additive in this work to avoid the abovementioned effect, since it prevented direct contact with water molecules because of competitive physisorption from the solution, stabilized the formed coatings, and declined their fragility. Figure 4 depicts the dynamics of phosphorescence change in \(\text{Sr}_{0.95}\text{Eu}_{0.02}\text{Dy}_{0.03}\text{Al}_2\text{O}_4\) entrapped in the alumina matrix during the drying process. It is shown that primary emission persists after drying. The graphs of excitation of the green-blue region at wavelengths from 400 to 480 nm and intensity of photoluminescence (PL), which were measured before drying, are displayed in Figure 4a,b, respectively. It is found that PL has two peaks at excitation wavelengths of 400 and 440 nm (the material glows in interval between blue and green regions). Upon drying, the photoluminescence of the composite shifted mostly from blue to green regions (Figure 4c,d). The curves depicted by solid lines from Figure 4c correspond to two states of phosphorescence, where the left line is photoluminescence before drying, the right line is photoluminescence after drying, and the intermediate lines are photoluminescence during drying. In our previous work, it was demonstrated that water is removed upon drying of the alumina gel, which results in this shift.

**Influence of the Matrix on Quenching of Phosphorescence.** Thermal quenching of crystallophore phosphorescence is connected not only with the impact of heating on a glowing center but also with the appearance of the new process—the filling of excited electron-free centers by electrons rising from the valence band, which is influenced by thermal energy. The resulting neutralized emissive centers can no longer play a role in further recombination processes. The dots, which were formed as a result of escape of electrons, move through the valence band, meet the centers of quenching, and localize to these. For the sustainable localization, it is necessary that the levels of quenching centers situated up on the valence band were noticeably higher than the levels of the glow centers. In this position of the quenching levels, electrons from the valence band cannot rise to the localized dots by the thermal path. The dots recombine with electrons from the conduction band. However, recombination close to the quenching center does not glow. Although it is
taken from the point of view that PDMS and alumina matrices have principal differences at their thermal conductivity properties (Table 1), it becomes clear that the activation of these processes proceeds in different ways. As shown in the obtained data (Figure 5a), the mechanism of phosphorescence quenching in the boehmite matrix has the character of a pseudo-first-order kinetic model, whereas the PDMS matrix has a zero-order character. Most likely, this is connected with the appearance of diffusion heat transfer processes in matrices, because their heat-conducting properties are different essentially, as depicted in Table 1. It is clearly seen in Figure 5b that the introduction of ML particles in matrices does not have an essential influence on phosphorescence lifetime: the form of graphs and lifetime values of composites are close to the original.

**Dependence of Contraction Forces on the Nature of the Matrix.** The development from the sol–gel state of boehmite to xerogel is a multistage process, which contains both ion-exchange process and drying. The bonds recombine, and the volume decreases in the alumina matrix upon drying because of solvent removal. Hence, the matrix compresses and squeezes the phase entrapped in it. The setup was constructed for the detection of the value of these forces (Figure 12), which is described in Experimental Details. The dependence of compressing action in time in the boehmite gel, which was measured during the drying process, versus cross-linking of the PDMS matrix is depicted in Figure 6 (left).

As illustrated in the left graph of Figure 6, the forces of capillary contraction thicken the structure of the alumina matrix during the drying process (stage I), followed by the convergence of its elements and providing the possibility of the appearance of numerous secondary cohesive and adhesive strengthening bonds (stage II) over the growth of coagulation contact between particles when dried. The intensity of these forces rises during drying and reaches the maximum at the border of conversion gel–xerogel. The last step of viscosity increase is characterized by total liquid removal, so that the forces of capillary contraction gradually disappear (stage III). For the PDMS matrix, those phenomena were not observed, which is assumed to take place because of independent effects from the stage of drying and density fluctuations of particle coagulation contact.

Macroscopic measurements of compression described above are equitable for volume \( V = 0.3 \) mL of both composites before drying. The compression of alumina (average diameter of particle is 15 nm) and PDMS (average molecular weight is 27,000, repeating unit molecular weight of 207.4 g/mol) per one particle of matrix was calculated to estimate the contraction forces. The assumptions of further calculations are as follows: (1) the compression force is evenly distributed throughout all units of the matrix

\[
F = F_0 \times N
\]  

(1)

where \( F \) is the compression force of the matrix, \( F_0 \) is the force per one unit (particle of alumina or PDMS molecule), and \( N \) is

| Table 1. Material Data of Alumina, PDMS, and Strontium Aluminate according to Previous Investigations |
|---------------------------------------------------------------|
|                     | alumina (boehmite) | PDMS | strontium aluminate |
| coefficient of thermal expansion, \( 10^{-6} \cdot K^{-1} \) | 5.50 | 3.10 | 9.54 |
| coefficient of thermal conductivity, W/(m·K) | 30 | 0.15 | 3.6 |
| references | 23 | 24 | 25, 26 |

**Figure 5.** (a) Thermal quenching of phosphorescence. (b) Lifetime values of active centers. The measurements were carried out in a ditch quartz cell by an Agilent Cary Eclipse fluorometer with \( \pm 0.05 \) °C precision and an excitation wavelength of 440 nm.

