# Mechanoluminescence of $(ZnS)_{1-x}(MnTe)_x$ nanophosphors excited by impact of a load

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## ARTICLE INFO

## ABSTRACT

$(ZnS)_{1-x}(MnTe)_x$ nanophosphors obtained by firstly preparing their precipitates using a wet chemical method, and then firing the precipitates at 850 °C for 10 h in a reduction atmosphere, exhibit intense fracto-mechanoluminescence. When a load is dropped on to the phosphor, initially the mechanoluminescence (ML) intensity increases linearly with time, attains a peak value at a particular time and later on it decreases with time. The crystal-structure investigated by X-ray diffraction confirms the formation of sphalerite phase of phosphors and shows that the average size of nanoparticles is 12 nm which is comparable to that obtained from TEM and SEM measurements. Both the peak ML intensity $I_m$ corresponding to the ML intensity verses time curve and the total ML intensity $I_T$ increase linearly with increasing impact velocity. Both the ML intensity and photoluminescence (PL) intensity are optimum for $x=0.05$ in $(ZnS)_{1-x}(MnTe)_x$ phosphor. The ML spectra of $(ZnS)_{1-x}(MnTe)_x$ phosphor are found to be similar to their photoluminescence spectra. Theoretical approaches were made for both the piezo-electrically induced electron bombardment model of ML and the charged dislocation model of ML. It is found that the piezoelectrically induced electron bombardment model provides a dominating process for the fracto ML of $(ZnS)_{1-x}(MnTe)_x$ phosphor. The ML intensity due to charged dislocations is less because of the low value of pinning time of dislocations near the crack tip. Expressions are derived for different parameters of fracto ML and their physical concepts are explored. From the time dependence of ML the relaxation time of the dropped load after the impact and the decay time of surface charges of $(ZnS)_{1-x}(MnTe)_x$ phosphor are determined and they are found to be 480 µs and 95 µs, respectively. As the ML intensity of $(ZnS)_{1-x}(MnTe)_x$ phosphor is higher as compared to ZnS:Mn phosphor, it can be used in ML damage sensor for structures and also in ML based structural health monitoring systems where ZnS:Mn phosphor is used presently.

## 1. Introduction

The luminescence produced during or after mechanical deformation of solids is known as mechanoluminescence (ML). 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]. The history of ML is long and varied. The first recorded observation of ML is contained in Sir Francis Bacon book "The Advancement of learning." Bacon, in 1605 reported that lumps of sugar emitted light when scraped. On the basis of the research work done in the past, the ML research can be divided into four generations [3,4] such as pre-PMT (photomultiplier tube) generation of ML (from beginning to 1950), early post-PMT

generation of ML (from 1951 to 1990), late post-PMT generation of ML (from 1991 to date), and future generation of ML (yet to come).

In the last two decades more emphasis has been given to study the origin and mechanisms of ML. The widely studied elastico-mechanoluminescent materials known to date are as follows [4–6]: ZnS:Mn: γ-irradiated alkali halide crystals, $SrAl_2O_4$:Eu, $SrAl_2O_4$:Eu, Dy, $SrAl_2O_4$:Ce, $SrAl_2O_4$:Ce,Ho, $SrMgAl_6O_{11}$:Eu, $SrCaMgSi_2O_7$:Eu, $SrBaMgSi_2O_7$:Eu, $Sr_2MgSi_2O_7$:Eu, $Ca_2MgSi_2O_7$:Eu,Dy, $CaYAl_3O_7$:Eu, $(Ba,Ca)TiO_3$:$Pr^{3+}$, $ZnGa_2O_4$:Mn, $MgGa_2O_4$:Mn, $BaAl_2Si_2O_8$:rare earth element, $Ca_2Al_2SiO_7$:Ce, $ZrO_2$:Ti,$CuZnO_5$:$Mn^{2+}$,$CaZr(PO_4)_2$:$Eu^{2+}$ and ZnS:Mn, Te phosphors. The EML has also been observed in the nanoparticles of ZnS:Mn, $SrAl_2O_4$:Eu and ZnMnTe. Certain materials such as $SrAl_2O_4$:Eu, $SrMgAl_6O_{11}$:Eu, $Ca_2Al_2SiO_7$:Ce, $ZrO_2$:Ti, etc. show such an intense EML that it can be seen in daylight with naked eye. The elastico ML has potential for sensing [7,8], imaging [6,9], multicolour light sources and multicolour displays [10–12].

