Impulsive excitation of mechanoluminescence in γ-ray irradiated ZnAl₂O₄:Dy phosphors synthesized by solution combustion technique

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ABSTRACT

The mechanoluminescence (ML) of γ-irradiated $ZnAl_2O_4$: Dy phosphor has been studied. $ZnAl_2O_4$ samples having different concentrations of Dy were prepared by solution combustion technique by using hydrazine as a fuel. ML was excited impulsively by dropping a load onto the sample. Two distinct peaks have been observed in the ML intensity versus time curve. Maximum intensity is obtained for 0.1 mol% of Dy doped $ZnAl_2O_4$ phosphor. ML spectra of the phosphors show two distinct peaks around 482 nm and 585 nm which is characteristic emission of Dy^{3+}. It is also observed that the ML intensity of the samples increases almost linearly with increasing mass of the sample and gamma ray doses given to the sample. Experimental results suggest that the ML excitation is related to the movement of dislocation with defect centres and it may be used for dosimeter applications. Copyright © 2013 VBRI press.

Keywords: Mechanoluminescence; dislocation; fuel; defect.

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Introduction

Mechanoluminescence is the light emission induced as a result of a mechanical action on a solid. About 36% of all inorganic and 19% of all organic compounds exhibit ML [1, 2]. Interest in ML phosphors has almost exclusively been academic in nature and no practical applications have been established due to the weakness of the ML intensity. The ML intensity depends on the deformation technique. ML can be generated by grinding, cleaving or scratching which produces a very dim ML. Recently, it has been shown that a high-intensity ultrasound in liquid slurries of sugar and other organic crystals could produce a 1000 times more intense ML than grinding [3], and ML materials with a high intensity have been developed, showing promising applications of this phenomenon in stress sensing techniques [4-6]. Good luminescence material should have high purity, better chemical homogeneity and high surface area in a rapid, inexpensive single step operation. The zinc aluminates ($ZnAl_2O_4$) offers many advantages, such as high thermal and chemical stability, hydrophobic behaviour, high mechanical resistance, low sintering temperature, and high quantum yields [7]. It is a wide-band gap semiconductor, which occurs naturally as the mineral gahnite and is a member of the spinel family; it can be used as transparent conductor, dielectric material, and optical material [8-10]. So we have used $ZnAl_2O_4$: Dy phosphors for ML study. The objective of this work is to study the ML properties of $ZnAl_2O_4$: Dy phosphor through solution combustion process by using hydrazine as a fuel because

for ML sensors and dosimeter use, ML properties should be known and optimum intensity of ML material is required. The present paper reports various ML properties in gamma-irradiated $ZnAl_2O_4$: Dy phosphors.

Experimental

Chemicals

The purity and manufacturing of the chemicals used for the preparation of $ZnAl_2O_4$: Dy are as follows: Zinc nitrate hexahydrate [$Zn(NO_3)_3.6H_2O$, purified], Aluminium nitrate nonahydrate [$Al(NO_3)_3.9H_2O$, extra pure], Dysprosium (III) nitrate pentahydrate [$Dy(NO_3)_3.5H_2O$, 99.9% pure] were procured from MERCK Specialist Pvt. Ltd., Mumbai, whereas Hydrazine hydrate (H_6N_2O, 80%), Johnson Matthey Company, MA were used as received.

The samples were prepared by solution combustion synthesis technique. Zinc nitrate, Aluminium Nitrate, fuel and the desired amount of dopant were taken in a glass beaker and dissolved in distilled water. Fuel hydrazine is taken as excess than stoichiometric ratio for the complete combustion. After stirring for about 20 min, precursor solution was transferred to a furnace preheated at 300 ºC and the porous products were obtained. Since in this method samples are prepared through the solution combustion route, better control over sample homogeneity and particle size would be obtained. Once the water boils off, the metal nitrate and fuel react and ignite; it undergoes dehydration followed by decomposition generating combustible gases. The volatile combustible gases ignite and burn with a flame and thus provide conditions for formation of phosphor with dopants. The large amount of escaping gases dissipates heat and thereby prevents the material from sintering and thus provides conditions for formation of crystalline phase. Also, as the gases escape they leave voluminous, foaming and crystalline fine powder occupying the entire volume of the firing container. 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. The combustion reaction described as follow:

$$Zn\ (NO_3)_2 + 2Al\ (NO_3)_3 + 10N_2H_4 \rightarrow ZnAl_2O_4 + 20H_2O\uparrow + 14N_2\uparrow$$
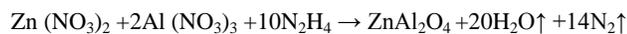
The prepared host lattice was characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical deffractometer (Cu-Kα radiation) at a scanning step of 0.01°, continue time 20s, in the 2θ range from 20-80 °. The gamma-ray-irradiation was carried out using ^{60}Co 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). Different filters were used to record ML spectra of the samples. All ML measurements were carried out after gamma irradiation.