**Figure 6.** Dependence of the compression forces on time during the process of drying of the initial matrices based on boehmite and PDMS in bulk (left) and per one particle of matrix (right).
the amount of units in the volume \( V \); (2) boehmite forms spherical nanoparticles with radius \( r = 7.5 \text{ nm} \), and its volume \( (V_p) \) is

\[
V_p = \frac{4}{3}\pi r^3
\]

Thus, \( F_0 \) can be found as

\[
F_0 = \frac{F}{C_M \cdot V \cdot N_i} \times \frac{V_p}{V_{\text{mol}}}
\]

For PDMS, one particle is considered as one molecule \( (V_p = V_{\text{mol}}) \), so the second fraction in eq 3 transforms to 1. The results of calculations are shown in Figure 6 (right graph). The stress of one particle of alumina in \( N \) is stated to be higher by two orders than the stress of one PDMS molecule. Consequently, the inorganic matrix should activate triboluminescence more intensively and suppress the absorption of mechanical load. Taking into account the value of operating forces on the model nanoparticle after entrapment in the alumina matrix, morphological transformation of trapped strontium aluminate nanoparticles was discovered. It is expected that this transformation is the edge dislocation of crystalline layers relative to each other. The determination of composition of eluted formations by the EDX mapping method (Figure 7) proves this conclusion. According to the data obtained, outgrowths with a similar composition to strontium aluminate form on the surface of alumina xerogel during the drying process. Their presence is explained by partial hydrolysis of trapped strontium aluminate particles and by the action of capillary contraction forces on these objects during the drying process. In this way, the consequence about the possibility of an excessive compressive load on the trapped objects in sol–gel systems over this process is established.

The viscometry graphs of alumina and PDMS matrices are displayed in Figure 8a. Alumina gelaes over 5 min, whereas PDMS cures for 10 min. This demonstrates that these materials harden fast enough to cause production, as soon as its cycle gives the required time for convenient processing.

Fluctuations of luminescence intensity depending on applied load were measured to acknowledge the aforementioned information. The change in emission intensity due to mechanical tension (triboluminescence) is shown in Figure 8b. According to the data obtained, the activation thresholds of triboluminescence for \( \text{Sr}_{0.95}\text{Eu}_{0.02}\text{Dy}_{0.03}\text{Al}_2\text{O}_4 \) entrapped in matrices with various chemical nature are significantly different. This proves the conclusions about the presence of residual tension in the system and the residual action of compression forces in inorganic sol–gel matrices contrary to organic ones. For instance, the activation threshold of triboluminescence for the PDMS matrix is 0.21 \( \text{Pa} \), whereas that for the alumina matrix is only 0.04 \( \text{Pa} \). It is obvious that the use of inorganic matrices, which condense with compaction of their skeleton, has a positive effect on the excitation of triboluminescence of the captured agent. Particularly, this may be applied as photon-induced coatings, which activate by applying pressure using a human finger (Figure 9).

One more perspective form of the application of highly sensitive ML composite is the advanced glowing detector on a product package. Namely, if some products, such as dairy and meat products, are spoiled, excess gas medium will generate inside a package with this product. Obviously, gas generation is a result of the vital activity of bacteria, and it is dangerous to consume such products. The additional pressure of this gas results in mechanical deformation of a package (swelling). Thus, because an alumina ML material is very active, we assumed that a triboluminescent label added on the cover of a fermented milk product can serve as the visual detector of its freshness (Figure 10).

First, a package with an ML indicator was exposed to UV irradiation to activate tribocrystals inside the composite material. In the case of a product before its expiration date, a very dim glow was observed (Figure 10c), because any pressure influenced the label. On the other hand, a package swelled after the expiration date and pressurized the cover with the...
an ML composite, so it glowed rather brightly. The experiment proves that the alumina-based triboluminescent material can help discourage customers from buying spoiled products due to visibility and impossibility to hide the fact of spoilage.

**CONCLUSIONS**

Overall, this investigation reports how matrices with different nature have an influence on the mechanoluminescent and morphological properties of corresponding composite materials, which consist of Sr$_{0.95}$Eu$_{0.02}$Dy$_{0.03}$Al$_2$O$_4$ dispersed in a matrix. The alumina xerogel and PDMS were chosen as inorganic and polymer matrices, respectively. As a result, the threshold of triboluminescence activation of the alumina composite was seen to require a rather weak external tension because of internal contraction phenomenon of the matrix, which takes place during the drying process. Because this phenomenon is absent in polymer compounds and these matrices absorb external tension, the boehmite triboluminescent material activates at load, which is lower by two orders, than the PDMS composite (0.04 Pa vs 0.21 Pa). Finally, authors expect that inorganic matrices will expand their application in mechanoluminescent devices, such as impact detectors or photonic displays, because most of the developed materials do not exceed their properties.

