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CORRELATION BETWEEN THERMOLUMINESCENCE AND MECHANOLUMINESCENCE OF γ-RAY IRRADIATED Dy DOPED $ZnAl_2O_4$ PHOSPHORS PREPARED BY SOLUTION COMBUSTION TECHNIQUE

K.K.Satapathy[1] and F.Khan[2]

[1]Department of Applied Chemistry, O.P. Jindal Institute of Technology, Raigarh 496001 India
[2]Department of Applied Chemistry, National Institute of Technology, Raipur 492001 India
Corresponding author Email: kabita.satapathy@gmail.com

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ABSTRACT:

Dy doped $ZnAl_2O_4$ phosphors have been synthesized by solution combustion technique by using urea as a fuel and its thermo luminescence (TL) and mechanoluminescence (ML) properties have been studied. Two distinct peaks were observed at around 165°C and 345°C in TL glow curve of $ZnAl_2O_4$: Dy phosphors. ML has been excited impulsively by dropping a load of mass 0.7 kg on to the phosphors from various heights. As the piston is dropped on to the sample, ML intensity initially increased with time attained an optimum value for a particular time then decreased again increases to a value then decreases and finally disappeared for all the samples. TL and ML intensity increased with gamma doses given to the sample. ML emission spectrum showed characteristic emission of Dy^{3+} ions. In order to study the influence of deformation on TL, TL was recorded after deforming the sample by dropping the load on to it. It is found that TL yield decreased markedly with increasing the height of the piston. Results suggest that though the mode of excitation is different in these two phenomena but similar states are responsible for TL and ML.

Keywords: Luminescence, Defects, Dislocation, Phosphors, Fuels

[I] INTRODUCTION:

Inorganic phosphors are widely used in a variety of applications such as lamp industry, radiation dosimetry, X-ray imaging, and colour display etc. [1]. $ZnAl_2O_4$ phosphors are more useful in field emission displays (FEDs) and vacuum florescent displays (VFDs) [2, 3]. It exhibit higher chemical stability than commonly used phosphors. Since $ZnAl_2O_4$ are oxide based phosphors, many of the degradation problems associated with other phosphors

are avoided. $ZnAl_2O_4$ has also paid considerable attention for electroluminescent thin film displays and optomechanical sensors [4-6]. $ZnAl_2O_4$ is a well-known wideband gap semiconductor, an active component of catalysts, and also acts as a convenient support for other metal oxides and dispersed metals [7-8]. TSL of Tb doped $ZnAl_2O_4$ phosphors has been investigated and it has been reported that the sample shows intense TL peak and two defect centre [9].

Mechanoluminescence (ML) is the phenomenon of light emission induced by any mechanical action on solids [10]. The investigation of mechanoluminescent materials exhibiting intense ML during their elastic deformation and fracture has attracted the attention of a large number of workers and some important applications of ML materials have been made such as visualization of stress distribution in solids, visualization of stress-distribution near the tip of a crack. Recently, some new materials exhibits ML have been reported. $Ca_2MgSi_2O_7$: Eu micro-particles emits green light under the application of a mechanical stress [11]. Impulsive excitation of ML of gamma ray irradiated $CaSO_4$: Eu phosphor has been studied [12]. ML of gamma-ray irradiated and Eu activated $BaSO_4$ phosphor was studied [13]. Using the ML technique, the impact parameters of the $SrAl_2O_4$: Eu film and ZnS: Mn coating is determined [14].

Since some of the TL materials also show ML [15], thus we have chosen $ZnAl_2O_4$: Dy phosphor as it is good TLD. Present paper reports correlation between TL and ML of $ZnAl_2O_4$: Dy phosphors prepared by solution combustion technique.

