CHAPTER IV

THEORETICAL APPROACH TO THE LONG DECAY ELASTICO MECHENOLUMINESCENCE OF PERSISTENT LUMINESCENT PHOSPHORS
4.1 INTRODUCTION

Till now, many elastico mechanoluminescent materials are known and they are as given below: ZnS:Mn, SrAl$_2$O$_4$:Eu, SrAl$_2$O$_4$:Ce, SrAl$_2$O$_4$:Ce,Ho, SrAl$_2$O$_4$:Er, SrAl$_2$O$_4$:Eu,Er, SrMgAl$_6$O$_{11}$:Eu, SrCaMgSi$_2$O$_7$:Eu, SrBaMgSi$_2$O$_7$:Eu, Sr$_2$MgSi$_2$O$_7$:Eu, Ca$_2$MgSi$_2$O$_7$:Eu,Dy, CaYAl$_3$O$_7$:Eu, (Ba,Ca)TiO$_3$:Pr$^{3+}$, ZnGa$_2$O$_4$:Mn, MgGa$_2$O$_4$:Mn, BaAl$_2$Si$_2$O$_8$:rare earth element, BaSi$_2$O$_3$N$_2$:Eu$^{2+}$, Ca$_2$Al$_2$SiO$_7$:Ce, ZrO$_2$:Ti and ZnMnTe. The rare earth element can be Eu. A few polymers and rubbers have also been reported by mechanoluminescent. The elastico ML has also been observed in the nanoparticles of ZnS:Mn, SrAl$_2$O$_4$:Eu and ZnMnTe. The ML of SrAl$_2$O$_4$:Eu, Dy phosphors have attracted the attention of many researchers because of the following facts: (i) Higher ML intensity, (ii) recovery of ML in deformed sample with UV-irradiation, (iii) appearance of EML, PML and FML, (iv) ML is observed in various items coating, thin film and bulk forms, (v) suitable material for stress indicator, (vi) ML intensity can be increased many times by changing activator and firing temperature, (vii) composite can be easily made by mixing SrAl$_2$O$_4$:Eu, Dy in polymers, (viii) nanocrystalline form also exhibit intense EML, PML and FML, (ix) the ML intensity of this phosphor depends on the ultraviolet doses, (x) in the elastic region, the ML intensity is proportional to pressure, (xi) the phosphors also exhibit the ML during the release of pressure, (xii) as SrAl$_2$O$_4$:Eu, Dy phosphor is used as a persistent luminescence material in watch dial and luminescent paint, and (xiii) the ML can be also excited by ultrasonic shocks. Akiyama et.al.(1998) were the first to report the elastico mechanoluminescence of Sr$_3$Al$_2$O$_6$:Eu, Dy in 1998. They have observed
that elastico ML in this phosphor is so strong that it can be seen in daylight with naked eyes and the total (integrated) ML intensity is about 500 times as high as that of sugar crystals (Akiyama et.al. 1999). Xu et.al. (1999), Akiyama et.al. (2002a,b) have shown that the stress distribution in solids can be visualized using the nondestructive elastico ML from \(\text{Sr}_3\text{Al}_2\text{O}_6:\text{Eu}\). Akiyama et.al. (1999) have reported recovery phenomenon of mechanoluminescence from \(\text{Ca}_2\text{Al}_2\text{Si}_7\text{O}_{17}:\text{Ce}\). Akiyama et.al. (2002) have studied intense deformation luminescence of \(\text{Sr}_3\text{Al}_2\text{O}_6:\text{Eu}\), in which the ML could be seen in daylight with naked eyes. Xu et.al. (2002) have reported that the elastico mechanoluminescence intensity increases linearly with the applied pressure. Sohn et.al. (2002) have used \(\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}\) to study the crack-tip stress field in ML material by introducing two rare-earth elements such as Dy and Nd which provide the appropriate trap levels. Sohn et.al. (2005) have reported pulsed-laser-deposited \(\text{SrAl}_2\text{O}_4:\text{Eu}, \text{Dy}\) thin film and it has been shown that such thin film can be used as a stress indicator. Kim et. al. (2003, 2005, 2007, 2008) have reported that the ML of \(\text{SrAl}_2\text{O}_4:\text{Eu},\text{Dy}\) can be used in the study of quasidynamic crack-propagation in solids. Xu et.al. (2004a, b, 2006) have studied the ML in strontium aluminates systematically using precisely controlled pure phase Eu-doped strontium aluminates of \(\text{SrAl}_{12}\text{O}_{19}, \text{Sr}_4\text{Al}_{14}\text{O}_{25}, \text{SrAl}_7\text{O}_{17}, \alpha-\text{SrAl}_2\text{O}_4, \beta-\text{SrAl}_2\text{O}_4, \text{SrAl}_2\text{O}_4\) and their mixed phases. Jia et. al. (2006) have studied the ML of \(\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}\text{Dy}^{3+}\) under various loading and unloading conditions. Nanko et.al. (2007) have synthesized \(\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}\) by conventional solid-state reactions process and have consolidated it by pulsed electric current sintering. The sintered \(\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}\) has shown the good photoluminescence by UV-light irradiation and mechanoluminescence by elastic deformation. Terasaki et.al. (2007) have reported that the elastico ML of \(\text{SrAl}_2\text{O}_4:\text{Eu}\) phosphor can drive a photocell system. Terasaki and Xu (2009) have fabricated an
accumulative and integrative mechanoluminescence recording system consisting of a mechanoluminescent material and a photosensitive material. Using the ML recording system, the applied stress was successfully recorded onto a picture film accumulative via the mechanoluminescence from the ML sheet, in which the recorded intensity exhibits an increase with increasing time and they have presented a number of stress applications. Terasaki et al. (2009) have investigated that the preparation method for a hybrid material which combines an ML material and TiO$_2$ photocatalyst nanoparticles without losing their original mechanoluminescence and photocatalysis properties. Yamada et al. (2007, 2008) have fabricated strongly adherent SrAl$_2$O$_4$:Eu films on the rough surface of an alumina substrate by a combination of the RF magnetron sputtering technique and a post-annealing treatment. It was found that the fabricated films possessed a strong immunity against friction, exhibiting no peeling, cracking and breaking in the films after ML measurements. Li et al. (2008 a, b, 2009) have demonstrated the dynamic visualization of stress distribution by ML sensing film of SrAl$_2$O$_4$:Eu. Zhang et al. (2008) have developed a novel elasticoluminescent material with CaAl$_2$Si$_2$O$_8$:Eu$^{2+}$. Zhang et al. (2008) have also reported a multifunctional ceramics, europium-doped feldspar MAI$_2$Si$_2$O$_8$:Eu (MASE,M=Ca,Sr,Ba) and demonstrated that this phosphor was capable of emitting high mechanoluminescence, strong photoluminescence, and electroluminescence. Zhang et al. (2008) have reported blue-greenish light emission from stress activated SrCaMgSi$_2$O$_7$:Eu. Fu et al. (2008, 2009) have prepared highly oriented SrAl$_2$O$_4$:Eu films with different thickness on inconel 600 substrate by radio frequency sputtering. The films exhibited an intensively green photoluminescence and high ML intensity. Chandra et al. (2009) have reported that, when rare earth doped strontium aluminate phosphor mixed
in an epoxy resin, is deformed elastically by applying a uniaxial pressure, then the mechanoluminescence intensity increases initially with time, attains a peak value $I_m$ later at particular time $t_m$, and decreases thereafter with time. Considering the piezoelectrically-assisted charge carrier detrapping model of ML, a theoretical analysis has been made to different characteristics of the ML of SrAl$_2$O$_4$:Eu,Dy phosphors. Kim et al. (2009) have reported a rate equation model for the loading-rate dependent ML of SrAl$_2$O$_4$:Eu,Dy (SAO), whereby the effect of the loading rate on the ML of SAO were investigated. Ono et al. (2010) have demonstrated the visualization of internal defect of a pipe using mechanoluminescent sensor. Li et al. (2011) have reported the real-time visualisation of the Portevin-Le-Chatelier effect with mechanoluminescent-sensing film. Wang et al. (2011) have developed a new smart damage sensor using mechanoluminescence SrAl$_2$O$_4$:Eu,Dy powder and polymer. They performed the detection of crack and the evaluation of the stress concentration and stress intensity factors using SAO film sensor. Zhang et al. (2011) have demonstrated that the ML technique has potential to be used in ultrasonic power measurements. Chandra et al. (2011) reported the mechanoluminescence glow curves of rare-earth-doped strontium aluminate phosphors. Chandra et al. (2012) reported that real-time mechanoluminescence sensing of the amplitude and duration of impact stress. Hyodo et al. (2010) reported that the EML materials can be used for the stress imaging of the orthopedic devices; they have potential of analyzing the suitable design of the artificial organs such as legs. Chandra (2012) has reported several applications of elastico mechanoluminescent materials.

