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Materials with mechanoluminescent properties and their use for registration of impact

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Abstract. In the present article, the questions of using the materials with mechanoluminescent properties as impact indicators are analyzed. The class of substances that exhibit mechanoluminescence (ML) the most intensively is revealed. Various designs of ML transducers are considered. The mechanism of ML radiation, which is based on the interaction between the mobile charged dislocations with the luminescence centers, formed by the activator atoms, are considered. Space charge of the moving dislocations causes tunneling of electrons to excited state with the subsequent radiating transitions. The problem of calculation of elasto-plastic strain of the transducer was solved by means of the microdynamic theory of plasticity. Equation of the intra center ML kinetics is given, with separate calculation results. The major features of the output optical signals of ML transducers on impact is analyzed.

1. Introduction

Mechanoluminescence is a physical phenomenon caused by the ability of luminescent materials to transform mechanical impact energy to optical radiation, typically of a visible range, but also of infrared or ultraviolet radiation in several cases. Many solid bodies prove a property to generate optical radiation on dynamic mechanical strain, generally the bodies with crystal structure [1]. Nearly a third of all solid bodies have ability to ML, however most of them have luminescence so weak that it cannot be detected by ordinary photodetectors.

Among a rather big group of the substances that possess ML properties, a special group of crystalline phosphors stands out. Crystalline phosphors are dielectrics with high resistivity that belong to the class of $A_{II}B_{VI}$ semiconductors with a wide band gap. The ML, as well as other types of a luminescence, occurs in crystalline phosphors because of small concentration of expressly injected impurities of other substances, usually metals. These impurities create the centers in a crystal lattice of the main substance, where luminescence takes place. Such centers of a luminescence (CL) are evenly distributed over the volume of a crystal. The brightest luminescence arises at crystals of chalcogenide group (CdS, ZnSe, ZnS, $CaWO_4$, $ZnSiO_4$). Except them, ML of properties are present in alkaline and haloid crystals of LiF, NaF, KCl, KBr, metals (Cu, Fe), organic compounds (sugar, anthracene, naphthalene) and some others ($SrAl_2O_4:Eu$, $BaAl_2Si_2O_8:Yb$, $Cs_2[Pt(CN)_4] \cdot H_2O$, SiC, $MgAl_2O_4$, $Y_2O_3:Eu$, $UO_2(NO_3) \cdot 6H_2O$).

Zincum-sulphidic compounds doped by various impurities possess the greatest intensity of ML, compared to other groups of materials. For example, it is noted that impurity of manganese produces the brightest ML with a wavelength 580 nanometers [2, 3]. Therefore luminescent materials on the basis of ZnS: Mn are of the greatest interest of studying. ZnS is one of the most important materials in



optoelectronics, which has a low absorption coefficient, is chemically inert, and is transparent in visible and infrared spectra. Optical ceramics based on ZnS is what the head fairings for aerospace technology are made of. It is appealing to use ML transformation for impact sensors in constructions with already available luminophors. It is also appealing to use such sensors where they can be easily embedded into the construction, for example, in a construction made of composite materials reinforced by glass fibers. The ML can be used for registration of impact influences that occur during the operation in structural elements of planes, rockets and other technology operating in extreme conditions to prevent the dangerous consequences from such influences [3].

ML sensors of impact influences work on a basis of direct transformation of the mechanical impact energy to the energy of a light impulse. Additional incentives for development of such sensors are provided by actively developing fiber-optical means of collecting measuring information. Such tools show high resistance to electromagnetic disturbances and high temperatures, intrinsic and explosion safety, small weight and size. However, their successful use requires creation of the sensors transforming various physical impacts to signals of the optical nature. ML sensors provide transformation of this exact kind. ML sensor consists of a transducer generating a light impulse, an optical channel in form of a multiple light fiber or a cable, and a photoreceiving device. The ML transducer can be concentrated or distributed across some area. Then for the concentrated sensor the photodetector has to be single-element; for distributed, matrix. The distributed ML transducer records the dynamic light images corresponding to complicated outline impact influences.

However, for successful application of ML sensors, it is necessary to know the transformation function of a pressure impulse to optical radiation. The development of transformation function is impossible without comprehension of the physical nature of ML in ZnS:Mn crystals. Based on a physical model, the mathematical model that adequately describes this phenomenon and allows calculation of the parameters of output optical signal depending on parameters of an impact impulse is created.