Fracto ML has also a great deal of potential to understand the following facts and devices: (i) Earthquake and mine failure [13],

(ii) earthquake lights [14,15], moonquake lights [16], (iii) dynamics and mechanics of fracture [17–19], (iv) design of damage sensors [20,21], (v) design of fracture sensors [22–24], (vi) fuse-system for army warhead [25,26], (vii) design of safety management monitoring system [27–30], identifying the suitable design of milling machines [31–33] and the understanding the process of grinding in milling machines [34]. Such potentials of fracto ML require deep understanding of the correlation between fracto ML and fracture.

The significance of the present study are as follows: (i) Similar to that of other II–VI semiconductors the fracto ML in $(ZnS)_{1-x}(MnTe)_x$ phosphor may also arise due to the piezoelectrification of newly created surfaces and due to the movement of charged dislocations [1], but to date it is not known whether the fracto ML of $(ZnS)_{1-x}(MnTe)_x$ phosphor is dominated by a piezoelectrification process or by the movement of a charged dislocation process, (ii) the ML intensity of $(ZnS)_{1-x}(MnTe)_x$ nanophosphor prepared by a wet chemical method is very high and it is nearly 5 times more as compared to that of ZnS:Mn phosphor. Therefore, such phosphor may replace ZnS:Mn phosphor in its use in damage sensor and mechanoluminescence structural health monitoring system, (iii) the fracto ML of nanophosphors has been least studied till now, and therefore, further studies in this direction may be interesting, (iv) the characteristics of the fracto ML of $(ZnS)_{1-x}(MnTe)_x$ phosphor are not known satisfactorily to date, and further experimental and theoretical studies are required in this direction, (v) the present paper derives expressions for the dependence of parameters of ML on different factors and clarifies the physical concepts of the parameters, and (vi) the nanometre size phosphors are preferred in a number of applications not only due to their particle size but also for smooth imaging of the stress distribution in solids. Thus, the present study provides a sufficient novel knowledge which are quite unknown till now.

## 2. Experimental

For the present study, initially the $(ZnS)_{1-x}(MnTe)_x$ precipitates were synthesized by the wet chemical method. In the synthesis of $(ZnS)_{1-x}(MnTe)_x$ precipitates, we used $Zn(CH_3COO)_2 \cdot 2H_2O$ (A.R. Himedia Laboratories., 99.5%), $Mn(CH_3COO)_2 \cdot 4H_2O$ (AR fine-chem Limited, 99.5%), $Na_2S \cdot 9H_2O$ (Flakes, Himedia Laboratories Pvt. Ltd.) and $TeO_2$ (Himedia Laboratories Pvt. Ltd. 97.0%) as the starting materials. Firstly, a certain molar proposition of $Zn(CH_3COO)_2 \cdot 2H_2O$ and $Mn(CH_3COO)_2.4H_2O$ (Mn/Zn molar ratio=5%) was dissolved in distilled water at room temperature with continuous stirring (solution 1). Similarly, $Na_2S \cdot 9H_2O$ and $TeO_2$ (Te/S molar ratio= 5%) were dissolved in distilled water with continuous stirring (solution 2). Then solution 1 and solution 2 were mixed together with continuous stirring, whereby we found the precipitates of the material. Then the resulting precipitates were washed with distilled water many times. After the washing we separated the precipitates by centrifugation and then the precipitates were dried in vacuum. Finally, the dried precipitates were mixed with activated charcoal, and then the precipitates were fired at 850 °C for 10 h. Such powder phosphor obtained was used for the ML measurements.

