

Mechanoluminescence Studies of Zinc Selenide Doped with Cu Phosphors

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Abstract

Mechanoluminescence (ML) frequently appears in our day today life. Children amuse themselves by chewing wintergreen candy in dark to see its mechanoluminescence. We often see the light emission during wearing or taking out a silky shirt from our body in dark. This is a light produced due to triboelectrification between our body and silky cloth. This is an example of mechanoluminescence. The appearance of ML in modern adhesives and other polymers has brought it to the attention of mothers using diaper tape, photographers unrolling films and the many users of duct tapes. In fact, mechanoluminescence is a type of luminescence, that is, told emission of light produced during mechanical deformation of solids.

The phenomenon of ML has been known for a long time. The ML was probably first discovered when human lived in caves, as many common minerals produced very bright ML emission. The first recorded discovery of ML was made in 1605 by Francis Bacon who reported in his writing "Advancement of learning" that hard sugar being nimbly scrapped with a knife would afford a sparkling light. The ML of sugar must have been observed before Bacon, as cane sugar was prepared since earliest time in India and Persia, and introduced to Europe in the twelfth century. The early sugar often formed a very hard mass which had to be clipped away from the container and any one carrying out this task at night would almost certainly have observed the luminescence.

KEYWORDS: Luminescence, Triboelectrification, Deformation, Polymers.

Introduction

Mechanoluminescence (ML) is a type of luminescence induced by the elastic deformation, plastic deformation and factor of crystal. ML can be excited by compressing, stretching, loading, rubbing, grinding, cutting, cleaving, shaking, scratching, or crushing of solid. It can also be excited by thermal shocks caused by drastic cooling or heating or by shock waves produced during exposure of sample to powerful infrared laser pulses or ultrasonic waves. ML also appears during the deformation caused by the phase – transition or growth of certain crystal as well as during separation of two dissimilar materials in contact.

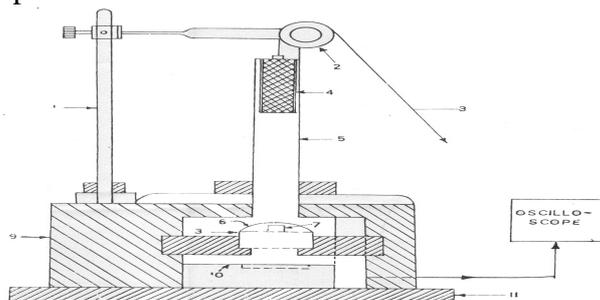


Fig 1. Schematic diagram of the experimental arrangement used for measuring ML.

Luminescence materials have drawn considerable interest and are recently being investigated by the scientists in through the world. Luminescence is the general term for the emission of visible and non visible electromagnetic radiation from a substance during or following the absorption of energy from suitable sources, such as high energy particles, UV radiations, X-rays etc. It generates because radiation is non thermal called “cold light”. Luminescence can be distinguished form thermal radiations as is does not follow Kirchoff’s and Wein’s Laws. It also differs from Rayleigh and Cerenkov emissions in respect of line delay between excitation and emission. The research on optical properties of luminescent materials has become the topic of both theoretical and experimental interest due to its wide technological importance. Among them Zinc Selenide doped with Cu (ZnSe: Cu) is one of the most important materials. Synthesis of material particles with narrow size distribution imposes a great challenge to the scientists. Different methods have been used, such as thick film, thin film, chemical deposition, vacuum deposition etc. Our ZnSe:Cu phosphors have been synthesized by vacuum deposition and mechanical grinding technique.

Experimental

ZnSe:Cu phosphors have been obtained by mixing the ZnSe and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in various concentration and placed inside the furnace at 800°C for one and half hour in silica boat. Now the material is cooled gradually with very slow rate.

In order to investigation the Mechano-and Electroluminescence of ZnSe:Cu phosphor, photomultiplier tube (PMT) RCA – 931, grating monochromatic HM-104, wide band amplifier and Aplab Oscillator are used. The emission intensity due to mechano- and electro excitations have been measured with mechano and electro luminescence arrangements, which are shown in fig 1 and fig 2.

Result

The heavily doped ZnSe: Cu phosphors exhibits intense ML. Fig 3 shows that ML spectra of ZnSe: Cu phosphors similar to EL spectra. No nitrogen emission is found in ML of ZnSe: Cu phosphors. The EL spectra do not change considerably with the frequency and strength of the applied electric field. It is found that EL brightness increases with the frequency of the applied electric field. It is known that emission of in ZnSe:Cu phosphor is from 1_G state to the 6_S state of Cu^{+2}

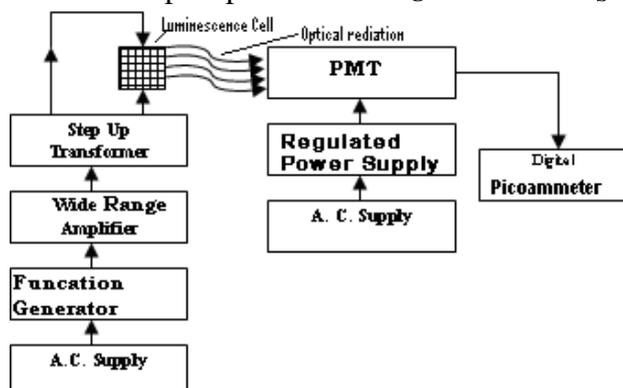


Fig 2. Experimental arrangement for the measurement of brightness of activator concentration

