Development of ZnS:Mn mechanoluminescent film for impact sensor

Piyush Jha* and Ayush Khare

Department of Physics, National Institute of Technology, GE Road, Raipur – 492 010, India

*Corresponding author’s e-mail address: piyushjha22@rediffmail.com

Abstract: This paper reports the elastico-Mechanoluminescence (EML) induced by the impact of a steel ball onto the composite film of ZnS:Mn phosphor. The film is prepared by pasting the mixture of ZnS:Mn phosphor and optical resin on polycarbonate substrate. The EML induced by impulsive excitation using a steel ball has been measured. The ML intensity linearly increases with square of impact velocity of the steel ball. The $t_m$ (temperature corresponding to maximum ML intensity) does not change with increasing impact velocity. The ML intensity is observed to recover after every impact of steel ball (height of fall = 20 cm) and does not require any irradiation. The outcome of present investigation is expected to be useful in extracting information about ML when a projectile with small contact area, such as steel ball makes an impact on the ML sensitive composite film.

1. Introduction

Pure zinc sulfide (ZnS) is a non-centric [1] and mechanoluminescent [2] material emitting the lightning lines characteristics of fracto-mechanoluminescence (FML). When doped with small percentage of strongly luminescent transition metal ions, such as copper, manganese [3-7] and even silver [4], zinc sulfide becomes strongly mechanoluminescent under deformation exhibiting a spectrum most similar to the electroluminescence (EL) spectrum caused by the dopant. ZnS doped with Mn is found to drastically enhance the mechanoluminescence (ML) properties [8].

ML or triboluminescence (TL) has been known for almost 400 years. One of the earliest references of this phenomenon was given by Francis Bacon’s in his writing “Advancement of Learning” in 1605. ML is categorized in three ways: elastico-mechanoluminescence (EML), plastico-mechanoluminescence (PML) and FML [9, 10]. PML and FML are destructive classes of ML, while EML is a non-destructive technique and is recoverable. In reality, before 1950 there were reports only on FML [11] in which the ML material was used for one time. So, it was realized to develop ML materials, which could be used for non-destructive applications. Recently, ZnS:Mn has been rigorously investigated for applications in the field of ML.

Xu et al. [12] demonstrated the EML from impact of a steel ball on ZnS:Mn film fabricated by ion plating or sputtering method. They reported that the prepared film was very sensitive to mechanical stimuli, and could act as a self-diagnosis material to detect mechanical stress remotely by visible light emission.

Recently, Jeong et al. [13] reported ML flexible composite films consisting of ZnS:Cu and polydimethylsiloxane (PDMS). This film was quite durable for repeated load and could bear repeated
mechanical stress of over ≈100000 cycle. In this film, the decrease in intensity after ~ 100 000 cycles was only ~35%; thus, maintaining 65% intensity of the initial ML.

Wang et al. [14] gave an outstanding example of EML to the scientific community in 2015. They made a flexible pressure sensor matrix (PSM) using ZnS:Mn, polyethylene terephthalate and ethylene–vinyl acetate, which were very useful in hand writing mapping. This flexible PSM recorded pressure/force applied at each pixel during signing.

Literature suggests that limited studies have been carried out on the EML of ZnS:Mn film induced by the impact of the moving steel ball till date [12, 13]. Therefore, there it is imperative to study EML produced by impact of the steel ball in more detail. In last three decades, many EML materials, such as Sr3Al2O6:Eu,Dy, SrAl2O4:Eu,Dy, CaAl2SiO7:Ce, SrAMgSi2O7 (A = Ca, Sr, Ba), CaZr(PO4)2:Eu, CaZnOS:Mn, etc. showing potential for light sources, sensors, colored displays, etc. [15-28] have been studied and developed [29-35]. Among other ML materials, ZnS:Mn is a very cheap in preparation, easily available, highly intense [8] and reproducible [12, 29].

The present paper reports the EML induced by impact of a steel ball on the ML of a film prepared by mixing ZnS:Mn with optical resin on polycarbonate substrate. The outcome of this study is useful to develop impact sensor where projectile with small contact area, such as steel makes an impact on the ML sensitive composite film.

2. Experimental

The starting materials ZnS, MnCl2, and NaCl were used for the preparation of microcrystalline ZnS:Mn phosphor. The particular amount of activator in the form of MnCl2 was mixed with the appropriate amount of ZnS. 4% NaCl was mixed into the mixture using a pestle and a mortar. The so prepared charge was transferred to a clean silica boat and fired at 1150°C for 1 h in nitrogen atmosphere. After combustion, the phosphor was taken out of the furnace and cooled to the room temperature (RT). The synthesized ZnS:Mn sample was cleaned for two to three times with distilled water and dried again.

