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Citation: Appl. Phys. Lett. 102, 241105 (2013); doi: 10.1063/1.4811160
View online: http://dx.doi.org/10.1063/1.4811160
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v102/i24
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Strong luminescence induced by elastic deformation of piezoelectric crystals

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(Received 26 April 2013; accepted 30 May 2013; published online 17 June 2013)

The luminescence induced by elastic deformation of solids, called the phenomenon of elastico-mechanoluminescence (EML), is observed in several materials. For applied pressure in the range of 17 MPa, certain crystals emit intense EML, which can be seen in day light with naked eye. In the present paper, we explore that, as the piezoelectric constant near the photo-generated electric dipoles formed by trapping of charge carriers in crystals is several times higher as compared to that at normal sites, the piezoelectrically induced detrapping of charge carriers and EML emission may take place for less value of the pressure applied onto the crystals. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4811160]

It is not a fiction, but a scientific fact that intense light emission takes place during simple elastic deformation of certain solid materials, where plastic deformation and fracture are not required. Such phenomenon of light emission induced by elastic deformation of solids is known as elastico-mechanoluminescence (EML).1,2 It is surprising that, when the disk-shaped specimen with diameter of 25 mm and thickness of 15 mm made by mixing any of the microcrystalline phosphors such as SrAl2O4:Eu, ZrO2:Ti, and Ca2Al2SiO7:Ce, in epoxy resin of epichlorhydrine, is compressed uniaxially by the pressure in the range of 17 MPa (applied force = 1000 N and contact area = 0.59 × 10−2 m2), then the light emission taking place from both surfaces of the disk is so intense that it can be seen in day light with naked eye.3–7 In general, the light emission induced by any mechanical action on solids is known as ML and the light emissions induced by elastic deformation, plastic deformation, and fracture of solids are called elastico ML (EML), plastico ML (PML), and fracto ML (FML), respectively.1,2 Whereas nearly 50% of all inorganic salts and organic molecular solids show ML during their fracture, comparatively a few solids exhibit ML during their elastic and plastic deformation.

In the recent past, systematic material research has been done and it has resulted in producing a variety of materials that emit an intensive and repeatable ML during their elastic deformation without any destruction.2 So far the most promising elastico mechanoluminescent materials are: rare-earth doped alkaline aluminates and silicates crystals appears for such a low value of stress where the normal piezoelectric field is nearly ten times less to cause the detrapping of charge carriers and therefore to cause the EML emission. Thus, it seems that the EML emission arises due to the piezoelectrically induced cation caused by some other process. The present paper explores a suitable mechanism of elastico ML and shows that the excitation of elastico ML takes place by the stress-induced polarization of photo-generated electric dipoles formed by the trapping of charge carriers in the crystals.

Figure 1 shows that, when a load is applied on to the ZnS:Mn nanoparticles’ film coated on to a quartz substrate, then initially the EML intensity increases with time, attains a peak value, and later on it decreases with time when the load tends to attain a fixed value.10 It is seen that, when the pressure is released, then the EML emission also takes place. It is evident from Figure 1 that when the load is applied for the second time, then also the EML emission takes place during the application and release of the applied pressure. This fact shows the reproducibility of EML. Corresponding to the application and release of pressure, two EML pulses I and II, respectively, are generated during one cycle of the applied pressure, and all of which are reproducible as shown in II and II′ in Figure 1. The EML intensity produced during the release of pressure is higher as compared to that produced during the application of pressure because the rate of release of pressure is higher as compared to the rate of application of pressure. However, the total EML intensity produced during the release of pressure is nearly equal to that produced during the application of pressure. The threshold pressure for the appearance of EML in ZnS:Mn crystals is nearly 5 MPa. The EML intensity of ZnS:Mn crystals increases linearly with the applied pressure as well as with the strain rate.10,12 The total EML intensity of ZnS:Mn crystals increases quadratically with the applied pressure.12 The EML spectra of ZnS:Mn crystals are similar to their photoluminescence and electroluminescence spectra.10 For the ML measurement, Xu, Watanabe, and Akiyama10 have prepared the thin film of...
ZnS:Mn nanoparticles on various substrates by physical vapor deposition of ion plating or sputtering method. The chemical composition determined by X-ray diffraction pattern showed that the Mn amount in the film was the same as in the source material, i.e., 1.5%. Moreover, the X-ray diffraction pattern showed only one strong diffraction peak at 28.49° in the 2θ range of 10°–90°, which was attributed to the (111) plane of ZnS, indicating that the film was highly oriented. The field emission scanning electron microscope (FE-SEM) and XRD techniques indicated that the ZnS:Mn film was composed of nano-sized crystallites with a mean size of 20 nm. In this case, the EML was excited by compressing the nanoparticles using a material testing machine. The EML spectrum was simultaneously measured during the application of stress by using a spectrometer attached to a photonic multichannel analyzer.