Botterman et al. (2012) have investigated strong non-destructive ML in BaSi$_2$O$_2$N$_2$:Eu. They found that when irradiated in advance with ultraviolet or blue light, this phosphor shows intense blue-green light
emission upon mechanical stimulation such as friction or pressure. The ML has an emission band peaking at 498 nm, which is 4 nm red-shifted compared to the steady-state photoluminescence. The origin of the ML is discussed and related to the persistent luminescence of BaSi2O2N2:Eu. The same traps are responsible for both phenomena. Based on the occurrence of ML in this phosphor, this is evident that the predominant crystallographic structure of BaSi2O2N2:Eu belongs to space group Cmc21. Fig. 4.13 shows typical mechanoluminescence (ML) behavior of stress-stimulated BaSi2O2N2:Eu during application of a force of 20 kN (64 MPa). The solid line shows the ML intensity (on a linear scale) and the dashed line shows the force profile.

Matsuo et.al.(2012) have studied phase transformation behavior and pseudoelastic deformation in SrAl2O4. They reported that Europium-doped strontium aluminate [SrAl2O4:Eu2+] (SAOE) emits green light under an applied mechanical stress. In order to clarify the relationship between ML and its structure, the microstructure, phase transformation behavior and structural change under a load on SAO ceramics were investigated. The microstructures were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It has been that SAO has a twin structure with three kinds of morphologies. The phase transformation behavior was investigated using differential scanning calorimetric (DSC) measurements and observation of the microstructures. It is indicated that the twin structures are formed by a thermo elastic martens tic transformation from a hexagonal (β) to a monoclinic (α) phase at about 670 °C. In addition, the structural change under a load was observed by in situ TEM nanoindentation. It is clarified that pseudoelastic deformation occurred in SAO. These results suggest that ML occurs with rearrangement of variants of α phase.
Yun et.al.(2013) have investigated Stress sensing performance using mechanoluminescence of SrAl2O4:Eu (SAOE) and SrAl2O4:Eu, Dy (SAOED) under mechanical loadings. The stress sensing performance of two well-known mechanoluminescence (ML) sensing materials, (1) SrAl2O4:Eu(SAOE) and (2) SrAl2O4:Eu,Dy(SAOED), has been experimentally studied. Under the same input loadings and strain rates, changes of the light intensity have been characterized in terms of sensitivity, repeatability and linearity. Effects of the strain rate on the light intensity changes have also been investigated for both ML sensing materials. SAOED appears to perform better as an ML stress sensor than SAOE because it shows higher sensitivity and no saturation of light during the loading history. Although SAOE showed saturation of light emissions, its initial sensitivity to loading was higher than that of SAOED. Therefore, SAOE appears to be more suitable for sensors for monitoring dynamic active cracks. Fig. 4.14 shows the compression tests of a light-emitting sample (SAOE). Fig. 4.15 shows relative peak light intensity and force versus time for SAOE and SAOED for five strain rates.

The elastico-mechanoluminescence (EML) properties of CaZnOS:Mn$^{2+}$ are investigated by Zhang et.al.(2013). They reported that the CaZnOS:Mn$^{2+}$ epoxy resin composite can simultaneously “feel” (sense) and “see” (image) various types of mechanical stress over a wide energy and frequency range (ultrasonic vibration, impact, friction and compression) as an intense red emission (610nm) from Mn$^{2+}$ ions. Further, the accurate linear relation between emission intensity and different stress parameters (intensity, energy and deformation rate) are confirmed. The EML mechanism is explained using a piezoelectrically induced trapped carrier excitation mode. All the results imply that
CaZnOS:Mn$^{2+}$ has potential as a stress probe to sense and image multiple mechanical stresses and decipher the stress intensity distribution. Fig. 4.16(a) shows ML intensity response of the CaZnOS:Mn$^{2+}$ film to impact stress applied by a free-falling ZrO2 ball with impact energy of 28.2 mJ. The inset shows the luminescence induced by mechanical impact, and Fig.4.16 (b) shows relationship between ML intensity and impact energy.

It is evident from the above description that, in the past, detailed study of the elastico ML produced during application of load on rare earth doped persistent luminescent material have been made; whereas, the ML of the persistent luminescent materials has not been studied. From the basic and the application points of view the theoretical study of the ML of rare earth doped persistent luminescent material induced by impact of a load is required. The present thesis/study reports in detail the characteristics of mechanoluminescence of SrAl$_2$O$_4$:Eu,Dy phosphors induced by the impact of a load for the first time. Instead of mixing the phosphor with resin, the compact masses of SrAl$_2$O$_4$:Eu,Dy phosphors were used and found to give more ML than the former. It has been shown that the day visible mechanoluminescence in SrAl$_2$O$_4$:Eu,Dy phosphors may be used in designing the impact stress and impact velocity sensors. It is noteworthy that the measurements of impact velocity and impact pressure have imperative applications in engineering and technology.
4.2 MECHANISM OF THE ELASTICO MECHANOLUMINESCENCE OF SrAl$_2$D$_4$:Eu AND OTHER PERSISTENT LUMINESCENT MATERIALS

Figure 4.1 shows the schematic diagram for the ML emission in SrAl$_2$O$_4$:Eu crystals. The steps involved in the EML emission in SrAl$_2$O$_4$:Eu crystals are as follows:

(i) UV-light induced excitation of the electrons of Eu$^{2+}$ ions from 4f level to the 5d level lying very close to the bottom of conduction band.

(ii) Subsequent oxidation of some Eu$^{2+}$ ions to Eu$^{3+}$ ions, and the trapping of released electrons at the oxygen vacancy levels located in the vicinity of the photo-generated Eu$^{3+}$ locations (Clabau et.al. 2005, 2006, 2008).

(iii) De-trapping 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 (Xu et.al. 2004).

(iv) Recombination of the electrons moving in the conduction band with the photo-generated Eu$^{3+}$ ions and generation of excited Eu$^{2+}$ (Clabau et.al. 2005, 2006, 2008).

(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 (Chandra and Chandra 2012, Botterman et.al. 2012, Yun et.al. 2013).
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 $d=10^{-11}$ Coulomb N$^{-1}$ (Ohsato et.al. a,b,c, 2012, Uchino 2003). The threshold pressure for the EML emission in SrAl$_2$O$_4$:Eu$^{2+}$ crystal is $1 \times 10^6$ Nm$^{-2}$. Thus, the piezoelectric charge density for the threshold pressure will be, $\rho = dP_{th} = 10^{-11} \times 10^6 = 10^{-5}$ Coulomb 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, $1.13 \times 10^6$ Vm$^{-1} = 1.13 \times 10^4$ V cm$^{-1}$. The dielectric constant of SrAl2O4:Eu crystals is 8 (Kurien 2005); hence, the internal electric field will be, $1.4 \times 10^3$ Vcm$^{-1}$. As the detrapping of charge carriers needs an internal electric field of the order of $10^4$ V cm$^{-1}$ (Cottaar et.al. 2010 and Ottaviani 1977) and the impact ionization needs an internal electric field of the order of $10^5$ V cm$^{-1}$ (Medling et.al. 2011 and Hitt et.al. 2000); the normal internal piezoelectric field of the order of $10^3$ Vcm$^{-1}$ produced by the threshold pressure may not cause the detrapping and impact ionization. The appearance of elastico ML by the threshold pressure of $1 \times 10^6$ Nm$^{-2}$ 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 (Chandra and Rathore 1995, Sage and Bourhill 2001) or due 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.