[II] EXPERIMENT:

The samples were prepared by solution combustion synthesis technique. The ingredients used were Zn $(NO_3)_2.6H_2O$, Al $(NO_3)_3.9H_2O$, urea and dysprosium nitrate. Zinc nitrate, Aluminium Nitrate, urea and the desired amount of dopant were taken in a glass beaker and dissolved in distilled water. The beaker was kept in a furnace set at 250 ºC. Once the water boils off, the metal nitrate and fuel react and ignite. The reaction is self-propagating and is able to sustain this high temperature long enough. The entire combustion process was over in about 5 min. Formations of the samples were confirmed by XRD pattern recorded by X-ray defractometer (PW-1710). The gamma-ray-irradiation was carried out using ^{60}Co source. ML was excited impulsively by dropping a load on the sample placed on a Lucite plate with different impact velocities. The luminescence was monitored by a 931A photomultiplier tube positioned below the Lucite plate and connected to storage oscilloscope (SM-340). All ML measurements were carried out after gamma irradiation. A PC based thermo luminescence analyser system (TL-1009I) was used for recording TL of gamma irradiated sample.

[III] RESULT AND DISCUSSION:

Figure 1 shows XRD pattern of the $ZnAl_2O_4$: Dy phosphors. XRD pattern obtained is almost similar to the JCPDS card No. 05-0669 and it may be concluded that small amount of impurity doped in the host material does not affect the XRD pattern.

TL glow curves of γ-ray-irradiated Dy doped $ZnAl_2O_4$ phosphors are given in Figure 2. Dy doped $ZnAl_2O_4$ phosphor shows two distinct peaks at around 165 and 345°C. In the TL glow curve each and every peak represent one type of trap present in the lattice. The observed TL glow curve appears to be superposition of at least two distinct centres. In $ZnAl_2O_4$, the most probable centres which can be observed are the V centres (a hole trapped at a cation vacancy) and F centres (an electron trapped at an anion vacancy). It is known that the cation disorder and non-

stoichiometric of aluminates like $ZnAl_2O_4$ provide a large number of lattice defects, which may serve as trapping centres. It seems that during the preparation of $ZnAl_2O_4$: Dy phosphor, two ions of Dy^{3+} replace three Zn^{2+} ions, creating Zn^{2+} ion vacancies. The Dy^{3+} ion can easily enter the lattice, in place of Zn^{2+} ion, as the ionic radius of Dy^{3+} (0.091 nm) is close to the ionic radius of Zn^{2+} ion (0.083 nm).

When the piston of mass 0.7 kg was dropped on to the 1 mg γ-ray-irradiated $ZnAl_2O_4$:Dy (0.1 mol%) phosphors, ML intensity initially increased with time attained an optimum value for a particular time then decreased again increase and finally disappeared (fig. 3).

Non-irradiated $ZnAl_2O_4$: Dy phosphors did not exhibit ML. Figure: 4 shows that ML intensity increased almost linearly with increasing the mass of the irradiated sample deformed for recording ML in the rage (0.5 to 2.5 mg) investigated.

Figure: 5 shows the dependence of ML intensity on γ-ray dose of $ZnAl_2O_4$: Dy (0.1 mol %) phosphors. ML intensity increased almost linearly with γ-ray doses given to the samples.

In order to find the luminescence centres responsible for ML emission, we have recorded ML spectrum. The corrected ML spectrum is given in figure 6. Two peaks at 482 nm and another at 585 nm were observed.

In order to find the thermal stability of ML it is recorded at various surrounding temperatures and shown in figure 7. It is found that ML intensity decreases with increasing the temperature of the sample, however, time corresponding to ML peak shifted towards shorter time value.

Some intermediate states are responsible for ML emission in this system as we know that mechanical energy can not be imparted to the trapped charge carriers directly. The origin of light emission are not due to the separation of the charges on the fracturing surfaces and piezoelectricity as the particle size is very small observed in XRD and $ZnAl_2O_4$ has a centrosymmetric structure (Fd3m). Therefore it seems that ML of $ZnAl_2O_4$: Dy is strongly related to the movement of dislocations and the recombination of activated electrons and holes. The movement of dislocations excites carriers from the filled traps and the subsequent recombination of the electrons and holes in luminescence centres (Dy^{3+}) [16].

ML emission spectrum contains two peaks at 482 and 585 nm. These are the characteristic emission of Dy^{3+} ions [17]. Probably energy released during/after impact may be transferred non-radiatively to Dy^{3+} ions causing their excitation and subsequent de-excitation of excited Dy^{3+} ions may give rise characteristic emission of Dy^{3+} ions.