2. Physical model of the excitation of ML

ML in crystals of class $A_{II}B_{VI}$ appears as a result of the movement of dislocations arising during a plastic strain caused by the impact influence. It was found [4], that dislocations in ZnS:Mn have rather big electric charge, which is explained by the considerable share of an ionic component in forces of interatomic communications. During the plastic strain, there happens an interaction of the electric field of the moving charged dislocations with CL, which leads to exciting of the CL with the subsequent radiating recombinations. Here the electrical model of the dislocation can be presented in the form of a cylinder of a space charge, center of which is filled with electrons.

In process of approaching of the dislocation center to the CL, it displaces in the electric field of the dislocation to a higher energy level. When the ground electronic levels overlap with the vacant levels of CL the electrons will tunnel from the occupied levels to the vacant ones. Traveling speed of dislocation is negligible in comparison with tunneling speed therefore it is possible to consider that during the tunneling process, the distance between the CL and the dislocation is constant and equal to r_{CL} , and tunneling happens in a constant electric field E_D of the cylinder of a space charge of the dislocation [5]. Tunneling probability in the homogeneous electric field of dislocation has an appearance [6]

$$P_T(r_{CL}) = \frac{[eE_D(r_{CL})]^4 \hbar^3 (1 - \Delta/E_{pb})^{0.5}}{4\sqrt{2}P_T G_d^2 E_{pb}^3 m_*^2} \exp\left[\frac{(E_{pb} - \Delta)^2}{4G_d^2}\right]; \quad (1)$$

$$G_d^2 = 2\Delta T \quad \text{if } k_B T > \hbar\omega; \quad G_d^2 = \frac{\Delta \hbar\omega}{2} \left[1 + \frac{2\pi^2}{3} \left(\frac{T}{\hbar\omega}\right)^2\right] \quad \text{if } \sqrt{8m_* C_l E_{pb}} < k_B T < \hbar\omega;$$

$$\Delta = \frac{3\pi^2 E_{pb} m_*}{2M_c} \left(\frac{\Omega_{cb}}{\hbar\omega}\right)^2,$$

where e - electron charge; \hbar - Planck's constant; Δ - the parameter characterizing energy of polarization of a crystal lattice; E_{pb} - the energy of a potential hill counted from a nonequilibrium excited level (conduction band) to its ground nonexcited level; P_T - tunneling probability; G_d^2 - parameter characterizing dispersion of energy of an electron; m^* - effective mass of an electron; k_B - Boltzmann constant; T - absolute temperature; $\hbar\omega$ - Debye energy of a phonon; C_l - speed of longitudinal elastic waves in a crystal; M_c - mass of the unit cell of a crystal; Ω_{cb} - constant of strain potential of a conduction band. Then the distance from CL to the center of dislocation at the time of tunneling will be determined by a formula

$$r_{CL} = q / 2\pi\epsilon\epsilon_0 E_D(r_{CL}),$$

where q - line density of a dislocation charge; ϵ - relative permittivity; ϵ_0 - vacuum permittivity. Then the radius of interaction of CL with dislocation can be calculated using a formula [5]

$$r_{in}(t) = \left[\frac{\pi r_{CL}^4 P_T(r_{CL})}{2V_D(t)} \right]^{1/3}, \quad (2)$$

where $V_D(t)$ - dislocation velocity; t - current time. Here the circumstance that the configuration of a dislocation space charge cylinder significantly changes at larger velocities is already considered. Radius of interaction r_{in} characterizes such area of excitation of CL where dislocation, moving with a velocity of V_D near CL, excites it with the probability of P_T . Setting the values of P_T close to 1, we at first determine $E_D(r_{CL})$, and then r_{CL} , at which tunneling happens. Radius of interaction of $r_{in}(t)$ is determined by a formula (2).

During a plastic strain the whole ensembles of dislocations move, interacting with CL and exciting them. If we assume that a dislocation excites each CL only once, then the speed of their exaltation will be determined by all volume of a crystal by the equation

$$\frac{dN_{CL}}{dt} = N_{CL} 2r_{in}(t) \tilde{N}_{mD}(t) \tilde{V}_D(t), \quad (3)$$

where N_{CL} - the total number of CL in volume of a crystal determined by a volume concentration of CL; $\tilde{N}_{mD}(t)$ - average density of the mobile dislocations; $\tilde{V}_D(t)$ - average velocity of the dislocations. The factor $2r_{in}(t)\tilde{N}_{mD}(t)\tilde{V}_D(t)$ shows the fraction of the excited CL from their total number and is defined as the volume with excited CL covered by moving dislocations in unit of time.

