

BaAl₂O₄: Dy phosphor: Synthesis and Mechanoluminescence characterization

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ABSTRACT: Dy doped BaAl₂O₄ phosphors were synthesized by solution combustion technique by using fuel carbohydrazide. Mechanoluminescence (ML) was excited impulsively by dropping a piston of 0.7 kg on to the phosphors. Two distinct peaks were observed in ML glow curve of the γ -ray irradiated BaAl₂O₄:Dy phosphors. Dependence of ML on various parameters as impact velocity of the piston dropped on to it, mass of the sample, gamma-ray doses given to the sample, fading of phosphors and ML spectra have been studied. ML emission spectrum showed characteristic emission of Dy³⁺ ion in this system. ML was observed optimum for the sample having 0.05 mol% of Dy in BaAl₂O₄ phosphors. XRD result confirms formation of the phosphor and surface morphology is seen by SEM. It may be speculated that recombination of the trapped charge carriers are responsible for ML in this system and as the it shows linear gamma ray response and low fading therefore it may be used for ML sensors and dosimeter.

Keywords: Mechanoluminescence, SEM, BaAl₂O₄, Defect.

I. INTRODUCTION

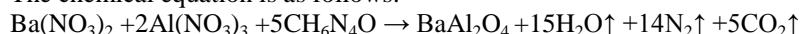
Luminescence induced during any mechanical action on solids is known as mechanoluminescence (ML) or triboluminescence. The mechanical treatment of crystals generally contributes a very rough interference. A great number of physical processes may occur within a very short time interval, which excite or 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 [1]. When the phosphor sample deposited on a glass substrate is elastically deformed by applying a load, then initially the ML intensity increases with time, attains a peak value at a particular time, and later on it decreases with time. The rise and decay characteristics of the ML produced during release of the load are also similar to those produced during the application of load. The ML of certain solids is so intense that it can be seen in day light with naked eye. In recent years the investigation of mechanoluminescent materials exhibiting intense ML intensity during their deformation has attracted the attention of a large number of workers. Rare earth doped strontium aluminate phosphors have been found useful in the real-time visualization of stress distribution in solids [2–4]. The ML materials show promising application to stress sensing techniques. The intense mechanoluminescent materials have been reported to be suitable for the real-time sensing of the strength and location of damages caused by the dynamic events in an object. The ML materials have also been found useful in the fuse system for army warhead [6–11]. Good luminescence material should have better chemical homogeneity and high surface area in a rapid, inexpensive single step operation. The BaAl₂O₄ offers high thermal and chemical stability, hydrophobic behaviour, high mechanical resistance, low sintering temperature, and high quantum yields. 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 and optical material [12]. The objective of this work is to study the ML properties of BaAl₂O₄: Dy phosphor synthesized by solution combustion process.

II. EXPERIMENTAL

The samples were prepared by solution combustion synthesis technique. The ingredients used were Ba(NO₃)₂.6H₂O, Al(NO₃)₃.9H₂O, carbohydrazide and dysprosium nitrate. Barium nitrate, Aluminium Nitrate, fuel 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 260°C. 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. This technique can produce a homogeneous product in a short amount of time, without the use of an expensive high-temperature furnace.

The chemical equation is as follows:



We observed greenish yellow flame during the combustion process and found white phosphor with low loss in weight on ignition.

Formations of the samples were confirmed by XRD pattern recorded by X-ray diffractometer (PW-1710). SEM measurement is carried out to observe the surface morphology of BaAl₂O₄: Dy phosphor (Model Hitachi S-3400N). The gamma-ray-irradiation was carried out using ⁶⁰Co 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 ray irradiation.

III. RESULT AND DISCUSSION

3.1 XRD characterisation

Figure 1 shows XRD pattern of BaAl₂O₄: Dy phosphors by using carbohydrazide as fuel. XRD pattern obtained is almost similar to the JCPDS card No. 73-1333 and it may be concluded that small amount of impurity doped in the host material does not affect the XRD pattern.

3.2 SEM study

An SEM study was carried out to investigate the surface morphology and crystallite sizes of the synthesized phosphor powder. The synthesis was carried out at 400°C by a combustion reaction. This shows that the combustion reactions of the mixtures took place well. The typical morphological image represented in Fig. 2 shows representative SEM micrographs taken for BaAl₂O₄ phosphor materials. The surface of the powder shows a lot of voids and pores, which may be formed by the evolved gases during combustion.