Mechanoluminescence in γ- ray irradiated sample

Luminescence induced during any mechanical action on solids is known as mechanoluminescence (ML). The mechanical treatment of crystals generally contributes a

very rough interference. A great number of physical processes may occur within a very short time interval, which excite or stimulate the process of photon emission. During the deformation of the solids, the mechanical energy is rather transformed into other form of energy which then constitutes the last state of excitation. Thus in reality the mechanoluminescence is a mechano induced luminescence. As ML emission is associated with stress, fracture and damage of solids, such inherent behaviour of ML material has exploited to fabricate mechanoluminescent stress, fracture and damage sensors. Many workers proposed their views on the mechanism of ML excitation. It may be expected that the ML excitation may be due to electric field produced during movement of charged dislocation. Also tunnelling of electrons from impurity level and trapping centers may take place during the deformation of phosphors. Free electrons produced in this process may recombine radiatively with holes and may consequently give rise to luminescence. Two types of devices are generally needed for ML measurements, for deforming the samples and for the spectral measurements. When the phosphors are exposed to ionizing radiation the defect centers are created. On increasing the γ dose, the defect centres increases and thereby the peak intensities also increased.
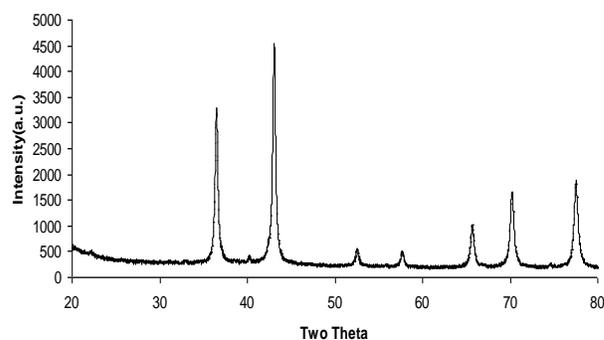

Fig. 1. XRD pattern of $ZnAl_2O_4$:Dy phosphor.

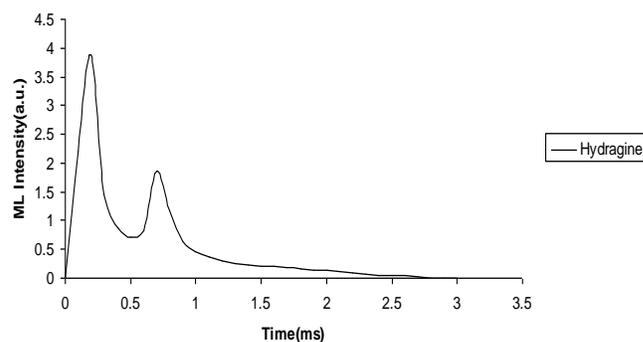**Fig. 2.** Time dependence of ML intensity of $ZnAl_2O_4$: Dy (0.1mol %) phosphors. γ-dose 1.1kGy.

Results and discussion

Fig. 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.

Fig. 2 shows the ML intensity versus time curve of gamma ray irradiated $ZnAl_2O_4$: Dy (0.1 mol %) phosphors. Two distinct peaks were observed when ML was excited by dropping a load of mass 0.7 kg on to the sample. ML intensity increases linearly with increasing the impact velocity of the piston 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.
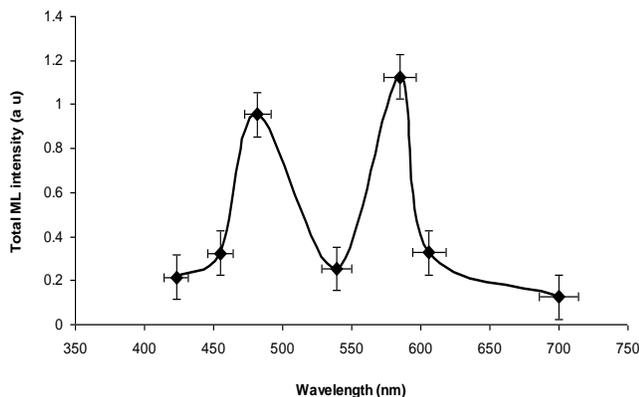
Fig. 3. ML emission spectra of γ-ray irradiated $ZnAl_2O_4$:Dy (0.1mol%) phosphors(Mass of the piston 0.7 kg, γ-ray dose 1.1 kGy, mass of the sample 1 mg, impact velocity 2.83 ms^{-1}).
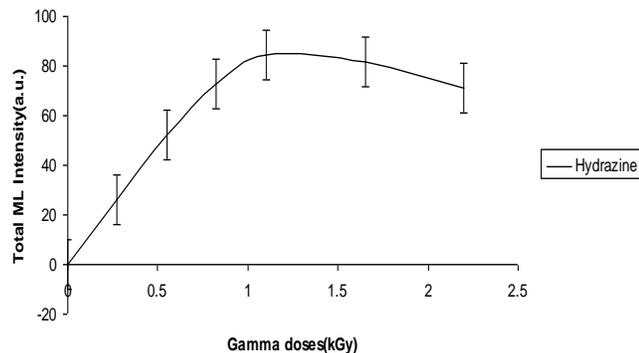
**Fig. 4.** Total ML intensity of $ZnAl_2O_4$: Dy(0.1mol%) as function of γ-ray doses given to the samples (mass of the sample 1mg, mass of the piston 0.7 kg, impact velocity 2.83 ms^{-1}).
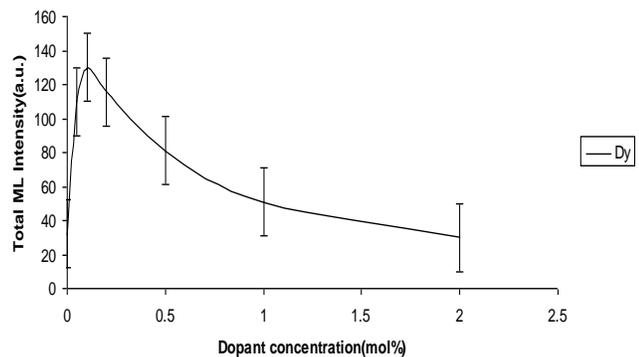
Fig. 5. Total ML intensity of $ZnAl_2O_4$:Dy as function of dopant concentration(mass of the sample 1mg, mass of the piston 0.7 kg, impact velocity 2.83 ms^{-1}).

