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Piezoelectrically-induced trap-depth reduction model of elastico-mechanoluminescent materials

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ABSTRACT

Considering the detrapping of charge carriers due to reduction in trap-depth caused by piezoelectric field produced by applied pressure, an expression is derived for the detrapping rate of electrons. Then, an expression is obtained for the rate of generation of excited ions produced during capture of detrapped electrons by Eu^{3+} ions in persistent luminescent materials or by the energy released during electron-hole recombination in ZnS:Mn crystals. Finally, an expression is explored for the elastico-mechanoluminescence (EML) intensity, which is able to explain satisfactorily the characteristics of EML for the application of static pressure as well as for impact pressure. The total number of detrapped electrons and the total EML intensity are found to increase linearly with the electrostatic energy of the crystals in piezoelectric field. It is shown that the EML intensity should increase with the EML efficiency, number of crystallites (volume of sample), concentration of local piezoelectric regions in crystallites, piezoelectric constant of local piezoelectric regions, average length of the local piezoelectric regions, total number of electron traps, pressing rate, and applied pressure, and it should be higher for the materials having low value of threshold pressure and low value of trap-depth in unstressed condition. On the basis of the piezoelectrically-induced trap-depth reduction model of EML reported in the present investigation novel intense elastico mechanoluminescent materials having repetitive EML with undiminished intensity for successive loadings can be tailored which may find applications in sensing, imaging, lighting, colored displays, and other mechano-optical devices.

1. Introduction

Mechanoluminescence (ML) is a type of luminescence induced by any mechanical action on solids. The cold light emissions induced by elastic deformation, plastic deformation, and fracture of solids are called elastico ML (EML), plastico ML (EML), and fracto ML (FML), respectively [1,2]. For a given pressing rate the elastico-mechanoluminescent materials present an accurate linearity of EML intensity against pressure in the elastic region and they offer the advantages of repetitive, wireless, non-destructive, reproducible, real-time and reliable stress sensing. So far the most promising elastico-mechanoluminescent smart materials are the rare-earth ions doped alkaline aluminates and silicates, ZnS:Mn, ZnS:Cu, and ZnS:Mn,Cu phosphors. In the past, some possible applications of ML have been reported for X-ray generators, [3,4] damage sensors, [5,6] fracture sensors, [7–9] stress sensors, [10–15] quasidynamic crack propagation in solids, [16–18] bioimaging, [19] etc. Recently, Jeong et al. [20] have demonstrated highly bright and durable mechanoluminescent flexible composite films with a brightness of $\approx 120\ cd/m^2$ and durability over $\approx$ 100,000 repeated mechanical stresses by using a combination of copper-doped zinc sulfide (ZnS:Cu) particles and polydimethylsiloxane (PDMS) elastomer. They have shown that the color of the EML produced by stretching the composite film containing ZnS:Cu,Mn and ZnS:Cu phosphors in a PDMS matrix, changes gradually from orange to green with increasing fraction of ZnS:Cu phosphor [21]. They expect that these findings can open a window for developing ML-based light sources and multicolor displays. Using ZnS-PDMS composite, Jeong et al. [22] have demonstrated the wind-driven ML device that produces significant brightness. They have reported that the wind-driven patterned colorful EML composites may find potential use in harvesting wind power for illumination and display systems. If the brightness of EML devices could be increased in the range of $1000\ cd/m^2$, the EML devices will be more important and useful. In this regard, nearly ten times more intense elastico-mechanoluminescent materials are required. Thus, the investigation of

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new intense elastico mechanoluminescent materials with repetitive EML intensity and self-recovery, and the investigation of new applications of elastico mechanoluminescent materials are still the challenges for researchers.