3. The equation of the energy luminosity of intracenteric ML

The equation (3) lies at the basis of the model of a ML sensor as a generator of light impulses. However it is necessary to consider the fact that radiating transitions with emitting the light quanta with energy $\eta = \hbar\nu$, corresponding to the maximum of a radiation spectrum, occur during a recombination, which is a transition of CL from an excited state in the ground one. Because the level of an excited state of manganese CL is not in the conduction band, but in the forbidden band, and excited electrons aren't collectivized, and remain near the activator atom, the attenuation of luminescence of such ML obeys the laws of an unimolecular reaction [7]. At the same time the fraction of the excited CL, returning to the ground state remains constant, and the curve of attenuation obeys the exponential law with a time constant τ

$$\Phi(t) = \eta \frac{1}{\tau} \exp\left(-\frac{t}{\tau}\right) \int_0^{t_\sigma} N_{CL} 2r_{in}(t) \tilde{N}_{mD}(t) \tilde{V}_D(t) dt, \quad (4)$$

where the integrand describes a kinetics of the exaltation of CL during the impact impulse of t_σ , and expression before integral describes kinetics of luminescence attenuation. Expression (4) represents the core equation of the luminosity of an intra-center ML as function of time. The obvious advantage of the

formula (4) is a possibility to carry out calculation of a power luminosity of ML of the transducer in absolute units of intensity of optical radiation.

4. Dislocation model of elasto-plastic strain

In the formula (4) the values defining dynamics of a plasto-elastic strain of ML transducer aren't determined. The most reasonable way of finding them is to use the microdynamic theory of plasticity [8, 9]. The intense strained state of the thin flat ML transducer for a case of the monoaxial pressure application is defined by the expression

$$\sigma_1 = E \left(\varepsilon_1 - \frac{4}{3} \varepsilon_p \right) = \sigma(t) - E \varepsilon_{1p}, \quad (5)$$

where σ_1 – the principal stress applied perpendicular to the transducer plane; E – elastic modulus; $\varepsilon_1 = \varepsilon_{1e} + \varepsilon_{1p}$ – total strain in form of a sum of elastic ε_{1e} and plastic ε_{1p} components; $\sigma(t)$ – impulse of impact pressure. Expression (5) shows that the stress increases with a growth of the general strain ε_1 and decreases with a growth of plastic strain ε_{1p} .

Within the dislocation theory the speed of a plastic strain is defined by Orowan's ratio [8]

$$\frac{d\varepsilon_p}{dt} = |\vec{b}| \tilde{N}_{mD}(t) \tilde{V}_D(t), \quad (6)$$

where $|\vec{b}|$ – Burgers vector module, that characterizes the distortion of a crystal lattice by dislocation. It is shown [8], that during a plastic strain only a part of the total number of dislocations \tilde{N}_{tD} is moving. And despite the fact that during a plastic strain the structure of a crystal contains a complicated set of forms and sizes of dislocation loops, the behavior of each any loop does not significantly differ from the behavior of an average one. Therefore, the behavior of an average loop will correspond in general to behavior of the whole distribution of loops. Correspondence between \tilde{N}_{mD} and \tilde{N}_{tD} can be described by the formula [9]

$$\tilde{N}_{mD} = \tilde{N}_{tD} \exp\left(-\frac{\tilde{N}_{tD}}{\tilde{N}_{cr}}\right), \quad (7)$$

where \tilde{N}_{cr} – critical value of the general dislocation density, corresponding to the termination of the yield stress platform on the diagram $\sigma(\varepsilon)$. The formula (7) shows that the part of mobile dislocations is a strictly decreasing function of the general dislocation density. And, so far $\tilde{N}_{tD} < \tilde{N}_{cr}$ with the increase of plastic strain \tilde{N}_{mD} increases, but when $\tilde{N}_{tD} > \tilde{N}_{cr}$, otherwise, with the increase of plastic strain \tilde{N}_{mD} decreases. The general dislocation density is bound to a plastic strain by the dependence

$$\tilde{N}_{tD} = \tilde{N}_{tD}^0 + M \varepsilon_p, \quad (8)$$

where \tilde{N}_{tD}^0 – average initial dislocation density; M – dislocations multiplication factor.

In the formula (4) average velocity of dislocations is determined by the formula [9]

$$\tilde{V}_D(t) = c_{tr} \exp\left(\frac{D_f}{\sigma_1}\right), \quad (9)$$

where c_{tr} – speed of shift waves propagation in a crystal; $D_f = 2\sigma_s$ – effective tension of internal friction; σ_s – static yield point.

Simultaneous solution of the equations (6)...(9) defines the intense strained state of ML transducer. Results of the solving are inserted into the equation (4) for determination of parameters of an output optical signal $\Phi(t)$.