Thereafter, the powder sample is mixed with optical resin in the ratio 1:1 and deposited on Lexan polycarbonate substrate using doctor blade method [36]. For the measurement of EML, a small ball having mass 5.02 g and diameter 1.04 cm was dropped from different heights (10 cm - 30 cm).

The photoluminescence (PL) spectrum at an excitation wavelength of 365 nm was recorded on Carry eclipse fluorescence spectrophotometer.

Figure 1. Schematic diagram of the experimental arrangement used for measuring the time dependence of ML in crystals (1-PVC pipe, 2- steel ball, 3-mechanoluminescent film, 4- photomultiplier tube, 5- stand, 6- sample holder, 7- wooden block, 8- iron base mounted on a table).

The EML was produced by dropping steel ball on ZnS:Mn film placed on the sample holder. The schematic diagram of experimental set-up employed for EML measurement is shown in Figure 1. The
light produced due to ML and transmitted through the transparent polycarbonate substrate was fed to an RCA-931A photomultiplier tube (PMT) placed just below the sample holder. The response time of PMT system was nearly 5 μs. The output of the PMT was then fed to a storage oscilloscope [27]. All the experiments were carried out at RT.

3. Results and Discussions

Figure 2 illustrates the time dependence of EML intensity for ZnS:Mn film at different impact velocities of steel ball. After the impact of a free-falling ball, initially the compression takes place at a faster rate, slows down in middle phase, and lastly goes into the elastic region. Correspondingly, as seen in Figure 2, initially the EML intensity increases with time, attains a peak value at a particular time $t_m$, and finally follows decay for longer time. In the time vs EML plot, only one peak was observed and the fast and slow decay times are recorded to be 0.511ms and 1.028ms, respectively[37].

![Figure 2](image1.png)

**Figure 2.** Time dependence of the ML intensity for ZnS:Mn film during impulsive excitation of the sample.

The steps involved in the EML emission from ZnS:Mn crystal are as follows [31]: (i) when the steel ball hits the ZnS:Mn film, the ML emission results from the contact area only (ii) piezoelectric field is produced because the crystal – structure of ZnS is non-centrosymmetric [1] (iii) due to the piezoelectric field, band bending occurs as a result of which de-trapping of electrons from filled-electron traps to the conduction band increases (iv) non-radiative emission of energy during the electron-hole recombination (v) release of energy during electron-hole recombination and excitation of Mn$^{2+}$ ions, and (vi) generation of light during the de-excitation of excited Mn$^{2+}$ ions.

![Figure 3](image2.png)

**Figure 3.** Variation of ML intensity with the square of impact velocity for ZnS:Mn film.
Figure 3 presents the variation of EML intensity with the square of impact velocity of the steel ball \((v^2)\). The linear relation is found between EML intensity and square of impact velocity of the steel ball. The EML intensity was measured by dropping the steel ball 10 times from each height. This finding establishes the suitability of present film to be developed as an impact sensor [27, 38].

The variation in EML intensity with successive number of dropping of steel ball from 20 cm height for ZnS:Mn film as shown in Figure 4. In case of FML of ZnS:Mn phosphor [39], the FML intensity is observed to diminish due to the decrease in newly created surface area with successive number of drops. But, in case of EML, the ML intensity is recovered after every impact of steel ball and does not require any irradiation. The recovery of EML intensity can be explained by the fact that charge carriers that lay in the vacant traps and are produced due to the detrapping caused by the piezoelectric field takes place by trapping of the charge carriers that drift in the field produced piezoelectric effect.

Figure 5 presents the PL spectrum of ZnS:Mn film excited by the light of wavelength= 365 nm in the same plot. The observed peak is corresponding to wavelength = 584 nm, which is attributed to \(4T_1\)-\(6A_1\) transition of Mn\(^{2+}\) ions [40].

4. Conclusions
The EML induced by steel ball on ZnS:Mn film has been investigated. When the ball impacts the ZnS:Mn film, initially the EML intensity increases with time, attains a peak value and then decreases. The linear relation is found between EML intensity and square of the impact velocity of the steel ball. This result reveals that in ML process, some part of the mechanical energy or piezoelectric energy is converted into the light energy, which is beneficial in the development of impact sensors. The EML intensity does not change significantly with number of droppings (up to 5 drops) of the steel ball. The PL spectrum is found to peak at 584 nm, which is attributed to \(4T_1\)-\(6A_1\) transition of Mn\(^{2+}\) ions.