Figure 2 shows the stress dependence of the EML intensity of SrAl2O4:Eu phosphors. It is seen that, after a threshold pressure of nearly 1 MPa, the EML intensity increases linearly with the applied pressure. The linear increase of the EML intensity with the applied pressure has also been found by other workers.9,13,14 The EML intensity of SrAl2O4:Eu phosphors also increases linearly with the strain rate; however, the total EML intensity of these crystals increases quadratically with the applied pressure.15 We have found that, when a load is applied number of times onto SrAl2O4:Eu phosphors, then the EML intensity decreases successively with the number of pressings. This result shows the detrapping of trapped charge carriers during the application of pressure. The diminished EML intensity caused by number of pressings can be recovered completely by the irradiation of SrAl2O4:Eu phosphors to UV-light. This fact indicates the trapping of charge carriers during the exposure of SrAl2O4:Eu phosphors to UV-light. The EML spectra of SrAl2O4:Eu,Dy crystals are similar to their photoluminescence and electroluminescence spectra.13 We have synthesized SrAl2O4:Eu phosphors by a solid state reaction process in the reduction atmosphere of Ar + 5% H2. For the EML measurement, the compact masses of the phosphors with dimension of 2 x 2 x 2 mm were exposed to UV-light, and then after 10 min, the EML was excited by pressing the UV-exposed sample at a fixed pressing rate. The EML intensity was measured using an RCA931A photomultiplier tube. The wavelength of the UV-light used for irradiation was 365 nm.

Figure 3 shows the schematic diagram for the EML emission in ZnS:Mn crystals. The steps involved in the EML emission in ZnS:Mn crystals are as follows:16 (i) production of piezoelectric field because the crystal structure of ZnS is non-centrosymmetric,17 (ii) detrapping of electrons from filled-electron traps to the conduction band (CB) as a result of band bending caused by the piezoelectric field, (iii) release of energy non-radiatively during the electron-hole recombination, (iv) excitation of Mn2+ ions by the energy released during electron-hole recombination, and (v) light emission during the de-excitation of excited Mn2+ ions.

Figure 4 shows the schematic diagram for the EML emission in SrAl2O4:Eu crystals. The steps involved in the EML emission in SrAl2O4:Eu crystals are as follows: (i) UV-light induced excitation of the electrons of Eu2+ ions from 4f level to the 5d level lying very close to the bottom of conduction band, (ii) subsequent oxidation of some Eu2+ ions to Eu3+ ions, and the trapping of released electrons at the oxygen vacancy levels located in the vicinity of the photo-generated

![FIG. 1. ML response of ZnS:Mn nanoparticles coated on quartz plate for the compression stress of 500 N, which was applied by material testing machine with a cross-head speed of 0.10 mm/min (after Xu, Watanabe, and Akiyama10). Reproduced by permission from Xu et al., Appl. Phys. Lett. 74, 1236 (1999). Copyright 1999 by The American Institute of Physics.](image1)

![FIG. 2. Dependence of EML intensity of SrAl2O4:Eu on the applied pressure (pressing rate = 10 MPa ms−1).](image2)

![FIG. 3. Schematic diagram for the EML emission in ZnS:Mn nanoparticles (1—detrapping of electron and its movement in the conduction band, 2—electron-hole recombination, 3—transfer of energy to Mn2+ ion and excitation of Mn2+ ion, and 4—emission of light).](image3)

![FIG. 3. Schematic diagram for the EML emission in ZnS:Mn nanoparticles (1—detrapping of electron and its movement in the conduction band, 2—electron-hole recombination, 3—transfer of energy to Mn2+ ion and excitation of Mn2+ ion, and 4—emission of light).](image4)
to some other processes. If there is nearly 10 times increase in the internal piezoelectric field of the order of $10^3$ V cm$^{-1}$ may be produced, which may cause sufficient band bending and subsequently the EML emission may take place.

