Functional materials based on the effect of mechanoluminescence for monitoring the state of load-bearing structures

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Abstract. Researches of light-generating converters based on zinc sulfide allowed us to describe the physical nature of the light signal. The description of the physical nature of light generation by semiconductors is based on the band theory of conductivity. This allowed us to determine the conditions for the possibility of registering mechanical impacts using mechanoluminescent pulse pressure sensors. One of the important conditions, as it turned out, is the presence of manganese impurities in the material, which become centers of light emission. Also a necessary condition for the appearance of luminescence is the hardness of the sensor element, it facilitates the transfer of mechanical stress to the crystal lattice of mechanoluminescent material and the changes in it with the release of energy as light. This property of these materials allows them to operate in generator mode and convert mechanical action into an optical signal without additional energy sources. As a result, theoretical and experimental data on the possibility of detecting pulsed mechanical action using distributed mechanoluminescent converters were obtained. As one of the directions of application of such converters, it is proposed to create composite materials with the insertion of light-conducting fibers with longitudinal light transmission, covered with mecanoluminophore particles. This will allow to create composite materials with a self-diagnosis function and the ability to connect to optical data channels for continuous monitoring of the technical condition of load-bearing structures of buildings. Such materials are devoid of such disadvantages as: the need for power supply or a reference light stream, sensitivity to electromagnetic interference, and a low degree of embeddability in the structure, inherent in the devices currently used.

1. Introduction
Currently, due to the high level of development of science, engineering and technology, the environment is being actively transformed by humans. This includes activities related to the construction of new structures and the operation of buildings and structures for various purposes already put into operation. The deterioration of buildings and structures is influenced by a large number of factors, some depending on human activity (activity near the constructed and operated buildings and structures), and some are not directly related to human influence (weather factors). With all this, the issue of monitoring the condition of buildings and structures is rather acute. State standards provide rules for the inspection and monitoring of the technical condition of buildings and structures [1]. So according to this document, regarding the monitoring of the condition of buildings, the
following types of work can be distinguished: a comprehensive survey of the technical condition of buildings; general monitoring of technical condition; monitoring the condition of the supporting structures of buildings and structures and others.

Various electronic devices and sensors are currently used to monitor the technical condition. For example: strain and stress sensors; acceleration and vibration sensors (accelerometers); tilt sensors (inclinometers); displacement sensors (mechanical, electronic, geo-positioning) [2,3]. Technical equipment and methods of its use suggest placing sensors and recording devices on the studied objects [4-6]. At the same time, a large amount of time and money is spent on performing these works, and the equipment must be removed at the end of the measurements. Such monitoring is exclusively periodic in nature and its results in rapidly changing external conditions can quickly lose their relevance. To solve this problem, it is necessary to constantly monitor the state of load-bearing structures of buildings and structures.

Continuous monitoring can be carried out by placing sensors in certain places of structures and then questioning them with the measuring system. This method has a significant drawback – it is necessary to lay cable communication lines and power supply in the case of electronic sensors, and laying fiber-optic data transmission lines in the case of optical sensors. In this case, these devices need a reference power supply voltage or light output to operate. This disadvantage is denied by sensors that use the effect of mechanoluminescence in their work.

Mechanoluminescence is the light emission of solids caused by mechanical action [7,8]. Based on this physical phenomenon, sensors are designed to detect various external influences (impacts, slippage, deformation, crack formation, and destruction). Of particular note is the generator operating mode of the sensors based on the effect of mechanoluminescence. They are not sensitive to electromagnetic interference and do not need to supply reference power or optical radiation. Known works [9-12], which propose the creation of mechanoluminescent (or triboluminescent) damage sensors. As controlled objects in the descriptions of the indicated inventions, the bridge supports bearing the building structures are also indicated.