Fig. 3 shows ML emission spectra of $ZnAl_2O_4$: Dy (0.1 mol%) phosphors. In order to find the luminescence centres responsible for ML emission, we have recorded ML spectrum. Two distinct peaks one around 482 nm and another around 585 nm were observed. ML emission observed is the characteristic emission of Dy^{3+}.

Fig. 4 shows the dependence of ML intensity on γ-ray dose of $ZnAl_2O_4$: Dy (0.1mol %) phosphors. ML intensity increased almost linearly with γ-ray doses given to the samples. **Fig. 5** shows the total ML intensity as a function of the dopant concentrations. It is clear that in all the samples ML intensity initially increased with increasing the dopant concentration attained an optimum value for a particular concentration of dopant then decreased with further increase in the dopant concentration. Optimum ML is found for 0.1 mol% dopant. **Fig. 6** 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.
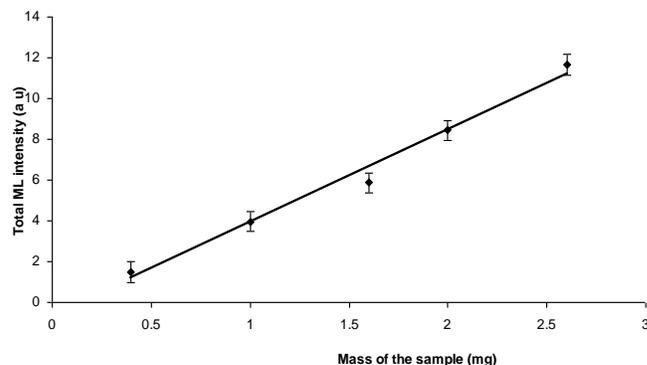
Fig. 6. Mass of the sample dependence of ML intensity of γ-ray irradiated $ZnAl_2O_4$:Dy (0.1mol%) phosphors(Mass of the piston 0.7 kg, γ-ray dose 1.1 kGy, impact velocity 2.83 ms^{-1}).

Mechanical energy cannot be imparted to the trapped charge carriers directly; therefore some intermediate states are responsible for ML emission in this system. The origin of light emission are not due to 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 (Fd-3m). Therefore it is suggested 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 centers (Dy^{3+}) [11]. 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) [12]. Since ML glow curve shows the characteristic emission of Dy^{3+}. This energy may

be transferred non-radiatively to Dy^{3+} ions causing their excitation and subsequent de-excitation of excited Dy^{3+} ions. When mass 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.

Conclusion

$ZnAl_2O_4$: Dy phosphors were synthesized by solution combustions method by using hydrazine as fuel. The starting materials were metal nitrates, fuel and dopant. Well crystallized powders were obtained at 388°C within 5 min. ML emission spectrum shows the characteristic emission of Dy^{3+} ions. Non irradiated $ZnAl_2O_4$ and $ZnAl_2O_4$: Dy phosphors do not show ML. ML intensity increases linearly with gamma-ray doses given to the sample and mass of the sample. The major advantages of the combustion process are improvement in processing time, energy saving and the fine particle nature of the combustion products. This fundamental work might be important in developing new luminescent devices applicable for ML sensors and ML dosimeter. Therefore $ZnAl_2O_4$: Dy may be used as a good ML phosphor. $ZnAl_2O_4$: Dy phosphor may be further studied with different fuels to know their effect on ML properties of the phosphors.

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