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 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. The enhanced piezoelectric constants of SrAl$_2$O$_4$:Eu crystals may be estimated in the following way. If the distance between two ends of the sites responsible for dipole formation is $L$ meter, then for the Young’s modulus $Y=1.02 \times 10^{11}$ Nm$^2$ (Nanko et.al. 2007 and Espinosa et.al. 2012); the change in the distance between two ends of the sites responsible for dipole formation by a unit stress will be, $L/Y=1 \times 10^{-11} \times L$ meter. 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 $M=q \times L = 1.6 \times 10^{-19} \times L \times 10^{-11} = 1.6 \times 10^{-30}$ L Coulomb meter. 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 $2.38 \times 10^{-30} \sigma L$. As the size of Sr$^{2+}$ ion is, $1.18 \times 10^{-10}$ m, $\sigma = \pi (1.18)^2 \times 10^{-20}$ m$^2=1.34 \times 10^{-20}$ m$^2$. Thus, the value of the activation volume $\Omega$ of the dipole comes out to be $\Omega= \sigma L= 1.34 \times L \times 10^{-20}$ 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 $d=M/ \Omega=1.12 \times 10^{-10}$ Coulomb 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 $5\times10^6$ Nm$^{-2}$ near the defect centres will be of the order of $10^4$ Vcm$^{-1}$. 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$^{3+}$ ions may produce excited Eu$^{2+}$ ions, whereby the de-excitation may give rise to the light emission characteristic of Eu$^{2+}$ ions.

Fig. 4.1 Schematic diagram for the ML emission in SrAl$_2$O$_4$:Eu, Dy (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) (after Chandra et.al., 2013).
4.3 THEORETICAL APPROACH TO THE ELASTICO MECHANOLUMINESCENCE OF PERSISTENT LUMINESCENT MATERIALS

For measuring the EML of persistent mechanoluminescent materials, the microcrystals or nanocrystals of the phosphors are mixed in epoxy resin and then the samples of suitable dimension are prepared using a mold. The EML in the sample is excited by applying a load or by the impact of a small ball from a low height. If $\Omega$ is the activation volume near an activator ion at around which the piezoelectric constant is high, $N_c$ is the number of crystallites in the sample, $N_l$ is the number of activators in a crystallite and $N_t$ is the concentration of traps, then the total number of traps in the sample is given by, $N_0 = \Omega N_c N_l N_t$.

Now, the following three cases of the EML excitation arise:

(I) EML under increasing stress and fixed stress condition
(II) EML under increasing and decreasing stress condition, and
(III) EML under impact stress condition.

In chapter III, section 3.4.1, we have described the EML under increasing stress and fixed strain condition for ZnS:Mn crystals using piezoelectrically induced de-trapping model of EML. The same theory is also applicable for the EML of persistent luminescent material. Thus, the EML expressions are as follows:

Case I: EML under increasing stress and fixed stress condition

For I:

$$I = \eta \sigma \mu n, \Omega N_c N_l N_I Z \alpha \tau B^2 d_0^2 \dot{P}(P - P_{in})$$

or, $I = \eta \sigma \mu n, \Omega N_c N_l N_I Z \alpha \tau B^2 d_0^2 \dot{P}^2(t - t_0)$

or, $I = \eta \sigma \mu n, \Omega N_c N_l N_I Z \alpha \tau B^2 d_0^2 Y^2 \dot{\varepsilon}^2(t - t_0)$

----- (4.1)
For fast decay:
\[ I_{df} = I_m \exp[-\phi(t-t_m)] \]  ----- (4.2)

For slow decay:
\[ I_{ds} = I_{0s} \exp\left[-\frac{(t-t_c)}{\tau_s}\right] = I_{0s} \exp[-\chi(t-t_c)] \]  ----- (4.3)

For Maximum Intensity:
\[ I_m = \eta \sigma m_e \Omega N_i N_e N_c \mu e \alpha Z \alpha \tau B^2 d_0^2 (P_m - P_{th}) \frac{dP}{dt} \]
\[ \text{or} \]
\[ I_m = \eta \sigma m_e \Omega N_i N_e N_c \mu e \alpha Z \alpha \tau B^2 d_0^2 Y (P_m - P_{th}) \dot{\epsilon} \]  ----- (4.4)

For Total Intensity:
\[ I_T = \frac{\eta \sigma m_e \Omega N_i N_e N_c \mu e \alpha Z \alpha \tau B^2 d_0^2 P_m^2}{2} \left(1 + \frac{2Y\dot{\epsilon}}{\phi P_m}\right) \]
\[ \text{or} \]
\[ I_T = \frac{\eta \sigma m_e \Omega N_i N_e N_c \mu e \alpha Z \alpha \tau B^2 d_0^2 P_m^2}{2} \left(1 + \frac{2\tau_m}{t_m}\right) \]  ----- (4.5)

Case II: EML under increasing and decreasing stress condition

For the increasing portion of pressure, \( I_m \) and \( I_T \) are given by Esq. (4.4) and (4.5), respectively. For the decay of EML intensity after \( t_m \), the following two conditions arise: (i) occurrence of the de-trapping in the localized piezoelectric region during the decay of piezoelectric charge, and (ii) occurrence of the EML decay from the filled shallow traps lying in the normal piezoelectric region of the crystals.

Condition I: Occurrence of the de-trapping in the localized piezoelectric region during the decay of piezoelectric charge

In this case, after \( t_m \), the pressure decreases with the rate \( \dot{P} \), and therefore, the time dependence of pressure can be expressed as
\[ P = \dot{P}[t_m - (t - t_m)] = \dot{P}(2t_m - t) \]  ----- (4.6)
where, $\dot{P} t_m$ is the maximum pressure $P_m$ and $\dot{P} (t-t_m)$ is the decrease of pressure with time after $t_m$.

From Eq. (4.6), $Q$ is given by

$$Q = d_0 P = d_0 \dot{P} (2t_m - t)$$

----- (4.7)

Now, from Eq. (4.7), $dQ/dt$, is given by

$$\frac{dQ}{dt} = -d_0 \dot{P}$$

----- (4.8)

Equation (4.1) indicates that for $Q >> Q_{th}$, the EML intensity $I$ is proportional to the product of $Q$ and $dQ/dt$. Thus, Esq. (4.7) and (4.8) give

$$I = Dd_0^2 \dot{P}^2 (2t_m - t)$$

----- (4.9)

where $D$ is the proportionality constant.

As $I = I_m$, at $t = t_m$, we get $Dd_0^2 \dot{P}^2 = I_m / t_m$, and therefore, the decay of EML intensity can be expressed as

$$I_{ds} = \frac{I_m}{t_m} (2t_m - t)$$

----- (4.10)

**Condition II: Occurrence of the EML decay from the filled shallow traps lying in the normal piezoelectric region of the crystals**

In the second condition, the decay of EML intensity can also be expressed using Eq.(4.3), where the EML intensity will decrease exponentially with time and the decay time of EML will be equal to the lifetime of electrons in the shallow traps lying in the normal piezoelectric region of the crystals, at which the piezoelectric field is less.