In luminescence, in addition to experimental observations, theoretical studies also play very important role to indentify the parameters and to clarify the processes responsible for the phenomenon. In this regard, in the past, some attempts have been made to understand theoretically the EML characteristics whereby the approaches are based on the increase of detrapping probability with the piezoelectric field [23,24]. Although such studies succeeded in identifying the dependence of EML intensity on certain parameters, they use many assumptions and approximations to correlate the theoretical and experimental results [23,24]. Furthermore, many parameters responsible for the EML emission could not be identified because the basic processes responsible for the detrapping were not considered. In fact, there is a need of such a new model that is based on the basic process of physics and it does not use many assumptions and approximations to explain the EML characteristics and experimental results. The present paper explores a new model namely, piezoelectrically-induced trap-depth reduction model of EML, according to which the trap-depth of charge carriers decreases with increasing piezoelectric field and after a threshold electric field, the trapped electrons become unstable and they get detrapped whose subsequent recombination with the hole centers excites the luminescence centers. On the basis of the piezoelectrically-induced trap-depth reduction model of elastico ML, expressions are derived which are able to explain satisfactorily the detrapping and recombination of charge carriers; and moreover, they explain satisfactorily the pressure, temporal, thermal, spectral and several other characteristics of elastico mechanoluminescent materials. It is shown that the EML intensity should increase with the EML efficiency, number of crystallites (volume of crystallites), concentration of local piezoelectric regions in crystallites, piezoelectric constant of local piezoelectric regions, average length of the local piezoelectric regions, total number of electron traps, pressing rate, and applied pressure, and it should be higher for the materials having low value of threshold pressure and low value of trap-depth in unstressed condition. This model is applicable to EML induced by application of static pressure as well as to the EML induced by impact pressure. On the basis of the model reported in the present investigation novel intense elastico mechanoluminescent materials having repetitive EML with undiminished intensity for successive loadings can be tailored which may find applications in sensing, imaging, lighting, colored displays, and other mechano-optical devices.

2. Mechanisms of the elastico-mechanoluminescence of persistent luminescent and other materials

The EML of persistent luminescent materials where the dopant is rare earth ions such as Eu^{2+} can be understood with respect to the following steps:

(i) When a pressure is applied, one surface of the local piezoelectric region produced due to the impurities in the persistent luminescent material becomes positively charged and the other surface becomes negatively charged.
(ii) The reduction in the trap-depth caused by the piezoelectric field causes detrapping of electrons whereby the detrapped electrons move to the conduction band.
(iii) Some of the detrapped electrons moving in the conduction band recombine with the Eu^{3+} ions produced previously by UV-irradiation of persistent luminescent materials such as $SrAl_2O_4$:Eu and subsequently generate excited Eu^{2+} ions [25–29].
(iv) The de-excitation of excited Eu^{2+} ions gives rise to the light emission characteristic of the luminescence centers.

The EML of ZnS:Mn crystals can be understood with respect in the following way:

(i) As a result of the applied pressure one surface of a local piezoelectric region produced due to the impurities in ZnS:Mn crystal gets positively charged and the other surface gets negatively charged.
(ii) Due to the reduction in trap-depth caused by the local piezoelectric field detrapping of electrons takes place, in which the detrapped electrons move to the conduction band.
(iii) Some of the detrapped electrons moving in the conduction band recombine with the holes, in which the energy released during the electron-hole recombination excites Mn^{2+} ions.
(iv) The de-excitation of excited Mn^{2+} ions gives rise to the light emission characteristic of the Mn^{2+} ions.

3. Modeling of elastico ML

When a crystalline structure absorbs energy from ionizing radiation, then creation of electron-hole pairs takes place. If sufficient energy is provided to electrons to break from the valence band and overcome the band gap, then these electrons jump to the conduction band, where they can move freely about the crystal. The holes created in the valence band can also move freely about the crystal. Most of the electrons moving in the conduction band may quickly lose their excitation energy and fall back to the valence band immediately and recombine with a hole or some of them may get trapped at defects within the crystalline structure. Some of the holes produced in the valence band may also get trapped at defects within the crystalline structure. The trapped electrons remain so until they are provided enough stimulation energy to overcome the trap and eventually recombine with a hole at a recombination center. These recombinations can give rise to the emission of light, i.e. luminescence. In case of an emission during stimulation, this phenomenon is referred to as 'optically stimulated luminescence' or 'thermoluminescence' depending on whether the stimulation source is light or heat. When certain irradiated solids are subjected to elastic deformation, then the detrapping of trapped electrons takes due to the transfer of trapped electrons to the conduction band because of the trap - depth reduction caused by the piezoelectric field produced due to the applied pressure [12–14]. The luminescence induced by the elastic deformation of solids is called elastico-mechanoluminescence.

If E_0 is the trap-depth or activation energy (eV) of electrons in the material in unstressed condition, n_0 the initial concentration of filled electron traps in the material, k the Boltzmann's constant and T the absolute temperature, then the number n_d of detrapped electrons is given by the following Boltzmann's statistical formula [30–32]:

$$n_d = n_0 \exp\left(-\frac{E_0}{kT}\right) \tag{1}$$

for $kT \ll E_0$, n_d is negligible; however, for increasing value of kT, n_d increases significantly.

In the measurement of EML of persistent luminescent materials, generally the microcrystalline or nanocrystalline phosphors