3.3 Mechanoluminescence characterisation

Figure 3 shows the ML intensity versus time curve of gamma ray irradiated BaAl₂O₄: Dy (0.05 mol %) phosphors. Two distinct peaks were observed when ML was excited by dropping a load of mass 0.7 kg on to it. 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. Figure 4 shows ML emission spectra of BaAl₂O₄: Dy (0.05 mol %) phosphors. In order to find the luminescence centres responsible for ML emission, we have recorded ML spectrum. In order to find the luminescence centres responsible for ML emission, we have recorded ML spectrum. Two distinct peaks one at around 482 nm and another at around 585 nm were observed. ML emission observed is the characteristic emission of Dy³⁺ which is due to the ⁴F_{9/2} → ⁶H_{13/2} and ⁴F_{9/2} → ⁶H_{15/2} transition of Dy³⁺ ions, respectively. Figure 5 shows that ML intensity increased almost linearly with increasing the mass of the sample deformed for recording ML, in the range (0.5 to 2.5 mg) investigated. When we increase the mass of the sample, the number of crystallites in the sample increases and thereby the ML intensity (I_m) and the total ML intensity (I_T) increase.

Figure 6 shows the dependence of ML intensity on γ-ray dose of BaAl₂O₄: Dy (0.05 mol %) phosphors. ML intensity increased almost linearly with γ-ray doses given to the samples. On increasing the γ-dose, the density of defect centres increases and when a sample of a given mass is deformed at a given impact velocity, I_m and I_T should increase with the density of defect centres. Figure 7 shows the dependence of total ML intensity (i.e. area below the ML intensity versus time curve) of BaAl₂O₄: Dy (0.05 mol %) phosphors on impact velocity. It is observed that the ML intensity initially increases with increasing impact velocity of the piston dropped on to the sample and seems to saturate at higher impact velocities.

We know that mechanical energy cannot be imparted to the trapped charge carriers directly; therefore some intermediate states are responsible for ML emission in this system. The origins of light emission are not due to the separation of the charges on the fracturing surfaces and piezoelectricity as BaAl₂O₄ has a centrosymmetric structure (Fd3m). Therefore it is suggested that ML of BaAl₂O₄: 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 (Dy³⁺). In BaAl₂O₄, 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). Since ML glow curve shows the characteristic emission of Dy³⁺, this energy may be transferred non-radiatively to Dy³⁺ ions causing their excitation and subsequent de-excitation of excited Dy³⁺ ions [13].

IV. CONCLUSIONS

BaAl₂O₄: Dy phosphor was synthesized via a solution combustion process from metal nitrates and organic fuel carbonylhydrazide. Well crystallized powders were obtained at 400°C within 5 min. The flame temperature and the amount of gaseous product released during combustion were key factors in determining the ML properties of synthesized phosphors. 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.

REFERENCES

- [1]. B P Chandra, D R Vij (Ed.), Luminescence of Solids, Plenum Press, New York, 1998, 361–389.
- [2]. C N Xu, T Watanabe, M Akiyama, X G Zheng, Appl. Phys. Lett., 1999, 74,2414.
- [3]. M Akiyama., C N Xu, M Taira, K Nonaka, T Watanabe, Philos. Mag. Lett., 1999,79,735.
- [4]. C N Xu, X G Zheng, M Akiyama, K Nonaka, T Watanabe, Appl. Phys. Lett., 2000,76,179.
- [5]. C Li, C N Xu, H Yamada, Y Imai, H Zhang, L Zhang, Key Eng. Mater., 2008,1407,368–372.
- [6]. Y Jia, M Ye, W Jia, Opt.Mater., 2006, 28,974.
- [7]. I Sage, L Huberstone, N Geddes, M Kemp, S Bishop, G Bourhill, Smart Mater. Struct., 2001,10,332.
- [8]. I Sage, R Badcock, L Humerstone, N Gedders, M Kemp, G Bourhill, Smart Mater. Srtuct., 1999, 8,504.
- [9]. G Bourhill, N I Geddes, I Sage, I Oswal, L Humberstone, R Badcock, P Llyod, N Willamson, M Kemp, J. Def. Sci., 2000, 5,433.
- [10]. I Sage, G Bourhill, J. Mater. Chem., 2001, 11,221.
- [11]. J G Dante, Reports by the Secretary of Army, USA, Patent no. 43722111983.
- [12]. L C V Rodrigues, R Stefani, H F Brito, M C F C Felinto, J Holsa, T Laamanen, M Malkamaki, M Lastusaari, Journal of Solid State Chemistry 183 (2010) 2365–2371
- [13]. E Tekin, A Ege, T Karali, P D Townsed, M Porik, Thermoluminescence studies of thermally treated CaB₄O₇:Dy, Radiation Measurements, 2010, 45(7), 764.