When mass or volume of the sample increases, the number of crystallites in the sample increase and thereby the peak ML intensity increases. Density of defect centres increases with increasing gamma ray dose given to the sample that‘s why total ML intensity (i.e. area below curve) increases with increasing gamma ray dose.

The time corresponding to ML peak is directly related to the lifetime of the holes in the valence band. Since the lifetime of the holes decreases with increasing temperature, the value of t_m also decreases.

[IV] CONCLUSIONS:

Non-irradiated $ZnAl_2O_4$ and $ZnAl_2O_4$: Dy phosphors do not show ML. ML intensity increases linearly with mass of the sample and gamma-ray doses given to the sample. Temperature dependence of the ML curve shows that ML is highly influenced by the surrounding’s temperature. Two distinct peak were observed in ML and TL glow curve of Dy doped $ZnAl_2O_4$ phosphors. TL glow curve of γ-ray-irradiated $ZnAl_2O_4$: Dy (0.1 mol %) sample recorded after deforming the sample indicates that the TL intensity of deformed sample is slightly

decreased. The decrement in TL is due to the emission of some energy in form of ML in this system. It indicates that TL in the phosphor is mechanically stable. Since ML emission in this system is induced by the gamma ray and ML increases with gamma ray dose it may use as mechanoluminescence dosimetry.

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Figures:

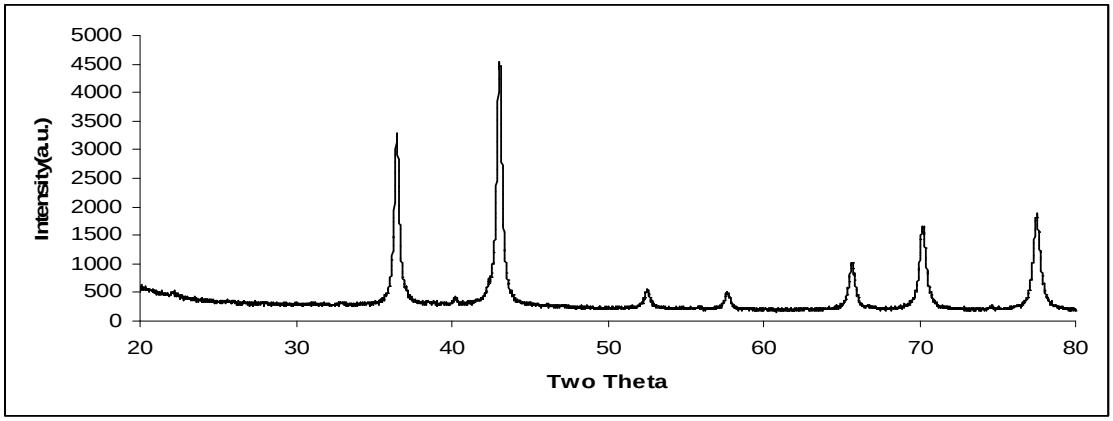

Figure: 1 XRD pattern of $ZnAl_2O_4$: Dy phosphor.