**Case III: EML under impact stress condition**

If a small ball of mass $m$ is dropped from a low height $h$ onto an elastic mechanoluminescent film coated on a substrate, then the velocity of impact is, $v_0 = \sqrt{2gh}$, where $g$ is the acceleration due to gravity. After
the impact, the velocity decreases with time. If $\tau_r$ is the rise time of the compression $x$, then the time dependence of the compression is given by

$$x = x_0 \left[ 1 - \exp \left( -\frac{t}{\tau_r} \right) \right] = x_0 \left[ 1 - \exp (-\xi t) \right] \quad \text{----- (4.11)}$$

where $x_0$ is the maximum compression and $\xi = 1/\tau_r$

Differentiating Eq. (4.11) and taking $dx/dt = v_0$, at $t = 0$, we get

$$x_0 = v_0 \tau_r = v_0 / \xi \text{. Thus, Eq. (4.11) can be written as}$$

$$x = \frac{v_0}{\xi} \left[ 1 - \exp (-\xi t) \right] \quad \text{----- (4.12)}$$

Consider a sphere of velocity $v_0$ mass $m$, radius $r$, and modulus of elasticity $Y$, impacting on an infinite flat plate. Using the Hertz model the force $f(x)$ needed to compress the sphere a distance $x$ can be expressed as (Correcher et.al. 2008, Heimbs et.al. 2009, Daraio et.al. 2004, Cross 1999, Burger et.al. 1995).

$$f(x) = -\frac{2Y \sqrt{r}}{3(1-\nu^2)} x^{3/2} \quad \text{----- (4.13)}$$

where $\nu$ is the Poisson ratio and for most metals it is 0.3.

The contact area $A_c$ made between the sphere and the base plate is a very useful parameter of impact and can be measured easily. By geometric arrangements, it can be shown that $A_c$ is directly related to the compression distance $x$ and it can be expressed as (Chandra 2011).

$$A_c = \pi r x \quad \text{----- (4.14)}$$

Thus, from Esqs. (4.36) and (4.37), the stress or pressure $P$ for the compression $x$ is given by

$$P = \frac{f(x)}{A_c} = \frac{2Y}{3(1-\nu^2)\pi \sqrt{r}} x^{1/2} \quad \text{----- (4.15)}$$

From Esqs. (4.12), (4.13), (4.14) and (4.15), the pressure $P$ at any time $t$ can be expressed as

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\[
P = \frac{2Y \sqrt{v_0}}{3\pi(1-\nu^2)\sqrt{r\sqrt{\xi}}} \left[1 - \exp(-\xi t)\right]^{1/2}
\]

or, \[ P = P_0\left[1 - \exp(-\xi t)\right]^{1/2} \] \hspace{1cm} ----- (4.16)

where \[ P_0 = \frac{2Y \sqrt{v_0}}{3\pi(1-\nu^2)\sqrt{r\sqrt{\xi}}} = \phi \sqrt{v_0} \]

where \[
\phi = \frac{2Y}{3\pi(1-\nu^2)\sqrt{r\sqrt{\xi}}}
\]

Differentiating Eq. (4.16), we get
\[
\frac{dP}{dt} = \frac{P_0 \xi \exp(-\xi t)}{2\left[1 - \exp(-\xi t)\right]^3} \] \hspace{1cm} ----- (4.17)

From Eq. (4.14), the contact area can be expressed as
\[
A_c = \pi r x = \pi r x_0 \left[1 - \exp(-\xi t)\right]
\]

\[
A_c = \pi r \frac{v_0}{\xi} \left[1 - \exp(-\xi t)\right] \] \hspace{1cm} ----- (4.18)

If \( H \) is thickness of the sample, then the effective volume \( V_e \) from there ML emission will take place is given by
\[
V_e = A_c H = H \pi r \frac{v_0}{\xi} \left[1 - \exp(-\xi t)\right] \] \hspace{1cm} ----- (4.19)

If \( N_p \) is the concentration of crystallites, then \( N_c \) can be expressed as
\[
N_c = N_p V_e = N_p H \pi r \frac{v_0}{\xi} \left[1 - \exp(-\xi t)\right] \] \hspace{1cm} ----- (4.20)

Now substituting the value of \( P \), \( dP/dt \), and \( N_c \) in Eq. (4.1), we get
\[
I = \frac{\eta \sigma m \Omega N_c N_c Z \alpha \beta^2 d_0^2 \rho_0 \left[1 - \exp(-\xi t)\right]^3 P_0 \xi \exp(-\xi t) N_p H \pi r \frac{v_0}{\xi} \left[1 - \exp(-\xi t)\right]}{2\left[1 - \exp(-\xi t)\right]^3}
\]

or, \[ I = \frac{\eta \sigma m \Omega N_c N_c Z \alpha \beta^2 d_0^2 \rho_0 \left[1 - \exp(-\xi t)\right]^3 P_0 \xi \exp(-\xi t) N_p H \pi r v_0 \left[\exp(-\xi t) - \exp(-2\xi t)\right]}{2} \]
or, \( I = \frac{\eta \sigma m, \Omega N, N, Z \alpha B^2 d_0^2 \phi^2 N \rho H \pi rgh [\exp(-\xi t) - \exp(-2\xi t)]}{2} \)

or, \( I = \frac{\eta \sigma m, \Omega N, N, Z \alpha B^2 d_0^2 \phi^2 N \rho H \pi rgh [\exp(-\xi t) - \exp(-2\xi t)]}{2} \) ----- (4.21)

As \( v_0 = \sqrt{2gh} \) where \( h \) is the height through which the ball is dropped on to the sample and \( g \) is the acceleration due to gravity.

(i) **Rise of EML Intensity**

For \( \xi t \ll 1 \) Eq. (4.21) can be written as

\[
I_r = \eta \sigma m, \Omega N, N, Z \alpha B^2 d_0^2 \phi^2 N \rho H \pi rgh \xi t \quad ----- (4.22)
\]

Eq. (4.22) Indicates that, when a small ball will be dropped into the film, then initially the EML intensity should increase linearly with time.

(ii) **Estimation of \( t_m \)**

The value of time \( t_m \) corresponding to the peak of EML intensity versus time curve can be obtained by differentiating Eq. (4.21) with respect to \( t \) and equating it to zero. Thus, we get

\[
\xi \exp(-\xi t) = 2\xi \exp(-2\xi t)
\]

or \( t_m = \frac{1}{\xi} \ln 2 \) ----- (4.23)

(iii) **Estimation \( I_m \)**

Substituting, the value \( t = t_m \), from Eq. (4.23) in Eq. (4.20), we get

\[
I_m = \frac{\eta \sigma m, \Omega N, N, Z \alpha B^2 d_0^2 \phi^2 N \rho H \pi rgh}{4}
\]

----- (4.24)

(iv) **Estimation of \( I_{TD} \)**

Using Eq. (4.21), the total EML intensity \( I_{TD} \) can be expressed as

\[
I_{TD} = \int \int 0^\infty \eta \sigma m, \Omega N, N, Z \alpha B^2 d_0^2 \phi^2 N \rho H \pi rgh [\exp(-\xi t) - \exp(-2\xi t)] dt
\]

or, \( I_{TD} = \frac{\eta \sigma m, \Omega N, N, Z \alpha B^2 d_0^2 \phi^2 N \rho H \pi rgh}{2\xi} \) ----- (4.25)
(v) Fast Decay of EML

Equation (4.21) can be written as

\[ I = \eta \sigma m, \Omega N_i N_e Z \alpha \tau B^2 d_0^2 \phi^2 N_p H \pi g h \exp(-\xi t) \exp[-\xi (t - t_m)] [1 - \exp(-\xi t)] \]

or, \[
\frac{I}{[1 - \exp(-\xi t)]} = \eta \sigma m, \Omega N_i N_e Z \alpha \tau B^2 d_0^2 \phi^2 N_p H \pi g h \exp(-\xi t) \exp[-\xi (t - t_m)]
\]

For \( \xi t \gg 1 \), Eq. (4.26), can be written as

\[ I_{df} = \eta \sigma m, \Omega N_i N_e Z \alpha \tau B^2 d_0^2 \phi^2 N_p H \pi g h \exp[-\xi (t - t_m)] \]

Equation (4.26) indicates that the plot between \( \ln I/(1-\exp(-\xi t)) \) versus \( (t-t_m) \) should be a straight line with negative slope \( \xi \). Equation (4.27) indicates that for longer duration of time the slope between \( \log I \) versus \( (t-t_m) \) should be a straight line with negative slope \( \xi \). Thus, the value of \( \xi \) can be determined from \( \log I \) versus \( (t-t_m) \) plot.