FIGURES

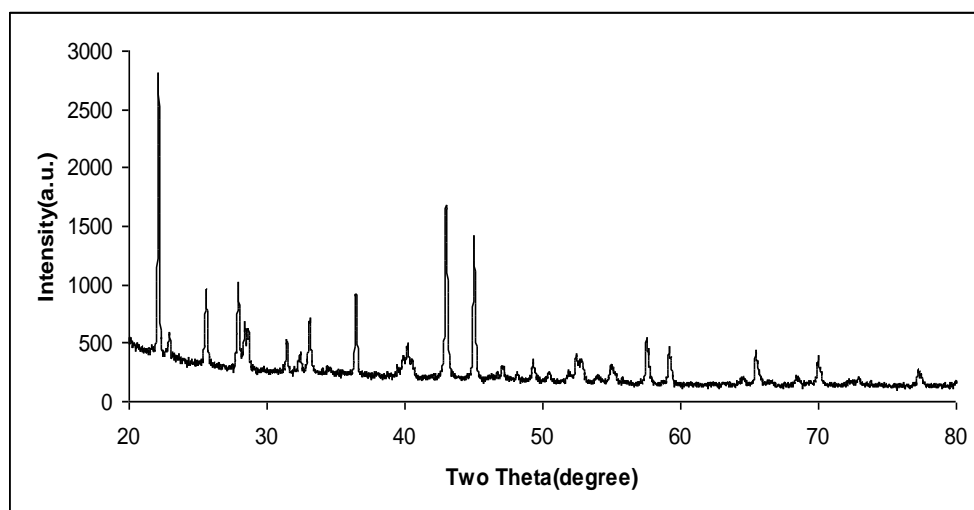


Figure 1 XRD pattern of BaAl₂O₄: Dy phosphor.