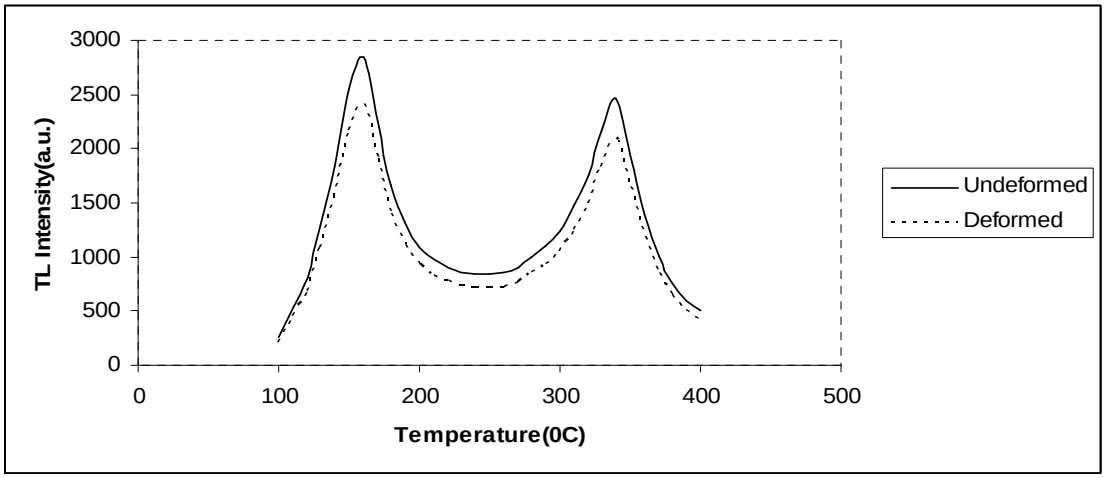

Figure 2. TL glow curves of gamma-ray irradiated $ZnAl_2O_4$: Dy (0.1 mol %) phosphors undeformed and deformed $ZnAl_2O_4$: Dy (0.1 mol %), Dropping a load of 0.7 kg on to the sample with the impact velocity 2.83 m/sec (Gamma-ray dose 1.1 kGy, mass of the sample 1 mg, rate of heating 5 °C/sec).

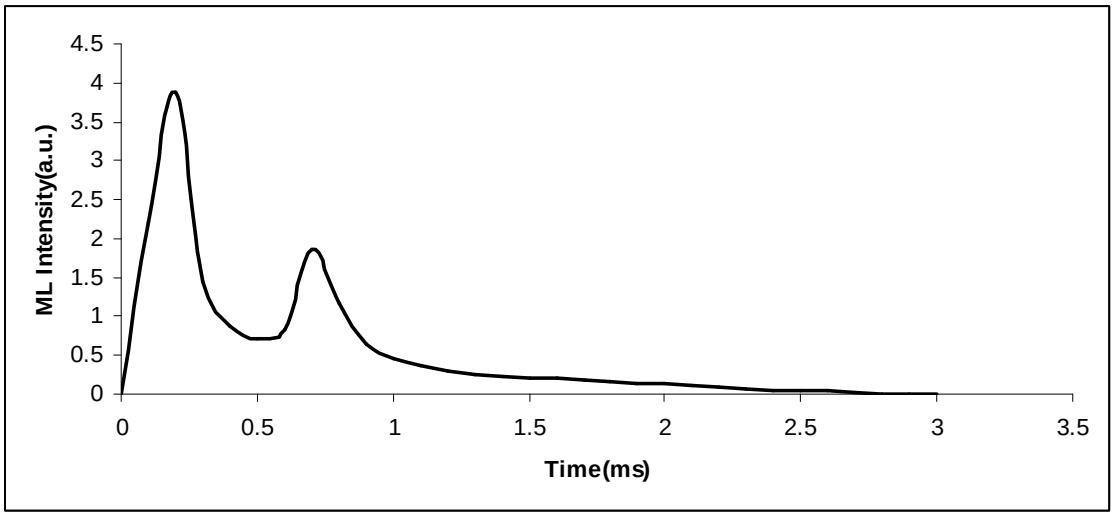

Figure3. Time dependence of ML intensity of γ-ray irradiated $ZnAl_2O_4$:Dy (0.1 mol%) phosphors (Mass of the piston 0.7 kg, γ-ray dose 1.1 kGy, mass of the sample 1 mg).