**EXPERIMENTAL DETAILS**

**Chemicals.** Aluminum isopropoxide (98%, Aldrich), strontium aluminate (europium- and dysprosium-doped, Aldrich), polyvinyl alcohol (PVA) ($M_w \approx 31,000$, Mowiol 4-88, Aldrich), Sylgard 184 (Aldrich), and nitric acid (65%, ACROS Organics) were used.

**Alumina Sol Synthesis.** The technique described in ref 27 was employed to synthesize the sol–gel boehmite matrix. Aluminum isopropoxide (8.2 g) was added to 50 mL of distilled water, which was heated to 90 °C. This step resulted in immediate formation of a white precipitate. After that, the obtained mixture was thoroughly stirred for 15 min at 90 °C. Thus, the formation of boehmite nanoparticles was stopped, and isopropanol, which was collected because of hydrolysis, was evaporated. Finally, 1 mL of concentrated nitric acid was poured into the mixture and cooled down to room temperature under continuous stirring.

**PDMS Synthesis.** The matrix based on PDMS was produced from Sylgard 184, which contains two parts: a polymer and a cross-linker. First, these parts were mixed at a weight ratio of 10:1 (base/curing agent). Then, the mixture was put in a vacuum oven to remove air bubbles and stop them from forming. After that, this matrix was applied to produce composites.

**Preparation of ML Samples.** The Sr$_{0.95}$Eu$_{0.02}$Dy$_{0.03}$Al$_2$O$_4$ powder was shredded preliminarily by a ball mill (0.03 g) up to 100 nm average diameter and immersed in concentrated boehmite sol (1 mL) with polyvinyl alcohol as a stabilizer (2 mL of 4% aqueous solution) or mixed with PDMS matrix (3 mL). Thus, the concentration of SrAl$_2$O$_4$: (Eu, Dy) in solutions was $4.78 \times 10^{-5}$ mol/mL. These mixtures were stirred thoroughly and left in air until complete drying and curing. The scheme of the process involved is shown in Figure 11. Thus, both thin films were obtained, which covered flexible substrates and individual thin films with low mechanical strength.

**Characterization.** A Tescan Vega3 electron microscope was employed for surface scanning of the created composites. X-ray structural analysis was made by a Bruker D8 Advance apparatus using Cu K radiation ($\lambda = 1.54$ Å); scanning was conducted at $20 \mu$ at a speed of 0.5° per minute. Measurements by dynamic light scattering were implemented by means of a Photocor Compact-Z analyzer at 25 °C. pH level was regulated by 0.1 M HCl or 0.1 M NaOH. Fluorescence emission spectra and spectra of excitation of colloidal solutions were measured through water. Thermal quenching of phosphorescence was measured in a ditch quartz cell by an Agilent Cary Eclipse fluorometer with ±0.05 °C precision. Viscosity gain of the alumina matrix was measured by a Fungilab Expert Series viscometer. Mechanoluminescence was detected by an Ocean Optics Flame spectrometer (Figure 12a). The tripod UV laser (power, $<300$ mW; $\lambda = 375$ nm) focused through a quartz window was fixed on the contact point of the examined sample and a texturometer was traversed to the sample, so that induced mechanoluminescence is present at the load point. Next, the texturometer traversed down to the sample while making the tension required for fast initiation of mechanoluminescence at the load point (Figure 12c). Meanwhile, luminescence intensity changes were detected by a Flame-S-UV-Vis spectrometer (Ocean Optics) and were transmitted to the computer. Thus, the dependence of luminescence intensity on the degree of loading was recorded. Compression forces were measured by an Instron 5943 strain gauge machine. The model of the experiment is shown in Figure 12b. The alumina or PDMS matrix (0.3 mL) was set between two planar surfaces made of nickel polished plates (diameter = 1.5 cm), which
were fixed in a strain gauge machine, at a distance of 1 mm (Figure 12d). After that, registration of contraction forces occurred, which are conditioned by compression of the matrix during condensation process and air drying.

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**Author Contributions**

A.V.V. and V.V.V. designed the study. D.A.I. and N.A.T. prepared the samples and made the SEM analysis. N.A.T. made the ML, viscosity, thermal quenching measurements. A.V.V. made the EDX mapping and contraction measurements. D.A.I., A.V.V., and N.A.T. wrote the paper. D.A.I., A.V.V., and V.V.V. analyzed the data and created the figures. All authors approved the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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