The piezoelectric constants of SrAl$_2$O$_4$ crystals have not been determined to date. In general, the piezoelectric constants of similar crystals are of the order of $d = 10^{-11}$ C N$^{-1}$. The threshold pressure for the EML emission in SrAl$_2$O$_4$:Eu$^{2+}$ crystals is $1 \times 10^6$ N m$^{-2}$ and the dielectric constant of SrAl$_2$O$_4$ crystals is $8$, and thus, the internal piezoelectric field as estimated previously for ZnS:Mn crystals comes out to be of the order of $10^4$ V cm$^{-1}$ for SrAl$_2$O$_4$:Eu$^{2+}$ crystals, which may not cause the detrapping and impact ionization. If there is nearly 10 times increase in the piezoelectric constant near the Eu$^{2+}$ centres, then the internal piezoelectric field of the order of $10^3$ V cm$^{-1}$ may be produced, which may cause sufficient band bending, and subsequently the EML emission may take place.

Although the change in crystal-structure near the defects is possible, 10 times increase in the piezoelectric constants near the defects may not be possible. It seems that the stress-induced polarization of photo-generated electric dipoles formed by the trapping of charge carriers in the crystals may enhance the local piezoelectric constants of the crystals. In ZnS:Mn crystals, the hole trapped in Zn$^{2+}$ vacancy and the electron trapped in S$^{2-}$ vacancy may form a photo-generated dipole. The enhanced piezoelectric constants of ZnS:Mn crystals may be estimated in the following way. If the distance between two ends of the sites responsible for dipole formation is L m, then for the Young’s modulus $Y = 0.67 \times 10^{11}$ N m$^{-2}$, the change in the distance between two ends of the sites responsible for dipole formation by a unit stress will be $L / Y = 1.49 \times 10^{-11}$ L m. If $q$ is the electronic charge, then the electric dipole moment M caused by the separation of positive and negative charges by a unit stress is given by $M = q \times 1.49 \times 10^{-11} \times 1.6 \times 10^{-19} \times 1.49 \times 10^{-11} = 2.38 \times 10^{-30}$ L C m. If $\sigma$ is the cross-sectional area of the dipole in m$^2$, then the activation volume $\Omega$ of the dipole comes out to be $2.38 \times 10^{-30}$ L m$^3$. Thus, the value of the activation volume $\Omega$ of the dipole comes out to be $\Omega = 1.7 \times 10^{-20}$ m$^3$. Therefore, the dipole moment per unit volume for the unit stress or the charge per unit surface area for the unit stress, that is, the piezoelectric constant is given by $d = M / \Omega = 1.4 \times 10^{-10}$ C N$^{-1}$. This estimated value of the piezoelectric constant $d$ is nearly 10 times higher than its value taken previously for the normal sites, and therefore, the local internal piezoelectric field produced by the threshold stress $5 \times 10^6$ N m$^{-2}$ near the defect centres will be of the order of $10^3$ V cm$^{-1}$. This order of the electric field may cause sufficient bending for the tunneling of electrons from negative ion vacancies or other traps to the conduction band and their subsequent capture in hole centres may produce sufficient energy for the excitation of Mn$^{2+}$ ions, whereby the de-excitation may give rise to the light emission characteristic of Mn$^{2+}$ ions.

In the case of SrAl$_2$O$_4$:Eu$^{2+}$ crystals, the hole trapped in Sr$^{2+}$ vacancy and the electron trapped in oxygen vacancy may form a photo-generated dipole; and also the hole trapped in Sr$^{2+}$ vacancy and Eu$^{3+}$ ion (or Dy$^{3+}$ ion in the case of SrAl$_2$O$_4$:Eu$^{2+}$, Dy$^{3+}$ crystals) may form the photo-generated dipole. Following the procedure used previously for ZnS:Mn crystals, the local piezoelectric constant arising due to the photo-generated electric dipoles is estimated for SrAl$_2$O$_4$:Eu$^{2+}$ crystals. If there is nearly 10 times increase in the internal piezoelectric constant near the Mn$^{2+}$ ions, then the internal piezoelectric field of the order of $10^4$ V cm$^{-1}$ may be produced, which may cause sufficient band bending and subsequently the EML emission may take place.

Eu$^{3+}$ cations, (ii) detrapping of electrons from filled-electron traps to the conduction band as a result of band bending caused by the piezoelectric field because SrAl$_2$O$_4$:Eu crystal is non-centrosymmetric, (iii) recombination of the electrons moving in the conduction band with the photo-generated Eu$^{3+}$ ions and generation of excited Eu$^{2+}$ ions, and (v) light emission during the de-excitation of excited activator ions.

The mechanism of EML described for SrAl$_2$O$_4$:Eu crystals is also applicable to other rare earth doped persistent luminescent crystals because the mechanism of the photoluminescence of these crystals is similar to that of the SrAl$_2$O$_4$:Eu crystals.