The crystal-structure and average size of particles were determined by X-ray diffraction (XRD) (Buker $D_2$-Phaser) analysis using Cu Kα radiation ($\lambda=1.54$ Å and $2\theta= 20$–$70°$) at room temperature. The particle size of $(ZnS)_{1-x}(MnTe)_x$ phosphor was also determined using a Transmission Electron Microscope (TEM; Hitachi model 7500, Ltd., Tokyo, Japan). Diluted nanoparticles were suspended in absolute ethanol and put on a carbon coated copper grid, and were allowed to dry in air for conducting TEM images. Zeiss EVO 18 SEM was used to observe the morphology and average size of the nanoparticles. Essential Specifications of ZEISS EVO 18 SEM are as follows: resolution – 3.0 nm@ 30 kV (SE with W ), 4.0 nm@30 kV VP mode; Acceleration Voltage – 0.2–30 kV; and

magnification $5 \times$ to $1,000,000 \times$. Sample Requirements for SEM are as follows: General Size – any dimension (height or diameter) less than 10 mm; Conductivity (electrical) – conducting or at least semiconducting. If sample is not electrically conducting, it requires carbon or gold coating.

In the present investigation the ML in $(ZnS)_{1-x}(MnTe)_x$ phosphor was excited using an impulsive technique reported previously [35]. The phosphor was used without any pre-irradiation such as UV, X-ray, γ rays, etc. In this technique, the sample of 4 mg was placed onto the upper surface of a transparent Lucite plate which was kept inside the sample holder below the guiding cylinder. Then, it was covered with a thin aluminium foil and fixed using an adhesive tape. This arrangement prevents the scattering of crystallite fragments during the impact of the load or piston on to the sample. The ML was excited impulsively by dropping a load onto the sample from different heights. The luminescence intensity was measured using RCA-931A photomultiplier tube (PMT) placed just below the Lucite plate. By changing the distance between the piston to be dropped and the sample placed on the Lucite plate, the impact velocity $\nu_o=\sqrt{2gh}$ of the load could be changed up to 313 cm/s. Since there is a negligible friction between the pulley and the guiding cylinder, the impact velocity $\nu_o$ was taken as $\sqrt{2gh}$, where $g$ is the acceleration due to gravity and $h$ is the height through which the piston was dropped. The strain-rate $\dot{\varepsilon}$ was determined by using the relation, $\dot{\varepsilon}=\nu_o /H=\sqrt{2gh}/H$, where $H$ is the thickness of the sample. The photomultiplier tube was operated at high voltage. The output of the PMT was fed to a digital storage oscilloscope. Care was taken that, except some specific studies, each phosphor sample should have the same mass; therefore, the mass of each sample was measured using a chemical balance. Furthermore, the samples were distributed in a particular area on the Lucite plate. The response time of a photomultiplier tube system was nearly 5 μs. The error found in the ML measurement was ± 5%.

We have found that $(ZnS)_{1-x}(MnTe)_x$ phosphor shows thermoluminescence (TL) in the range from 50 °C to 350 °C. As the trapped electrons are responsible for both the thermoluminescence (TL) and elastico ML of $(ZnS)_{1-x}(MnTe)_x$ phosphor, they were heated at 350 °C for 30 min and cooled slowly to room temperature in dark and they were kept in dark. When the TL and elastico ML were tested in such annealed phosphor, they did not show TL and elastico ML because the detrapping of electrons from traps during the process of annealing had already taken place. Such annealed phosphor show TL and elastico ML when they were exposed to UV-light or visible light in the wavelength of absorption. The TL was measured using a TL unit. For the measurement of EML a homogeneous mixture of $(ZnS)_{1-x}(MnTe)_x$ phosphor was formed in colourless nitrolacqer and then the luminescent layers of nearly 1 mm thickness and diameter 4 mm$^2$ were coated on thick glass plates, in which the nitrolacqer was hardened at 200 °C. 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. When the sample was pressed at a uniform rate the EML started nearly at 2 MPa and then increased linearly up to 25 MPa, which is in the elastic region.

It is to be noted that, in the present investigation we have measured fracto-mechanoluminescence where the luminescence is produced due to the fracture of crystallites during the impact of a load from different heights. As the crystallites annealed at 350 °C were used, there is no possibility of elastico ML and plastico ML, and the luminescence observed by impact of a load on to the crystallites is only due to the creation of new surfaces, i.e., fractoluminescence. If the load dropped on to the sample is 400 g and the impact velocity is 300 cm/s (suppose), then the momentum is $1.2 \times 10^5$ g cm/s. The ML response shows that the momentum is