



SYNTHESIS AND MECHANOLUMINESCENCE

CHARACTERISATION OF RARE EARTH DOPED PHOSPHATE BASED PHOSPHOR

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ABSTRACT

Eu and Dy doped LaPO₄ phosphors for mechanoluminescence dosimetry for ionizing radiations, were prepared by a solid state diffusion method and its mechanoluminescence (ML) have been studied. ML intensity varied with dopant concentration and it is optimum for the sample having 2 mole % of dopant. ML has been excited impulsively by dropping a piston of mass 0.6 kg on the phosphors with various impact velocities. As the piston was dropped on to the sample, ML intensity initially increased with time attained an optimum value for a particular time then decreased and finally disappeared. ML intensity increased almost linearly with the impact velocity of the piston dropped on to the sample, however, time corresponding to ML peak shifted towards shorter time value with increasing impact velocity of the piston dropped on to it. ML emission spectrum showed characteristic emission of Eu and Dy ions.

Keywords: *Luminescence, Mechanoluminescence, Phosphates.*

I. INTRODUCTION

Mechanoluminescence(ML) is a type of luminescence induced during or following any mechanical action on solids. It can be excited either by grinding, rubbing, cutting, cleaving, shaking, scratching, compressing or by impulsive crushing of solids. ML can also be excited by thermal shocks caused by drastic cooling or heating of materials or by the shock waves produced during exposure of samples to powerful laser pulses. ML phenomenon produced under different mechanical actions are sometime given specific names, such as triboluminescence, piezoluminescence, elastico and fracto luminescence, respectively.

Mechanoluminescence(ML) is used to describe the whole variety of processes in which light is emitted due to application of mechanical energy on solids. At present this effect is used widely in investigation of deformation and fracture of solids. This technique offers a number of interesting possibilities such as detection of cracks in solids and for mechanical activation of various traps present in the solids.

A number of reports on ML properties of irradiated alkali halides exists [1, 2, 3, and 4]. Chandra et al [5] paper reports the theory of mechanoluminescence (ML) produced during cleavage of elemental and III–V semiconductors. It seems that the formation of crack-induced localized states is responsible for the ML excitation produced during the cleavage of elemental and III–V semiconductors. According to this mechanism, as the atoms are drawn away from each other in an advancing crack tip, the decreasing wave function overlap across the crack may result in localized states which are associated with increasing electron energy. If the energy of these localized states approaches that of the conduction band, transition to the conduction band via

tunnelling would be possible, creating minority carriers, and consequently the electron-hole recombination may give rise to mechanoluminescence. Aman et al [6] reports the development of mechanoluminescence-based method for monitoring of size reduction processes in stirred media mill is described. Quartz particles are used as feed material that consists of aggregates and primary solid particles. Analysis of breakage in such system is problematic because it is very difficult to distinguish aggregates from primary particles. On the other hand, only stressing of primary particles between mill beads causes the mechanoluminescence impulses. (Ba,Ca)TiO₃:Pr³⁺ diphase ceramics with the self-assembled piezoelectric/phosphor/piezoelectric sandwich architectures have been synthesized using the solid-state reaction method. Their structure, elastically-mechanoluminescence (EML) property, and trap energy levels are characterized[7]. Mechanoluminescence (ML) in a CaAl₂SiO₈:Eu²⁺ phosphor was greatly enhanced by partial Sr²⁺ substitution for Ca²⁺; ML intensity reached a maximum at Sr²⁺ content of 40 mol %. Moreover, ML was not observed at Sr²⁺ content of 80 mol % or higher[8]. The promising green oxynitride phosphor, Ba₃Si₆O₁₂N₂:Eu²⁺, was synthesized at 1350 °C for 5 hours under a reducing N₂/H₂ (5%) atmosphere by using the solid-state reaction method. The phase purity was investigated by varying the nominal compositions, and the pure phase was achieved by carefully controlling the Si/Ba and O/Ba ratios[9]. Photoluminescence, luminescence and mechanoluminescence studies were carried out in a Li₃PO₄ microcrystalline powder doped with different rare earths[10]. Synthesis and thermo luminescence properties of SrAl₂O₄ (EU) phosphor irradiated with cobalt-60, 6 MV and 16 MV photon beams [11]. Ag nanoparticles coated CaTiO₃: Eu phosphor obtained from charge attracting process shows higher PL intensity and enhanced heat dissipation than the uncoated ones due to the LSPR effect and heat conduction of Ag nanoparticles reported by Zhenhua et al[12]

But no systematic study have been made of mechanoluminescence of phosphate based phosphor. In this present paper Eu and Dy doped LaPO₄ for mechanoluminescence dosimetry for ionizing radiations, the sample was preparation by a solid state diffusion method.