(vi) Slow decay of EML

During the deformation of crystals some of the de-trapped electrons moving in the conduction band get trapped at the shallow traps lying in the normal piezoelectric region of the crystals where the piezoelectric field is less and later on such trapped electrons are thermally released form the traps and their subsequent capture in the excited state of activator ions such as Eu\(^{2+}\) gives rise to the light emission. In this case, if \( \tau_i \) is the lifetime of electrons in the shallow traps lying in the normal piezoelectric region of the crystals, then the slow decay of EML intensity is given by

\[ I_{si} = I_0 \exp \left[ -\frac{(t-t_c)}{\tau_i} \right] = I_0 \exp \left[ -\psi(t-t_c) \right] \]

where \( \psi = 1/\tau_i \), \( t_c \) is the time at which the fast decrease of EML intensity becomes negligible ,and \( I_0 \) is the EML intensity at \( t = t_c \).
It is to be noted that, in this case, the shallow traps in which the lifetimes of charge carriers are of the order of one second or higher can not take part as they behave as stable traps for the pressure pulse duration of microseconds.

(vii) Dependence of $I_m$ and $I_{TD}$ on $H$

As $x_0 = v_0 / \xi$, $F_0 = BQ_0 = Bd_0 P_0 = \frac{2B^2d_0^2Y^2\sqrt{v_0}}{3\pi(1-v^2)\sqrt{r}\sqrt{\xi}}$

Eqs. (4.24) and (4.25) can be written as

$$I_m = \frac{\eta \sigma \mu e \tau B^2 d_0^2 Y^2 H \Omega N_i N_e Z_{agh}}{9\pi(1-v^2)^2 r_\xi^2}$$

----- (4.29)

and,  $$I_{TD} = \frac{2\eta \sigma \mu e \tau B^2 d_0^2 Y^2 H \Omega N_i N_e Z_{agh}}{9\pi(1-v^2)^2 r_\xi^2}$$

----- (4.30)

It is evident from Eqs. (4.29) and (4.30) that, both $I_m$ and $I_{TD}$ should increase linearly with the height $h$ through which the ball is dropped onto the mechanoluminescent films.
4.4 EXPERIMENTAL SUPPORT TO THE PROPOSED THEORY

Akiyama et al. (2002) have prepared SrAl$_2$O$_6$: Eu,Dy phosphors by mixing appropriate quantities of $\alpha$-Al$_2$O$_3$, SrCO$_3$, Eu$_2$O$_3$, Dy$_2$O$_3$ and H$_3$BO$_3$. The thoroughly mixed powders were sintered at 1300 $^\circ$C for 4h in a reduction atmosphere (Ar+5% H$_2$) and they were ground and composites of diameter of 25 mm and thickness of about 15mm were made by mixing 1.0 g of sintered powders and 3.5 g of epoxy resin of epichlorihydrine using a silicon mold.

Xu et al. (2004) have synthesized SrAl$_2$O$_6$:Eu phosphors by a solid state reaction process using high purity SrCO$_3$, Al$_2$O$_3$ and Eu$_2$O$_3$ as starting materials. The powder sample was dispersed uniformly in an optical epoxy and then a rectangular composite with a dimension of 55 x 29 x 14 mm was formed by a silicon mold. Jia et al. (2006) have prepared SrAl$_2$O$_4$:Eu, Dy by mixing SrCO$_3$, Al$_2$O$_3$, Eu$_2$O$_3$, Dy$_2$O$_3$ and H$_3$BO$_3$ and grinding. Then, the mixture was pressed into pellets. The pellets were pre-sintered in a furnace at 900$^\circ$C for 2h in air and then the pre-sintered pellets were ground and sintered again at 1400$^\circ$C for 2h in a reducing atmosphere of N$_2$ + 5% H$_2$. Fu et al. (2009) have deposited SrAl$_2$O$_4$:Eu films onto the quartz glass substrate by a combination of the RF magnetron sputtering technique and post-annealing treatment.

Akiyama et al. (2002) have prepared ZrO$_2$: Ti phosphor from ZrO$_2$ and 0.1 mol% TiO$_2$ powder. These powders were mixed in ethanol and sintered at 1500$^\circ$C for 4h in organ atmosphere. CaAl$_2$ SiO$_7$:Ce phosphor was prepared by mixing CaCO$_3$, $\alpha$-Al$_2$O$_3$, SiO$_2$, CeO and H$_3$BO$_3$ powders and then sintering at 1300$^\circ$C for 4h in reduction atmosphere (Ar +5% H$_2$) (Akiyama et al.1998). Wang et al.(2005) have synthesized (Ba,Ca)TiO$_3$:Pr$^{3\text{+}}$ phosphors using conventional solid-state reaction
technique. Zhang et al. (2009) have prepared Sr₂Mg Si₂O₇:Eu, SrCaMgSiO₇:Eu and SrBaMgSi₂O₇:Eu phosphors by mixing appropriate quantities of SrCO₃, CaCO₃, BaCO₃, SiO₂, MgO and Eu₂O₃, in which the powders were initially fired for 1h in air and then sintered at 1200°C for 4h in (Ar+5%H₂) atmosphere.

The EML was excited by pressing the specimen using a material testing machine or power press machine with a force gauge or a vise. Jia et al. (2006) used a hydraulic press for pressing the samples. For impulsive excitation of EML in SrAl₂O₄:Eu film on a quartz glass substrate, Fu et al. (2009) dropped a ZrO₂ ball of mass about 0.088 g and diameter 0.30 cm from a height of 2.5 cm.

The EML intensity was measured using a photomultiplier tube. In some cases the EML intensity was measured using a photon counting system comprising a photomultiplier tube and a photon counter controlled by a computer. The EML spectra were recorded using a spectrometer. In some cases, the EML emission light was guided to the photomultiplier tube using a quartz glass fiber and the EML spectra were obtained using a photon multichannel analyzer system. Jia et al. (2006) recorded the EML spectra using a spectrometer connected to a computer for real-time data-acquisition.

Fig. 4.2(a) shows the typical elastico mechanoluminescence behavior of stressed Sr₃Al₂O₆:Eu,Dy during application of force of 1000 N, Fig. 4.2 (b) shows the EML emission during the release of load and Fig. 4.2(c) shows the force versus time curve (Akiyama et.al. 2002). In this measurement the specimen diameter was 25 mm and the thickness was 15 mm. It is seen that when the load is applied, then the EML intensity initially increases with time, attains a peak value and then it decreases with time, initially at a fast rate and later on at a slow rate. When the load is released, the EML emission also takes place, in which
initially the EML intensity increases with time, attains a peak value and later on it decreases initially at a fast rate and then at a slow rate. In the case of release of pressure, the EML intensity is several times less as compared to that obtained during the application of pressure. For Sr$_3$Al$_2$O$_6$:Eu, Dy the value of fast decay time $\tau_1$ is 0.10 sec and the value of slow decay time $\tau_2$ is 4.03 sec. For the release of pressure the value of fast decay time is 0.33 sec and the value of slow decay time is 4.1 sec.

Fig. 4.2 (a) Typical elastic mechanoluminescence behavior of stressed Sr$_3$Al$_2$O$_6$:Eu, Dy during application of force of 1000 N, (b) EML during release of load (after Akiyama et. al., 2009), (c) force versus time curve (d) plot of log I versus $(t-t_m)$ for the EML produced during the application of force, and (e) plot of log I versus $(t-t_m)$ for the EML produced during the release of load.
Fig. 4.3(a) shows the time dependence of the intensity of EML obtained during the application of force of 1000 N on Sr$_2$Al$_2$O$_6$:Eu,Dy phosphors in which the specimen diameter was 25 mm and thickness was about 15 mm and the pressing rate was slow (Akiyama et.al. 1999). From the slopes of log I versus (t-t$_m$) plot shown in Fig.3 (b), the values of $\tau_1$ and $\tau_2$ are determined and they are found to be 1.03 sec and 4.14 sec, respectively.