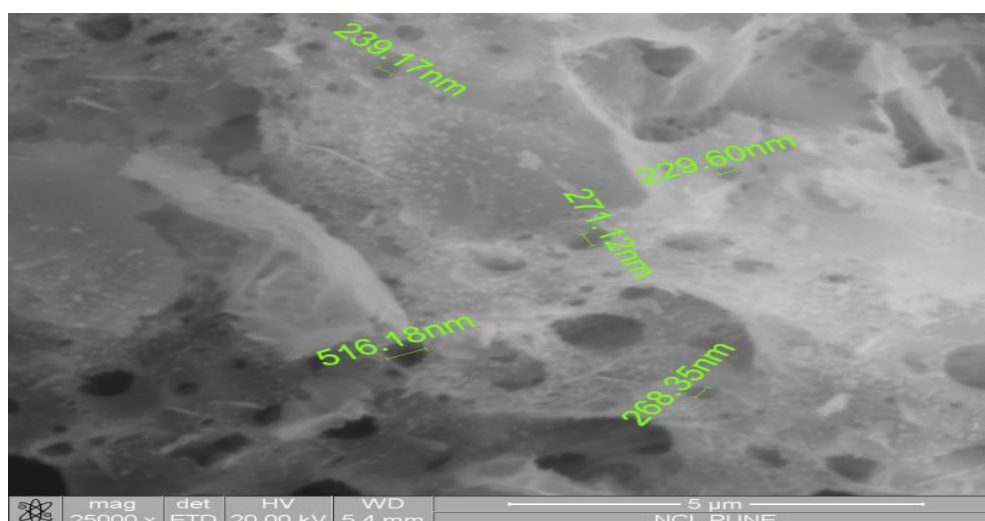


Figure 2 SEM image of BaAl₂O₄:Dy

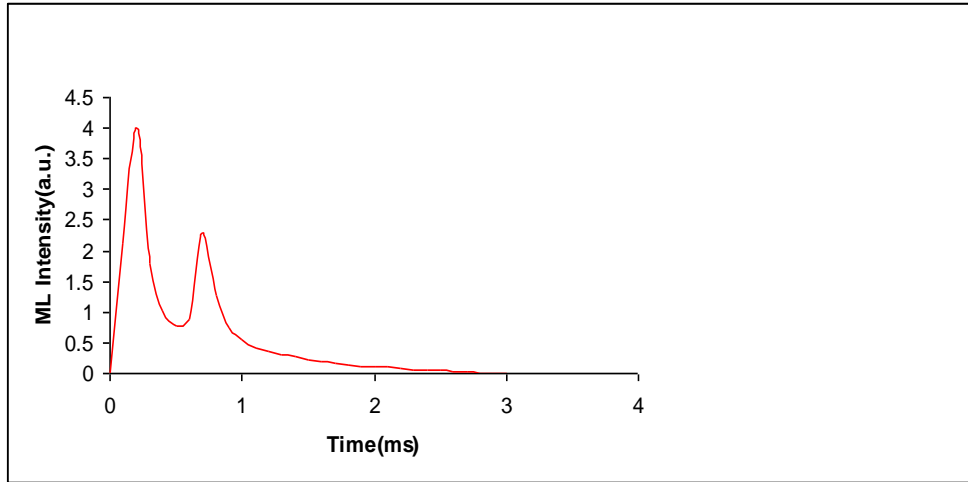


Figure 3 Time dependence of ML intensity of BaAl₂O₄:Dy(0.05mol %) phosphor. (γ -dose 1.1kGy.)

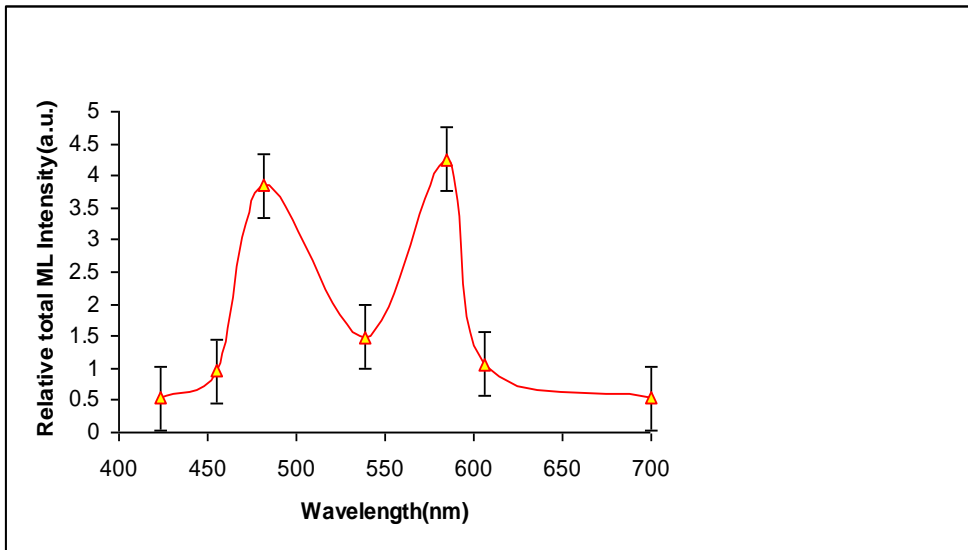


Figure 4 ML emission spectrum of BaAl₂O₄:Dy(0.05mol %) phosphor.

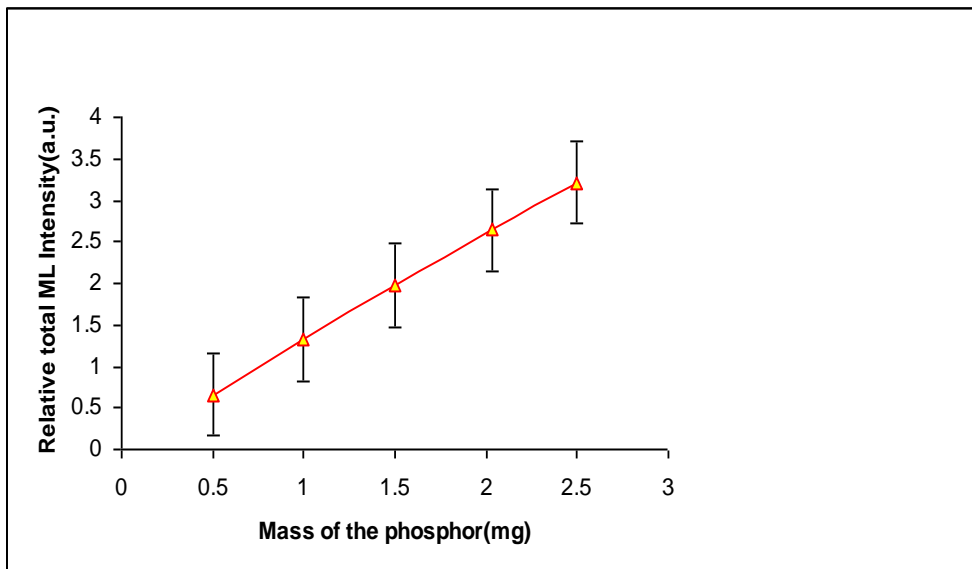


Figure 5 Dependence of total ML intensity of BaAl₂O₄:Dy(0.05mol %) phosphor on mass of the phosphor (γ -ray dose 1.1 kGy, mass of the piston 0.7 kg, impact velocity 2.83 ms⁻¹).