Acknowledgement
The authors acknowledge the financial support received from Science and Engineering Research Board (SERB), a statutory board under Department of Science and Technology, Government of India (Grant No. PDF/2018/000335) under National Post-Doctoral Fellowship (N-PDF) scheme.
References

[1] Scarmozzino R 1970 *Lett. Nuovo Cim.* 4 825
[2] Bredikhin S I and Shmurak S Z 1974 *JETP Lett.* 19 367
[3] Chandra B P, Dubey P K and Datt S C 1986 *Phys. Stat. Sol. (a)* 97 K59
[4] Meyer K, Orbikat D and Rossberg M 1970 *Krist. Tech.* 5 5
[5] Scarmozzino R, 1971 *Sol. St. Commun.* 9 1159
[6] Alzetta G, Chudacek I and Scarmozzino R 1970 *JETPLett.* 19 367
[7] Vardanyan R A, Veselko S G and Kirakosyan G G 1989 *Sov. Phys. Sol. State* 31 24
[8] Xu C N, Watanabe T, Akiyama M and Zheng X G 1999 *Mater. Res. Bull.* 34 1491
[9] Chandra B P 1998 *Luminescence of Solids*, ed D. R. Vij (Plenum Press, New York) p. 36
[10] Chandra B P 2011 *Mechanoluminescent Smart Materials and their Applications*, in *Electronic and Catalytic Properties of Advanced Materials*, ed A. Stashans, S. Gonzalez and H. P. Pinto, (Transworld Research Network, Trivandrum, Kerala, India), p. 1
[11] Jha P and Chandra B P 2014 *Lumin.* 29 977
[12] Xu C N, Watanabe T, Akiyama M and Zheng X G 1999 *Appl. Phys. Lett.* 75 1236
[13] Jeong S M, Song S, Lee S K and Choi B 2013 *Appl. Phys. Lett.* 102 051110-1
[14] Wang X, Zhang H, Yu R, Dong L, Zheng A, Zhang Y, Liu H, Pan C and Wang Z L 2015 *Advanced Materials* 27 2324
[15] Akiyama M, Xu C N, Nonaka K and Watanabe T 1998 *Appl. Phys. Lett.* 73 3046
[16] Xu C N, Watanabe T and Akiyama M 1999 *Appl. Phys. Lett.* 74 2414
[17] Xu C N, Liu Y, Akiyama M, Nonaka K and Zheng X G 2000 *SPIE Proc.* 4220 344
[18] Terasaki N, Xu C N, Imai Y and Yamada H 2007 *Jpn. J. Appl. Phys.* 46 2385
[19] Jeong S M, Song S, Lee S K and Choi B 2013 *Appl. Phys. Lett.* 102 051110-1
[20] Akiyama M, Xu C N, Matsui H and Nonaka K 1999 *Appl. Phys. Lett.* 75 2548
[21] Zhang H, Terasaki N, Yamada H and Xu C N 2009 *Jpn. J. Appl. Phys.* 48 04C109-1
[22] Zhang J C, Xu C N and Long Y Z 2013 *Opt. Exp.* 21 13699
[23] Zhang J C, Xu C N, Kamimura S, Terasawa Y, Yamada Hand Wang X 2013 *Opt. Exp.* 21 1276
[24] Jeong S M, Song S, Lee S K and Ha N Y, 2013 *Adv. Mater.* 25 6194
[25] Jeong S M, Song S, Joo K, Kim J, Hwang S H, Jeong J and Kim H 2014 *Energy Environ. Sci.* 7 3338
[26] Xu C N, Yamada H, Wang X and Zheng X G 2004 *Appl. Phys. Lett.* 84 3040
[27] Jha P and Chandra B P 2013 *J. Lumin.* 143 280
[28] Jha Piyush 2016 *Lumin.* 31 1302
[29] Chandra B P, Xu C N, Yamada H and Zheng X G 2010 *J. Lumin.* 130 442
[30] Chandra B P 2011 *J. Lumin.* 131 1203
[31] Chandra V K, Chandra B P and Jha P 2013 *Appl. Phys. Lett.* 102 241105-1
[32] Chandra V K, Chandra B P and Jha P 2013 *Appl. Phys. Lett.* 103 161113-1
[33] Chandra B P, Chandra V K and Jha P 2014 *Appl. Phys. Lett.* 104 031102
[34] Chandra B P, Chandra V K and Jha P 2015 *Physica B* 461 38
[35] Chandra B P, Chandra V K and Jha P 2015 *Physica B* 463 62
[36] Berni A, Mennig M, Schmidt H, 2004 *Sol–Gel Technologies for Glass Processors and Users*, (Dordrecht: Kluwer Publications) p 89–92
[37] Chandra B P, Chandra V K, Jha P and Sonwane V D 2016 *Physica B* 491 12
[38] Chandra B P, Chandra V K and Jha Piyush 2015 *Sens. Actuators* A230 83
[39] Chandra B P, Chandra V K, Jha Piyush, Pateria Deepti and Baghel R N 2016 *Lumin.* 32 67
[40] Osipyan Y A, Petrenko V F, Zaretskii A V and Whitworth R W 1986 *Adv. Phys.* 35 115