![Typical elastico mechanoluminescence behavior of stressed Sr$_3$Al$_2$O$_4$:Eu, Dy during application of load of about 1000N(after Akiyama et. al.,1999)](image)

![Plot of log I versus (t-t$_m$) for the EML produced during the application of force.](image)
Fig. 4.4(a) shows the EML emission of SrAl$_2$O$_4$:Eu composite of dimension 55 x 29 x 14 mm, in which initially the force increases linearly with time and then after attaining a maximum value, the force decreases linearly with time (Xu et.al. 2004). It is evident from the figure that, when the pressure increases, then the EML intensity increases and when the force decreases linearly, then the EML intensity decreases exponentially with time. From the slope of log I versus (t-t$_m$) plot shown in Fig.4 (b), the value of $\tau_1$ is determined and it is found to be 1.19 sec.

Fig.4.4 (a) Response curve of the elastic mechanoluminescence of $\alpha$-SrAl$_2$O$_4$: Eu (after Xu et. al., 2004),

Fig.4.4 (b) Plot of log I versus (t-t$_m$) for the EML produced during the decrease of force at a fixed rate.
Fig. 4.5(a) shows the EML emission from SrAl$_2$O$_4$:Eu, Dy composite of diameter 28mm and thickness 8 mm (Jia et.al. 2006). It is seen from Fig. 4.5(b) that, when at pressure of 8 kPa is applied, then initially the EML intensity increases with time, attains a peak value and latter on it decreases with time. From the slope of log I versus (t-t$_m$) plot shown in Fig. 4.5(c), the value of $\tau_1$ is determined and it is found to be 0.77 sec.

![Graphs showing EML intensity versus time and log I versus (t-t$_m$) plot](image)

Fig. 4.5(a) EML intensity versus time curve for SrAl$_2$O$_4$:Eu, Dy composites for the pressure of 8 kPa (after Jia et al., 2006), (b) time dependence of the EML intensity for the applied pressure of 6 kPa, and (c) plot of log I versus (t-t$_m$) for the EML produced during the application of the pressure of 8 kPa.
Fig. 4.6(a) shows the EML emission from Ca$_2$Al$_2$SiO$_7$:Ce phosphors pellet of diameter 25 mm and thickness 15 mm (Akiyama et al., 1998). It is seen that when a load of 1500 N is applied, initially the EML intensity increases with time, attains a peak value and then it decreases with times. From the slopes of log I versus (t-$t_m$) plot shown in Fig. 4.4 (b), the values of $\tau_1$ and $\tau_2$ are determined and they are found to be 3.22 sec and 8.61 sec, respectively.

![Graph](image1.png)

![Graph](image2.png)

Fig. 4.6(a) Typical elastico mechanoluminescence behavior of Ca$_2$Al$_2$SiO$_7$:Ce during application of a force of 1500N (after Akiyama et al., 1998) (b) plot of log I versus (t-$t_m$) for the EML produced during the application of force.
Fig. 4.7 (a) illustrates the EML intensity versus time of SrMgAl$_6$O$_{11}$:Eu composite of diameter 25 mm and thickness 7 mm (Akiyama et.al. 2003). It is seen from the figure that, when a pressure of at 130 N is applied, then the EML intensity increases with time, attains a peak value and latter on it decreases with time. It is evident from the Fig. 4.7 (b) that also the EML emission occurs during the release of pressure. Fig. 4.7(c) and Fig. 4.7 (d) show that, both for the pressing and release of pressure, initially the EML intensity decreases at a fast rate and then it decreases at a slow rate For pressing the value of fast decay time is 0.18 sec and the value of slow decay time is 0.81 sec. For the release of pressure, the values of fast decay time and slow decay time are found to be 0.17 sec and 0.80 sec, respectively.

**Fig. 4.7 (a) Typical elastico mechanoluminescence behavior of SrMgAl$_6$O$_{11}$:Eu composite during application of a force of 130 N, (b) during release from the load (after Akiyama et. al., 2003),**
Fig. 4.7 (c) Plot of log I versus (t-t_m) for the EML produced during the application of force,

Fig. 4.7 (d) Plot of log I versus (t-t_m) for the EML produced during the release of load.

Fig.4.8(a) illustrates the EML intensity versus time curve of (Ba, Ca) TiO$_3$:Pr$^{3+}$ composite for the application of a force of 1000 N on a specimen of diameter 25 mm and thickness 15 mm (Wang et.al. 2005). From the slopes of log I versus (t-t_m) plot shown in Fig.8(b), the values of $\tau_1$ and $\tau_2$ are determined and they are found to be 1.18 sec and 3.46 sec, respectively
Fig. 4.8 (a) Transient response with a compressive load up to 1000 N for a 25 mm diameter sample of (Ba$_{1-x}$Ca$_x$) TiO$_3$:Pr$^{3+}$ with $x = 0.30$. Red light emission is visible to the naked eye (after Wang et. al., 2005)

Fig.4.8 (b) Plot of log I versus (t-t$_m$) for the EML produced during the application of force
Fig. 4.9(a) shows the EML versus time curve of composite ZrO$_2$:Ti sample disc of diameter 25 mm and thickness 15 mm (Akiyama et al. 2002). Fig. 4.9(b) shows that also the EML emission takes place during the release of pressure. It is evident from Fig. 4.9(c) and Fig. 4.9(d) that, both for the pressing and release of pressure, initially the EML intensity decreases at a fast rate and then it decreases at a slow rate. For pressing the value of fast decay time is 4.10 sec and the value of slow decay time is 5.19 sec. Those values for the release of pressure are found to be 0.26 sec and 0.5.50 sec, respectively.

Fig. 4.9 (a) Typical elastico mechanoluminescence behavior of ZrO$_2$:Ti during application of load of 150N and during release from load (b) during release from the load (after Akiyama et al., ref. 2002).
Fig. 4.9(c) Plot of log I versus (t-t_m) for the EML produced during the application of force,

Fig. 4.9(d) Plot of log I versus (t-t_m) for the EML produced during the release of load.
A very interesting result in support of the model proposed in the present investigation is found from the pressure dependence of the EML intensity of Sr$_2$MgSi$_2$O$_7$:Eu (SMSE), SrCaMgSiO$_7$:Eu (SCMSE) and SrBaMgSi$_2$O$_7$:Eu (SBMSE) phosphors (Zhang et al. 2009). It is seen from Fig. 4.10 that, whereas the EML intensity of SBMSE phosphors increases linearly with stress, that of SMSE and SCMSE phosphors increase non-linearly. The EML intensities of SMSE and SCMSE phosphors are of the same order, but that of SBMSE phosphor is comparatively moderate. This fact shows higher EML emission for the crystals having higher value of the coefficient of deformation de-trapping, which is consistent with the basic principle of the present investigation (Eq. 4.11). The peaks of the EML spectra lye at 460, 490 and 440 nm for SMSE, SCMSE and SBMSE phosphors, respectively.

![Fig. 4.10 Dependence of the EML intensities of SrCaMgSi$_2$O$_7$:Eu (SCMSE), Sr$_2$MgSi$_2$O$_7$:Eu (SMSE) and SrBaMgSi$_2$O$_7$:Eu (SBMSE) crystals on stress (after Zheng et al., 2009). (The load values are changed to stress by taking the contact angle between the disk-shaped sample and the load to be $\theta = 18^\circ$, and therefore, the contact area = 0.59 cm$^2$) (after Zhang et al., 2009).](image)
Fig. 4.11 shows that the EML intensity of $\text{Sr}_3\text{Al}_2\text{O}_6$:Eu, Dy composite decreases with increasing number of pressings (Akiyama et.al. 2002). It is also seen that when the sample is exposed to UV light, then the recovery of EML intensity takes place.

Fig. 4.11 Dependence of luminescence intensity of $\text{Sr}_3\text{Al}_2\text{O}_6$:Eu, Dy on repetitive pressure of 1000N and effect of UV light irradiation. The UV wavelength was 365nm (after Akiyama et. al., 2002).