This paper provides a theoretical description of the principles of operation and the possibility of creating mechanoluminescent damage sensors and functional materials with built-in distributed mechanoluminescent sensors to ensure continuous monitoring of the state of load-bearing structures of buildings and structures. As the luminescent material in the researched sensors, zinc sulphide ZnS is used.

2. Methods
Excitation of luminescence in this class of substances is explained by the band theory of conduction. According to the band theory for ZnS-phosphors, there are three main zones – valence, forbidden, and conductivity. Electrons located in the valence or conduction bands belong to the crystal as a whole. The impurity atoms of activators and coactivators form in the forbidden zone local levels of luminescence centers and electron capture centers from the forbidden zone.

The band model allows one to interpret the processes associated with the migration of electrons and holes over distances of the order of several lattice constants and more. When studying intracenter processes, lattice vibrations cannot be neglected; therefore, in this case, a model of potential curves is used [13]. According to this model, the transition of a valence electron to an excited state causes changes in the forces of interaction between the nearest atoms forming an oscillatory system. The basis of the consideration of electronic transitions in such a system is the Frank-Condon principle [14], according to which the relative position of atomic nuclei does not have time to change during the electronic transition (~10^-15 s). Electronic transitions in the energy diagram are shown by arrows. The upward direction of the arrow corresponds to the absorption of energy \( E_2-E_{10} \) (transition \( E_{10} \rightarrow E_2 \)). In an excited state, the system remains for some time (of the order of 10^-8 s or more), sufficient to establish equilibrium (\( E_2 \rightarrow E_{20} \)). In this case, the vibrational energy \( \Delta E=E_2-E_{20} \) is transferred to the base lattice and leads to heating of the crystal. The return of the system to the ground state (\( E_{20} \rightarrow E_1 \)) is accompanied by the emission of a quantum of light.
Zone energy schemes of ZnS-phosphorus with various activators are shown in Figure 1. Local levels of Cu, Mn activators, Cl coactivator, and defects are located in the band gap of the crystal. The introduction of an activator creates an emission center, the main level of which $E_{10}$ is located near the valence band, and the level of excitation $E_2$ in the conduction band. The donor level of the $E_{CC}$ coactivator forms capture centers and is located near the bottom of the conduction band. In an unexcited state, the $E_{10}$ levels are filled with electrons, and the $E_2$, $E_{20}$, $E_{CC}$ levels are free. Levels $E_{10}$ and $E_2$ correspond to the equilibrium states of the unexcited and excited glow center. When energy is absorbed equal to or greater than $E_2 - E_{10}$, the electron makes a transition to the excited state $E_2$. If the $E_2$ level is located in the forbidden zone (Figure 1a: activation of Cu), then the center may not go into the equilibrium state of $E_{20}$ due to the possibility of electron detachment and ionization of the emission center. Such an electron is able to migrate along the base lattice. There are two ways for a free electron: either localize at the level of the capture center or recombine with an ionized luminescence center [13,14].

![Figure 1. Zone diagram of ZnS with luminescence centers (a) - recombination; (b) - intracenter luminescence: EC - light emission centers; CC - capture center; ExC - extinguishing center; $E'_1...E'_n$ - split levels; $E_{10}$ - the main level filled with electrons; $E_2$ - free level of the excited state](image)

In the manganese emission centers, both local excited levels $E_{20}$ and $E_2$ are located in the forbidden zone, and both main $E_{10}$ and $E_1$ are located in the valence band, near its edge. Therefore, the emission of manganese emission centers (EC) is not accompanied by ionization, which is confirmed experimentally [15]. This feature of Mn centers can be associated with the difference in ion radii, which is greater for the Mn$^{2+}$ ion ($r_{\text{Mn}^{2+}} = 0.80$ Å) than for the Zn$^{2+}$ ion it replaces ($r_{\text{Zn}^{2+}} = 0.74$ Å), and for the Cu$^+$ ion and Zn$^{2+}$ they are equal ($r_{\text{Cu}^+} = r_{\text{Zn}^{2+}} = 0.74$ Å).