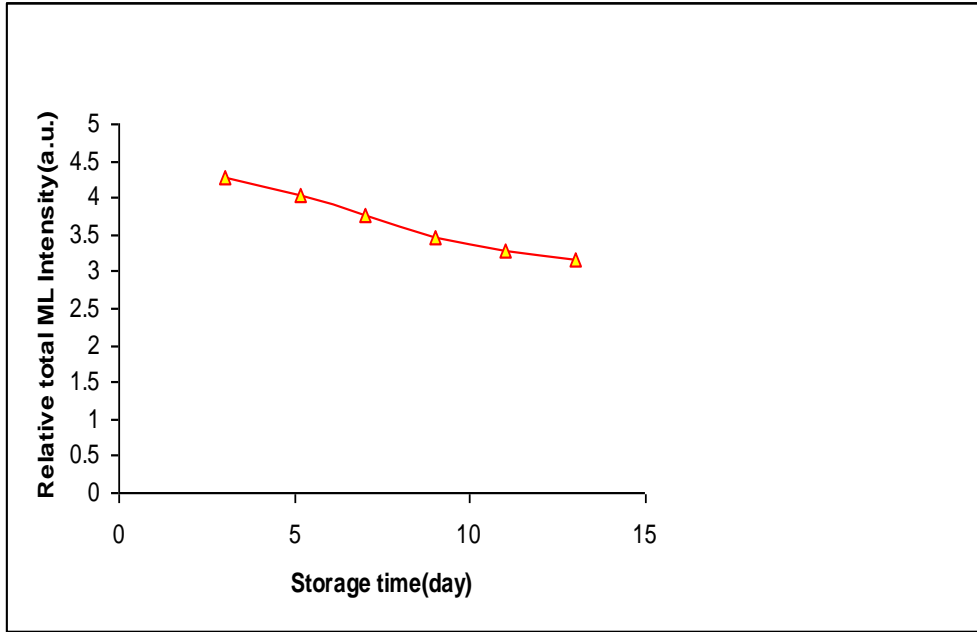


Figure 6 Total ML intensity of BaAl₂O₄: Dy(0.05mol %) as function of γ -ray doses given to the sample (mass of the sample 1mg, mass of the piston 0.7 kg, impact velocity 2.83 ms⁻¹).

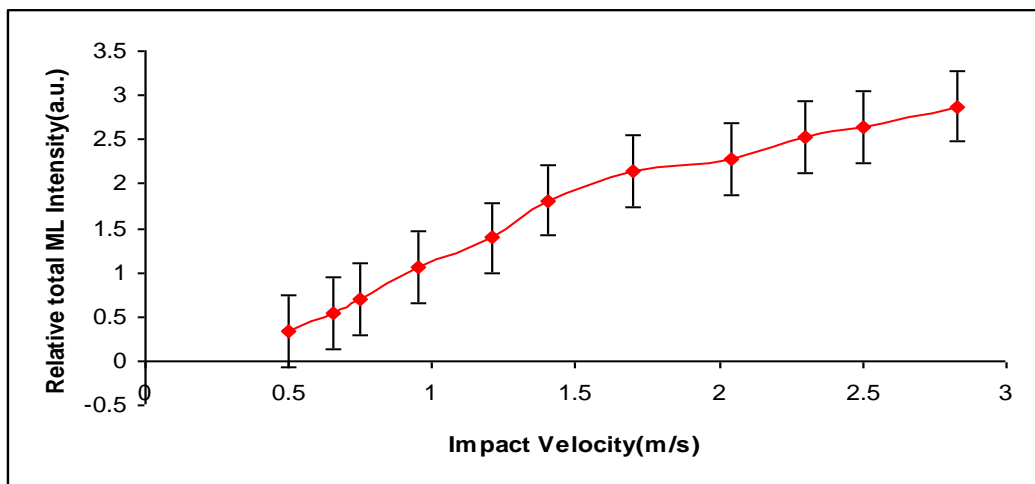


Figure 7 Dependence of total ML intensity of BaAl₂O₄:Dy(0.05mol %) on impact velocity (γ -dose 1.1 kGy).