5. Results of modeling and discussion of the results

The solution of the equations (4)...(9), united in a system was carried out in MATLAB. As a matter of estimation convenience, calculations of luminosity were carried for a single platform of a ML transducer, with surface area 1 mm^2 . The width of the transducer was chosen as $20 \mu\text{m}$, which corresponds to available experimental exemplars of transducers. Exemplars consisted of two layers of ML powder applied on a thin clear film and stuck to each other. The ML material was the industrial electrolumiphor of the ELS-580S type made on the basis of ZnS:Mn, Cu with weight content of Mn of 1%. The maximum of a radiation spectrum of manganese CL is $\lambda_{\text{max}}=580 \text{ nm}$, $\eta=2.2 \text{ eV}$. The time constant of attenuation was defined experimentally and estimated as $\tau=150 \mu\text{s}$. Features of the radiation output were considered by special coefficients. Entrance impact influence was described by a single impulse of pressure $\sigma(t)$ of semi-sinusoidal form, with varying amplitude σ_A and duration t_σ . The results of modeling of a power luminosity of the ML transducer are given in figures 1 and 2.

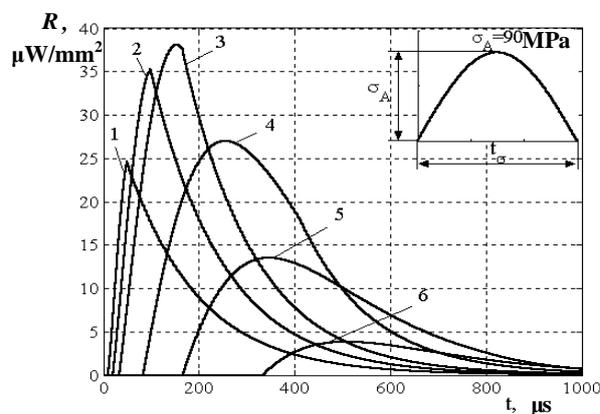


Figure 1. Estimated dependences of a power luminosity $R(t)$ of ML transducer under an influence of pressure impulses of identical amplitude $\sigma_A=90 \text{ MPa}$ and varying duration t_σ :

- 1 - $t_\sigma=60 \mu\text{s}$; 2 - $t_\sigma=120 \mu\text{s}$;
- 3 - $t_\sigma=200 \mu\text{s}$; 4 - $t_\sigma=500 \mu\text{s}$;
- 5 - $t_\sigma=1000 \mu\text{s}$; 6 - $t_\sigma=2000 \mu\text{s}$

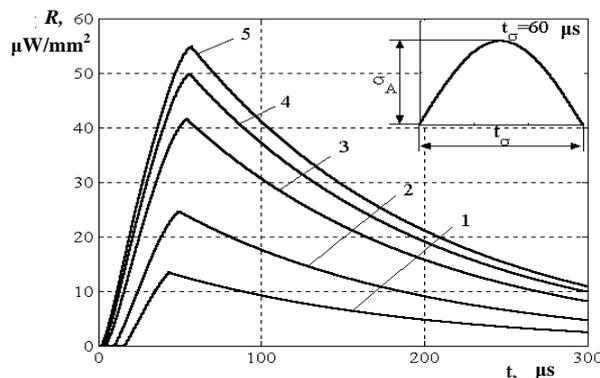


Figure 2. Estimated dependences of a power luminosity $R(t)$ of ML transducer under an influence of pressure impulses of identical duration $t_\sigma=60 \mu\text{s}$ and varying amplitude σ_A :

- 1 - $\sigma_A=60 \text{ MPa}$; 2 - $\sigma_A=90 \text{ MPa}$;
- 3 - $\sigma_A=180 \text{ MPa}$; 4 - $\sigma_A=270 \text{ MPa}$;
- 5 - $\sigma_A=360 \text{ MPa}$

The analysis of the received relations shows that the intensity of ML is sufficient for recording by its photo diodes. The form of an output optical signal considerably differs from the pressure pulse shape. Amplitude and duration of impulses of luminosity have the strong dependence not only from pressure impulse amplitude, but also from its duration. With a decrease of amplitude and duration of an impulse of pressure, a delay of emergence of radiation is observed. This is explained by the fact that pressure has to reach the level equal to a yield point of material at which intensive movement of dislocations begins. This means that the phenomenon of ML has threshold character.

Duration of the influence has a strong impact on the radiation intensity, and with the increasing duration, the intensity significantly falls, which means that under a static influence ML does not occur.

Comparison of the calculated data with the results of experiments [10] showed that difference between them does not exceed 10%, which serves as the proof of adequacy of the developed ML model.

Therefore, the developed model may serve as a theoretical basis for development and application of ML transducers of impact influences.

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