Thus, the special structure of manganese EC leads to the fact that in them the return from the excited to the ground state is possible only by the radiative transition (transition $E_{20} \rightarrow E_1$, shown in figure 1b). For copper and similar emission centers, the return to the ground state is possible both by...
radiative transition \((E_2 \rightarrow E_1)\) transition, shown in Figure 1 a) and by non-radiative transition \((RB \rightarrow ExC \rightarrow VB)\), which reduces the radiation output.

This difference seems to explain the greater sensitivity of ZnS: Mn to mechanical excitation of luminescence compared to other zinc-sulfide compounds.

A special stand was developed and manufactured to research the capabilities of tactile sensitive elements [16].

Here, the light field was registered using a video camera connected to a personal computer. A film flat round mechanoluminescent sensor element with a diameter of 56 mm was used. The force on the sensor was exerted by dropping or moving an object, such as a steel ball (diameter 32 mm, weight 110 g) on the surface of the sensor element with an arbitrary clamping force.

3. Results and Discussion

As a result, the movement of the glowing area was recorded. The combined image of several consecutive frames of the glow is shown in Fig. 2.

![Figure 2](image)

The result of combining individual video frames. Can see: 1) modulation of the brightness and area of the glow due to uneven pressure force; 2) local changes in the direction of the trajectory of movement; 3) uneven speed of movement.

Analysis of the results of the experimental research [16] shows that under the influence of an external mechanical force, a light emission occurs in the sensitive element of the ZnS:Mn phosphor. The amount of light flux is proportional to the amount of applied mechanical action.

Receiving and processing such data in real time can give very complete information about the interaction of the sensed surface of the item with an external object, in other words it will create a tactile dynamic image of the situation of contact interaction with a specific object.

Thus, the possibility of using mechanoluminescent sensing elements with area-distributed sensitivity for visualization and registration of pulse pressure fields with different time and amplitude parameters has been experimentally shown.

4. Conclusions

A promising area of application of mechanoluminescent sensor elements is the development of composite materials and structures that have the property of self-diagnosis [17, 18]. In general, composites are materials consisting of carbon-graphite or quartz fibers filled with epoxy compounds [10]. Such materials have high strength and rigidity with low mass and radio transparency. Currently, composites in the form of panels are widely used in mechanical engineering, aircraft and rocket engineering, in the construction of bridges, sports facilities, etc.

However, composites have a disadvantage, which is manifested in the fact that under various impacts, deformations and fractures can be observed on the side opposite to the application of the
impact. On the outside, after the termination of exposure, the composite panels return to their original state, and the site of damage may not be detected by a routine external inspection.

As a result of studying the nature of the phenomenon of mechanoluminescence, a model for converting mechanical energy into light radiation energy was developed. This model describes energy transitions occurring in mechanophosphor. The determination of the physics of the light emission process allowed us to determine the requirements for sensitive elements designed to register external mechanical influences. In particular, to overcome the shortcomings of existing electronic systems for monitoring the condition of buildings, it is proposed to add mechanoluminescent materials to the epoxy compound and create a structure that provides radiation transmission via optical fibers to the photodetector system [19, 20]. An example of a composite material with built-in mechanoluminescent sensor areas and optical fibers with lateral light transmission is shown in Fig. 3.

![Figure 3. The implementation of mechanophosphor optical fiber with lengthwise light input into the optical waveguides in the composition of the composite material.](image)

Here, distributed optical fiber systems and mechanoluminescent materials with different radiation spectra are used for reliable recognition of a specific damage site [17].

As a positive property, it is worth noting the presence of a threshold character of the dependence of the luminescence intensity on the applied pressure. This circumstance ensures that the sensors are insensitive to minor loads and vibrations during the operation of the products. Integration of functions within a single structure allows you to create built-in sensitive elements (sensors) that have the ability to selectively determine both the degree of damage to the composite panel and the specific location of the damage.

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