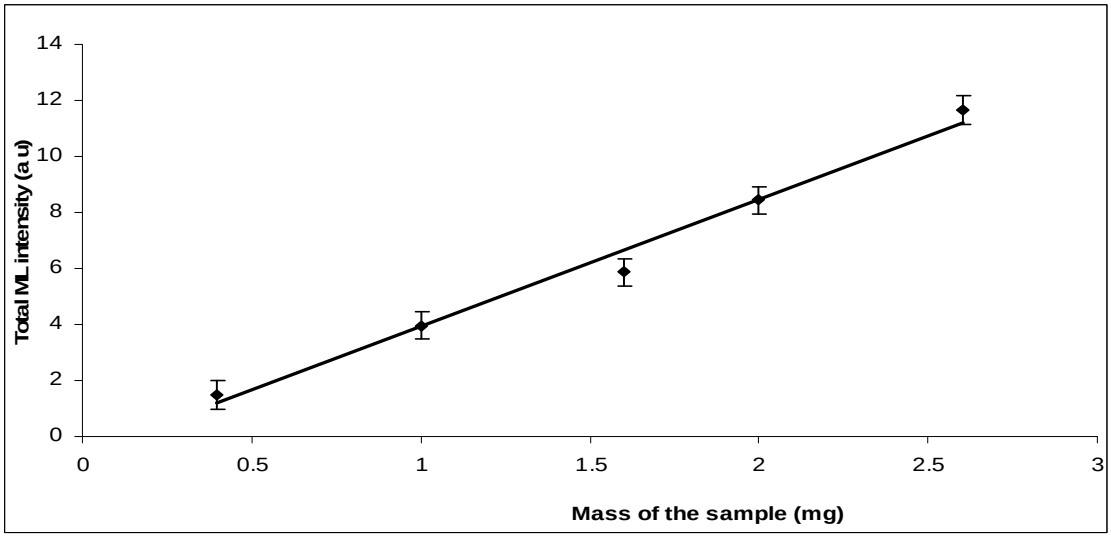

Figure4. Mass of the sample dependence of ML intensity of γ-ray irradiated $ZnAl_2O_4$:Dy (0.1mol%) phosphors(Mass of the piston 0.7 kg, γ-ray dose 1.1 kGy, impact velocity 2.83 ms^{-1}).

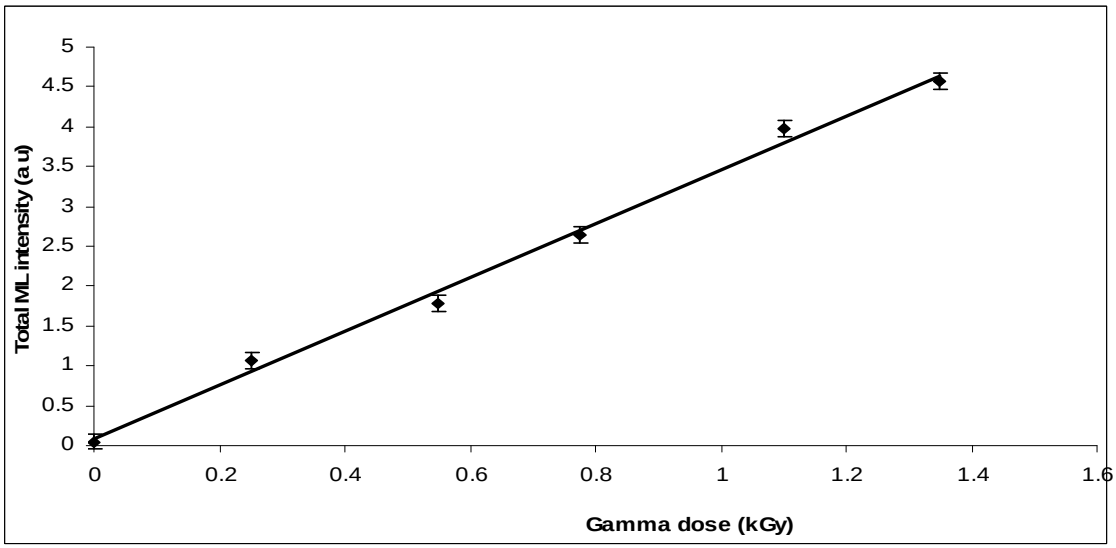

Figure5. Gamma ray dose dependence of ML intensity of $ZnAl_2O_4$:Dy (0.1mol%) phosphors(Mass of the piston 0.7 kg, mass of the sample 1 mg, impact velocity 2.83 ms^{-1}).