Fig. 4.12(a) shows the EML intensity versus time curve for the impact stress condition, in which the EML in $\text{SrAl}_2\text{O}_4$:Eu$^{2+}$ thin film on quartz glass substrate was excited by dropping a small ball of ZrO$_2$:Ti of approximate mass 0.088 gm from a height of 2.5 cm (Fu et.al. 2009). From the slopes of log I versus (t-t$_m$) plot shown in Fig.4.12 (b), the values of $\tau_1$ and $\tau_2$ are determined and they are found to be 36$\mu$s and 140$\mu$s, respectively.
Fig. 4.12(a) Mechanoluminescent glow curve of SrAl$_2$O$_4$:Eu thin film produced during the impact of a small ZrO$_2$ ball from a low height and ML image (inset)(Fu et.al. 2009).

The peaks of the EML spectra are found to lie at 510, 520, 420, 512, 617 and 478 nm for Sr$_3$Al$_2$O$_6$:Eu, Dy SrAl$_2$O$_4$:Eu, Dy, CaAl$_2$SiO$_7$:Ce, SrMgAl$_6$O$_{11}$:Eu, (Ba, Ca) TiO$_3$:Pr$^{3+}$, and ZrO$_2$:Ti, respectively. The EML spectra of composites are found to be similar to the corresponding photoluminescence and electroluminescence spectra (Wang et.al. 2005, Akiyama et.al. 2003, Xu et.al. 2004, Jia et.al. 2006, Kim et.al. 2007, Akuiyama et.al. 2002 a, b, 1999, Fu et.al. 2009).
Fig. 4.12 (b) Plot of log I versus (t–t_m) for SrAl_2O_4 :Eu for decreasing value of load.

Fig. 4.13. Typical mechanoluminescence (ML) behavior of stress-stimulated BaSi2O2N2:Eu during application of a force of 20 kN (64 MPa). The solid line shows the ML intensity (on a linear scale) and the dashed line shows the force profile. Inset: Photograph taken after “writing” the name LUMILAB on a layer of BaSi2O2N2:Eu powder (Botterman et al., 2012).
Fig. 4.13 shows the typical mechanoluminescence behavior of the ML of UV-irradiated PaSi$_2$O$_2$N$_2$:Eu phosphors mixed in transparent epoxy in which the ML was induced by applying a force of 20 kN (64 MPa) after a lapse of certain time after the UV-irradiation (Botterman et.al. 2012).

Fig. 4.14 shows that the ML intensity increases with increasing value of the load applied on to SrAl$_2$O$_4$:Eu (Yun et.al., 2013). Yun et.al.(2013) have studied the pressure dependence of the ML intensity of SrAl$_2$O$_4$:Eu and SrAl$_2$O$_4$:Eu,Dy phosphors for different strain rates. As shown in Fig. 4.15, they have found that for a given strain rate, initially the ML intensity increases with the applied force, then it attains an optimum value for a particular value of the applied pressure, and later on the ML intensity decreases with further increase in the value of the applied force. They have also found that the ML intensity increases with the strain rate.

Fig. 4.16 shows the ML response of the CaZnOS: Mn$^{2+}$ film; in which ML was excited by dropping a small ball of ZrO$_2$ of mass 18 mg from a fixed height (Zhang et.al., 2013). It is seen that only one ML pulse is obtained corresponding to a single impact. When a ball freely drops onto the CaZnOS:Mn$^{2+}$ film the impact ML intensity initially increases with time, attains a peak value, and then it decreases with time. The inset in Fig. 4.16(a) shows the corresponding Impact ML image, in which an intense red gleam was observed. From the slopes of semilog plot of I verses (t-t$_m$) shows in Fig. 4.16(b), the values of $\tau_1$ and $\tau_2$ are determined and they are found to be 2.62 ms and 8.44 ms, respectively.
Fig. 4.14 Compression test of a light-emitting sample (SAOE) (after Yun et.al., 2013).
Fig. 4.15 Relative peak light intensity and force versus time for SAOE and SAOED for five strain rate (after Yun et.al., 2013).
Table 4.1 shows the values of $\tau_1$, $\tau_2$, $\lambda_m$ and relative EML intensity of phosphors. SrMgAl$_6$O$_{11}$:Eu and SrAl$_2$O$_4$:Eu are the most intense EML phosphors.

It is to be noted that in some phosphors only one decay time of EML is observed whereas in some phosphors both the fast and slow decays of the EML are observed. The fast decay is related to the machine constant; however, the slow decay is related to the material constant. When the cross-head compressing the sample stops immediately after switching off the electrical power, initial part of the decay remains absent and only one decay time is observed. But, when after stopping gradually his electrical power the cross-head continues to move for some time with reducing rate, then both the fast decay time as well as slow decay time of EML are observed. In this case, the value of fast decay time $\tau_1$ depends
on the quality of the machine and thus, it is a machine constant. However, the slow decay time \( \tau_2 \) is related to the lifetime of electrons in the shallow traps lying in the normal piezoelectric region of the crystals. Therefore, the slow decay time is a material constant.

In case of the EML excitation of a film by impact stress, the fast decay time is related to the time-constant for the decrease of pressing rate of crystals and the slow decay time is related to the lifetime of charge carriers in the shallow traps lying in the normal piezoelectric region of the film.

In fact, a good agreement is found between the theoretical and experimental results.
Table 4.1

Fast decay time $\tau_1$, slow decay time $\tau_2$, wavelength $\lambda_m$ of the EML spectra and EML intensity of phosphors

<table>
<thead>
<tr>
<th>Material</th>
<th>Mechanic Action</th>
<th>$\tau_1$ (Fast decay time) (sec)</th>
<th>$\tau_2$ (Slow decay time) (sec)</th>
<th>$\lambda_m$(nm)</th>
<th>EML intensity (cps) (ref. [7])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Sr$_3$Al$_2$O$_6$:Eu,Dy (Fast pressing rate) (ref. [20])</td>
<td>Pressing</td>
<td>0.10</td>
<td>4.03</td>
<td>510</td>
<td>870</td>
</tr>
<tr>
<td>1. Sr$_3$Al$_2$O$_6$:Eu,Dy (slow pressing rate)(ref. [6])</td>
<td>Release</td>
<td>0.36</td>
<td>4.17</td>
<td>510</td>
<td></td>
</tr>
<tr>
<td>1. Sr$_3$Al$_2$O$_6$:Eu,Dy (slow pressing rate)(ref. [6])</td>
<td>Pressing</td>
<td>1.03</td>
<td>4.04</td>
<td>510</td>
<td></td>
</tr>
<tr>
<td>2. SrAl$_2$O$_4$:Eu (ref. [9])</td>
<td>Pressing, then release Hydraulic</td>
<td>-</td>
<td>1.05</td>
<td>520</td>
<td>12285</td>
</tr>
<tr>
<td>2. SrAl$_2$O$_4$:Eu (ref. [9])</td>
<td>Pressing</td>
<td>-</td>
<td>0.80</td>
<td>520</td>
<td></td>
</tr>
<tr>
<td>2. SrAl$_2$O$_4$:Eu, Dy (ref. [13])</td>
<td>Pressing</td>
<td>3.22</td>
<td>8.61</td>
<td>402</td>
<td>120</td>
</tr>
<tr>
<td>3. Ca$_2$Al$_2$SiO$_7$:Ce(ref. [21])</td>
<td>Pressing</td>
<td>0.18</td>
<td>0.81</td>
<td>512</td>
<td>24783</td>
</tr>
<tr>
<td>4. SrMgAl$<em>6$O$</em>{11}$:Eu (ref. [8])</td>
<td>Pressing</td>
<td>0.17</td>
<td>0.80</td>
<td>512</td>
<td></td>
</tr>
<tr>
<td>5. (Ba, Ca)TiO$_3$:Pr$^{3+}$ (ref. [7])</td>
<td>Pressing, then release</td>
<td>0.40</td>
<td>2.93</td>
<td>617</td>
<td></td>
</tr>
<tr>
<td>6. ZrO$_2$:Ti (ref. [22])</td>
<td>Pressing</td>
<td>3.07</td>
<td>5.21</td>
<td>478</td>
<td>69</td>
</tr>
<tr>
<td>7. SrAl$_2$O$_4$:Eu(Thin film) (ref. [25])</td>
<td>Impact stress</td>
<td>$36 \times 10^{-6}$</td>
<td>$140 \times 10^{-6}$</td>
<td>520</td>
<td></td>
</tr>
</tbody>
</table>
4.5 CONCLUSIONS

The important conclusions drawn from the present investigations are as given below:

(i) When a mechanoluminescent sample of a suitable dimension formed by mixing the microcrystalline or nanocrystalline persistent luminescent materials in epoxy resin is deformed at a fixed pressing rate, then the elastico mechanoluminescence (EML) emission takes place after a threshold pressure, in which the EML intensity increases linearly with the applied pressure. When the applied pressure is kept constant or decreased linearly, then the EML intensity decreases with time, in which, the EML intensity initially decreases at a fast rate and later on with a slow rate or sometimes it decreases exponentially having only one decay time.