Table I: ML activity of ZnSe:Cu
Cu phosphor with different activator concentration

S. No.	Activator concentration (ppm)	ML activity Normalized with regard to that of ZnSe : Cu (5000 ppm)
1.	100	1.1/12 = 0.09
2.	300	2.3/12 = 0.19
3.	600	2.5/12 = 0.21
4.	1000	3.2/12 = 0.27
5.	5000	4.7/12 = 0.39

The dependence of ML and EL intensity on the concentration in ZnSe: Cu phosphors studies. Fig 2 shows that ML and EL efficiency is maximum for 2480 ppm of Cu Initially the EL brightness increases in activator concentration after a particular concentration of activator the EL brightness decreases with concentration of the activator.

Discussion

It is known that activators II – VI compounds exhibit ML during their elastic, plastic and fracture deformation since the ML was excited impulsively in the present investigation, the fracture of phosphors crystallites was the major facts responsible for the ML emission during the impulsive deformation of the phosphors several crystallites were fractured and ML pulse observed was the superposition of the ML response to several mobile cracks in the micro crystallites.

The fact is that ML in ZnSe: Cu phosphor is deformation induced EL, is supported by the following result.

- (i) The ML and PL spectra are same.
- (ii) The stress (σ) dependence of ML follows the relation. $I_{ML} = I_{ML}^0 \exp\left(\frac{C}{\sqrt{\sigma}}\right)$
- (iii) And the voltage dependence EL follows the relation $I_{EL} = I_{EL}^0 \exp\left(\frac{C}{\sqrt{V}}\right)$
- (iv) The ML excitation start after a minimum stress and EL excitation after a minimum value of electric field and
- (v) both the ML and EL intensities decreases with temperature.

Initially brightness in phosphors increases with the increases in the activator concentration because the number of luminescence centers increase in the phosphors. After a particular concentration of activator, the EL and ML brightness decreases due to concentration quenching according and excited. The Figure 3 shows that ML spectra of phosphors are same EL spectra as well as PL spectra. No nitrogen emission was found in ml of ZnSe: Cu phosphors.

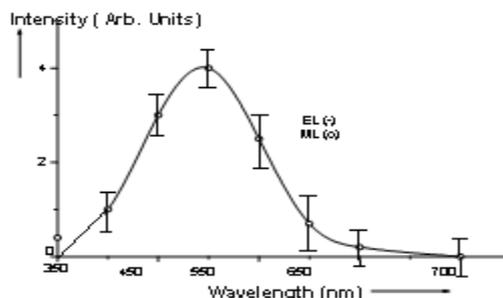


Fig 3. ML (o) and EL (-) spectra of heavily doped ZnSe: Cu phosphor.

Since the crystals of ZnSe: Cu piezoelectric and they also contain charged dislocations. The ML may either be due to the piezoelectrification or it may be due to the movement of charged dislocation or may be due to both processes. For small grain size of phosphors or at low temperature where dislocation can not move during the deformation, the piezoelectric origin of ML should be dominating. When phosphor crushed inside water, they still show ML. this shows that ML should be intrinsic in origin and it should not be related to electrostatic field developed between top and bottom of the phosphors. The ML should be related to the piezoelectric charge developed near the mobile cracks in each individual grain size of micron order.

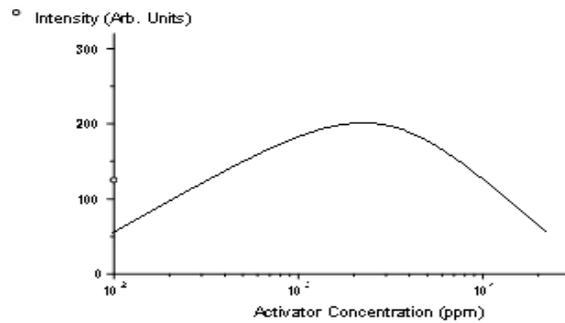


Fig 4. Effect of activator concentration of ZnSe: Cu phosphor.

The ML Excitation should be related to the piezoelectric charge induced due to stress near the lip of the mobile cracks of the phosphor. The field produced during the ML excitation is sufficient to cause ML excitation. Luminescence centre return to ground state with the emission of photon only if there is activator along with the sphere of radius R_0 atom the central activator atom. In other words it is assume that activator atoms interact with each other in such a way that. If the distance between them is similar than R_0 , they quantly each other and turn the probability of radiationless transition. Radiationless transition increases with the increasing concentration of the activator. As such the EL and ML brightness are maximum for a particular concentration of the activator.

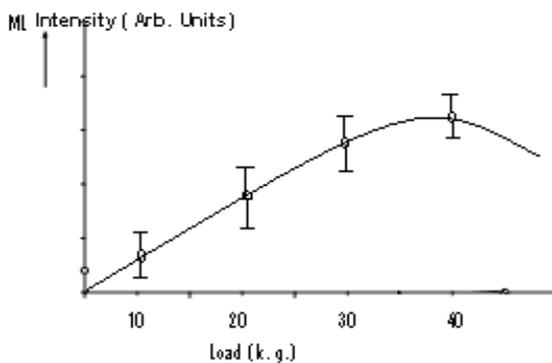


Fig. 5. ML intensity with different load

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