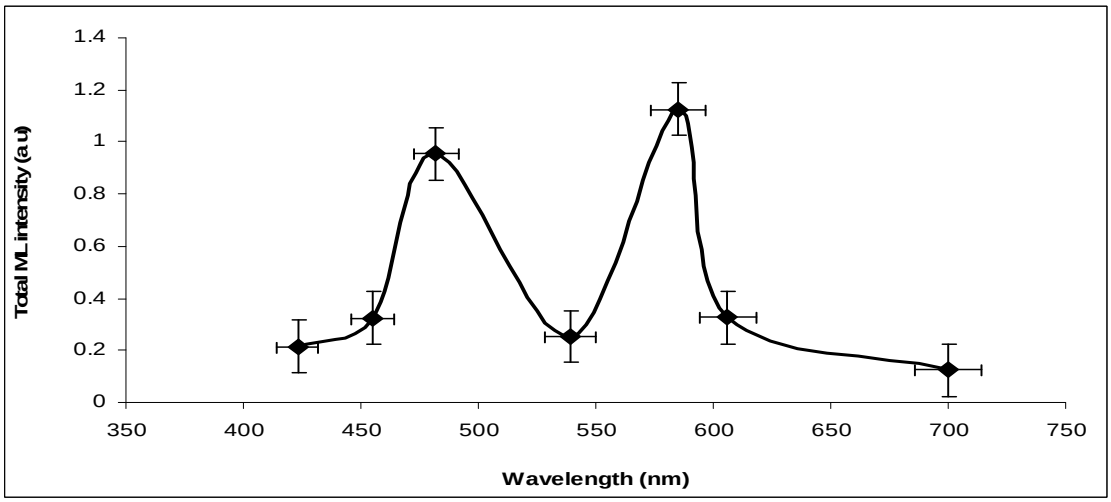

Figure6. ML emission spectra of γ-ray irradiated $ZnAl_2O_4$:Dy (0.1mol%) phosphors(Mass of the piston 0.7 kg, γ-ray dose 1.1 kGy, mass of the sample 1 mg, impact velocity 2.83 ms^{-1}).

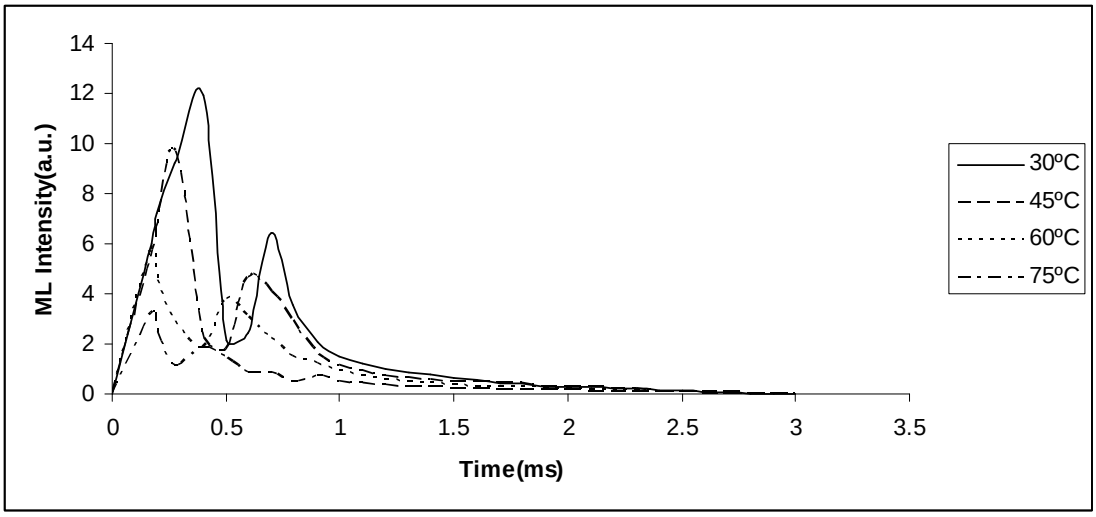

Figure7. Time dependence of ML yield of gamma-ray irradiated (1.1 kGy) $ZnAl_2O_4$:Dy (0.1mol%) phosphors for different temperature.(Mass of the piston 0.7 kg, γ-ray dose 1.1 kGy, mass of the sample 1 mg, impact velocity 2.83ms^{-1}).