(ii) When a small ball is dropped from a low height onto the film or coating of persistent luminescent materials, initially the EML intensity increases with time, attains a peak value and later on it decreases initially at a fast rate and then at a slow rate. In this case, the peak of EML intensity and the total EML intensity increase linearly with the height through which the ball is dropped onto the film.

(iii) The detrapping of electrons from oxygen vacancies and other traps by the local piezoelectric field near the defect centres, particularly near the activator ions in persistent luminescent crystals such as SrAl$_2$O$_4$:Eu and subsequent capture of the detrapped electrons moving in the conduction band by the Eu$^{3+}$ ions, may produce excited to the Eu$^{2+}$ ions and the subsequent de-excitation may give rise to the light emission characteristics of Eu$^{2+}$ ions. However, in certain persistent luminescent crystals, the detrapping of holes may
takes place by the local piezoelectric field and the subsequent electron-hole recombination may give rise to the light emission.

(iv) On the basis of the piezoelectrically-induced detrapping model based on the successive detrapping of electrons from exponentially distributed traps a theoretical approach is made to the dynamics of light emission induced by elastic deformation of persistent luminescent materials such as \( \text{Sr}_3\text{Al}_2\text{O}_6: \text{Eu}, \text{Dy} \), \( \text{SrAl}_2\text{O}_4: \text{Eu} \), \( \text{SrAl}_2\text{O}_4: \text{Eu}, \text{Dy} \), \( \text{Ca}_2\text{Al}_2\text{SiO}_7: \text{Ce} \), \( \text{SrMgAl}_6\text{O}_{11}: \text{Eu} \), \( \text{Ba}, \text{Ca})\text{TiO}_3: \text{Pr}^{3+} \), and \( \text{ZrO}_2: \text{Ti} \) crystals and \( \text{SrAl}_2\text{O}_4: \text{Eu} \) films. It is found that the EML intensity depends on several parameters such as pressure, pressing rate or strain rate, temperature, density of filled electron traps, piezoelectric constant near defect centres, etc.

(v) The EML emission during the application of pressure is caused by the de-trapping of thermally stable filled traps near activator ions. On the other hand, the EML emission during the release of pressure is caused by the thermally unstable shallow traps lying in the normal piezoelectric region of the crystals, which get filled during the de-trapping of thermally stable traps at the time of the increase of pressure.

(vi) Whereas the fast decay time is related to the time-constant of stopping the crosshead of the material testing machine employed to compress the sample, the slow decay time of EML is related to the lifetime of electrons in the shallow traps lying in the normal piezoelectric region of the crystals, which get filled during the detrapping of thermally stable traps at the time of increase of pressure.

(vii) Whereas, in the case of the EML induced by impact stress, the fast decay time is related to the time-constant for the decrease of pressing rate, and the slow decay time is related to the lifetime of
charge carriers in the traps lying at the localized piezoelectric region of the luminescent materials, which get filled with the increase of pressure during the detrapping of thermally stable traps.

(viii) The EML emission during the successive applications of pressure takes place due to the detrapping of retrapped electrons in the vacant electron traps near activator ions, in which retrapping is caused by the thermal release of electrons from the filled shallow traps lying in the normal piezoelectric region of the crystals.

(ix) At low pressure the crystals having higher values of the coefficient of deformation de-trapping exhibit higher EML intensity.

(x) On the basis of the piezoelectrically-induced de-trapping model based on the successive de-trapping of exponentially distributed traps, the expressions are derived, which are able to explain the dependence of EML intensity on different parameters and that of the dynamics of EML. The proposed model is also able to explain satisfactorily the physical concepts of the threshold pressure for the EML emission, the characteristic piezoelectric field, the coefficient of deformation de-trapping, and the occurrence of nonlinearity in the EML intensity with stress for the certain crystals at higher stresses and higher EML intensity in the crystals having higher coefficient of deformation de-trapping.

(xi) The present study may be helpful in harnessing the use of the intense persistent elastico mechanoluminescent materials with long lasting time.

(xii) The comparison between the theoretical and experimental results indicates that there is a good agreement between the theoretical and experimental results.
The expressions derived are as given as follows:

**Case I: EML under Increasing Stress and Fixed Stress Condition**

\[
I = \eta \sigma \mu \epsilon \Omega N_c N_i N_c Z \alpha \tau B^2 d_0^2 \hat{p} (P - P_{th})
\]

or

\[
I = \eta \sigma \mu \epsilon \Omega N_c N_i N_c Z \alpha \tau B^2 d_0^2 \hat{p} (t - t_0)
\]

\[
I_{df} = I_m \exp\left[ -\phi (t - t_m) \right]
\]

\[
I_{ds} = I_{0s} \exp\left[ -\frac{(t - t_c)}{\tau_s} \right] = I_{0s} \exp\left[ -\chi (t - t_c) \right]
\]

a. \[
I_m = \eta \sigma \mu \epsilon \Omega N_c N_i N_c Z \alpha \tau B^2 d_0^2 (P_m - P_{th}) \frac{dP}{dt}
\]

or

\[
I_m = \eta \sigma \mu \epsilon \Omega N_c N_i N_c Z \alpha \tau B^2 d_0^2 Y(P_m - P_{th}) \dot{\varepsilon}
\]

b. \[
I_r = \frac{\eta \sigma \mu \epsilon \Omega N_c N_i N_c Z \alpha \tau B^2 d_0^2 P_m^2}{2} \left( 1 + \frac{2\varepsilon}{t_m} \right)
\]

**Case II: EML under increasing and decreasing stress condition**

Condition I: Occurrence of the de-trapping in the localized piezoelectric region during the decay of piezoelectric charge

\[
I = D d_0^2 \dot{\varepsilon}^2 (2t_m - t)
\]

\[
I_{ds} = \frac{I_m}{t_m} (2t_m - t)
\]

**Case III: EML under impact stress condition**

\[
I = \eta \sigma \mu \epsilon \Omega N_c N_i N_c Z \alpha \tau B^2 d_0^2 \phi^2 N_p \Delta H \pi g h [\exp(-\xi t) - \exp(-2\xi t)]
\]

\[
I_r = \eta \sigma \mu \epsilon \Omega N_c N_i N_c Z \alpha \tau B^2 d_0^2 \phi^2 N_p \pi g h \xi
\]

\[
t_m = \frac{1}{\xi} \ln 2
\]

\[
I_m = \frac{\eta \sigma \mu \epsilon \Omega N_c N_i N_c Z \alpha \tau B^2 d_0^2 \phi^2 N_p \Delta H \pi g h}{4}
\]

\[
I_{df} = \frac{\eta \sigma \mu \epsilon \Omega N_c N_i N_c Z \alpha \tau B^2 d_0^2 \phi^2 N_p \Delta H \pi g h}{2\xi}
\]

\[
I_{ds} = \frac{I_0 \exp\left[ -\frac{(t - t_c)}{\tau_t} \right]}{I_0} = \frac{I_0 \exp\left[ -\psi (t - t_c) \right]}{I_0}
\]

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