The piezoelectric constant $d$ of ZnS:Mn crystals is $3.2 \times 10^{-12}$ C N$^{-1}$ and the threshold pressure $P_{th}$ to cause ML in ZnS:Mn crystals is $5 \times 10^6$ N m$^{-2}$. Thus, the piezoelectric charge density for the threshold pressure will be $\rho = d \times P_{th} = 3.2 \times 10^{-12} \times 5 \times 10^6 = 1.6 \times 10^{-5}$ C m$^{-2}$. The piezoelectric field will be $F = \rho / \varepsilon_0$, where $\varepsilon_0$ is the permittivity of free space, equal to $8.85 \times 10^{-12}$ C$^2$ N$^{-1}$ m$^{-2}$. Thus, the external electric field $F$ developed near the surface of crystals will be $1.8 \times 10^8$ V m$^{-1}$. The dielectric constant of ZnS:Mn crystals is $8.6$, hence, the internal electric field will be $2.1 \times 10^3$ V cm$^{-1}$. As the detrapping of charge carriers needs an internal electric field of the order of $10^3$ V cm$^{-1}$ (Refs. 26 and 27) and the impact ionization needs an internal electric field of the order of $10^3$ V cm$^{-1}$ produced by the threshold pressure may not cause the detrapping and impact ionization. The appearance of elastico ML by the threshold pressure of $5 \times 10^6$ N m$^{-2}$ in crystals indicates that the local piezoelectric field near Mn$^{2+}$ ions in ZnS:Mn crystals should be nearly 10 times higher, where the piezoelectric constant should be high. The higher piezoelectric constant may arise due to the change in the local structure near the impurities or to some other processes. If there is nearly 10 times increase in the piezoelectric constant near the Mn$^{2+}$ ions, then the internal piezoelectric field of the order of $10^4$ V cm$^{-1}$ may be produced, which may cause sufficient band bending and subsequently the EML emission may take place.

![FIG. 4. Schematic diagram for the ML emission in SrAl$_2$O$_4$:Eu (1—excitation of Eu$^{2+}$, 2—electron movement in CB, 3—electron trapping, 4—electron release, 5—electron movement in CB, 6—electron-capture by Eu$^{3+}$, and 7—light-emission).](image)
SrAl$_2$O$_4$ crystals for the Young’s modulus $Y = 1.02 \times 10^{11}$ N m$^{-2}$. Also, in this case, the local piezoelectric constant comes out to be of the order of $1 \times 10^{-10}$ C N$^{-1}$, which is nearly 10 times higher than its value taken previously. Therefore, the local internal piezoelectric field produced by the threshold stress near the defect centres will be of the order of $10^4$ V cm$^{-1}$. This order of the piezoelectric field may cause sufficient bending for the tunneling of electrons from oxygen vacancies or other electron traps to the conduction band and their subsequent capture by Eu$^{2+}$ ions may produce excited Eu$^{3+}$ ions, whereby the de-excitation may give rise to the light emission characteristic of Eu$^{2+}$ ions.

In the case of ZnS:Mn, the decrease in the number of filled electron traps by successive pressings and the decrease in the number of free hole traps by the electron-hole recombination may be recovered by the breaking of bonds in the crystals because ZnS is a semiconductor, and therefore, the density of free electrons in the conduction band and the density of free holes in the valence band should remain constant at a given temperature.

The reasons for the absence of elastico ML in many materials are as follows: (i) the charge carriers in the trapping sites may not be stable, (ii) the piezoelectric field may be less to cause the detrapping of charge carriers, (iii) the energy produced during the electron-hole recombination may be decaying through some non-radiative path, (iv) the photo-generated dipoles may be lying along the direction perpendicular to the direction of applied uniaxial pressure, (v) the photo-generated dipoles may be lying along the direction at which the piezoelectric constant of the crystal is minimum or zero, and (vi) the threshold stress for the EML emission may be exceeding the limit of elasticity. There may also be other reasons for the absence of EML in the crystals.

As the piezoelectric constant near the photo-generated electric dipoles formed by trapping of charge carriers in the crystals is several times higher as compared to that at normal sites, the piezoelectrically induced detrapping of charge carriers may take place for low value of the pressure applied on to the crystals. This concept of EML excitation is able to explain satisfactorily the characteristics of EML and it may be helpful in tailoring the smart elastico-mechanoluminescent materials having higher EML intensity and good reproducibility without any permanent deformation in the crystals.

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