The present chapter reports the detailed and systematic investigation of impulsive excitation of ML in γ – irradiated impurity Eu and Dy activated LaPO₄ phosphor.

II. SYNTHESIS

For preparation of LaPO₄, Ammonium dihydrogen phosphate was dissolved in nitric acid. Suitable amounts of the impurity Dy₂O₃, Eu₂O₃ were also dissolved in nitric acid. The above solutions were mixed together and the mixed solution was dried at 80°C and crushed for 1 hour. The resultant material was then mixed thoroughly with appropriate amount of La₂O₃. The crushed powder was heated at 400°C for 4 h in an air atmosphere, and then resulting powder was again crushed for 1 h to powder then heated to 900°C for 7 hour in an air atmosphere. The resulting powder was again crushed and fired at 400°C for one hour and quenched to room temperature. All the samples have been obtained as quenched samples.

III. RESULT AND DISCUSSION

Fig.1(a,b) shows the time dependence of ML intensity of LaPO₄:Eu and LaPO₄:Dy sample for different concentration of impurity. It is clear that the ML intensity increases with increasing concentration of impurity,



attains an optimum value for 2 mole %. However, there is no considerable change in t_m (i.e. the time corresponding to ML peak).

Fig.2(a,b) shows the ML glow curves of γ – irradiated $\text{LaPO}_4:\text{Eu}$ and $\text{LaPO}_4:\text{Dy}$ samples, (1 mole %) samples for different impact velocities of the piston. It is seen that the ML intensity increases with increasing impact velocity. However, the time corresponding to the ML peak(t_m) shifts towards shorter time values with increasing impact velocity.

Fig.3 shows the dependance of total ML intensity on the impact velocity. Total ML intensity initially increased with impact velocity.

Fig.4(a,b) shows ML has been excited impulsively by dropping a load of height 30cm on to the phosphors from various loads. 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 than decreases and finally disappeared for all the samples. ML intensity increased with loads given to the sample.

Fig.5 shows the dependance of total ML intensity on the mass of the piston. Total ML intensity initially increased with mass of the piston.

Fig. 6 shows the effect of storage at room temperature on total ML intensity of γ –irradiated $\text{LaPO}_4:\text{Eu}$ and $\text{LaPO}_4:\text{Dy}$ samples.

It is observed that the ML intensity of γ – irradiated impurity activated some $\text{LaPO}_4:\text{Eu}$ and $\text{LaPO}_4:\text{Dy}$ samples initially increases with increasing concentration of impurity doped, attains an optimum value for a particular concentration. When the concentration of impurity is increased, initially the number of luminescent centre and the formation of defect centre increase, thereby increasing the ML intensity. Later on when the concentration exceeds a particular level, the concentration quenching starts and the efficiency of radiative transition decreases. The critical concentration of impurity for which the ML intensity attains an optimum value is higher (1 mole %) for the sample , it is observed that the ML intensity of γ – irradiated impurity activated some phosphate based phosphor initially increases with increasing concentration of impurity doped, attains an optimum value for a particular concentration. When the concentration of impurity is increased, initially the number of luminescent centre and the formation of defect centre increase, thereby increasing the ML intensity. Later on when the concentration exceeds a particular level, the concentration quenching starts and the efficiency of radiative transition decreases. It is believed that the factors leading to an increase in the probability on non-radiative transitions results as a decrease in the critical concentration related to the optimum luminescence efficiency. It is believed that the factors leading to an increase in the probability on non-radiative transitions results as a decrease in the critical concentration related to the optimum luminescence efficiency.

It is clear that the ML intensity increases with increase in mass of the load without any appreciable change in time corresponding to ML peak.

It is clear that the total ML intensity initially increases linearly with increasing impact velocity of the piston then it attains a saturation value for higher value of impact velocity

When we increase the mass or volume of the sample, the number of crystallites (N_c) in the sample increases and thereby the peak ML intensity (I_m) and the total ML intensity (I_T) increase.



IV. CONCLUSION

ML intensity varied with dopant concentration and it has been obtained optimum for the sample having 2 mole% of dopant. As the piston was dropped on to the sample, ML intensity initially increased with time attained an optimum value for a particular time then decreased and finally disappeared. ML intensity increased almost linearly with the impact velocity of the piston dropped on to the sample, however, time corresponding to ML peak shifted towards shorter time value with increasing impact velocity of the piston dropped on to it. ML emission spectrum showed characteristic emission of Eu and Dy ions.

FIGURE

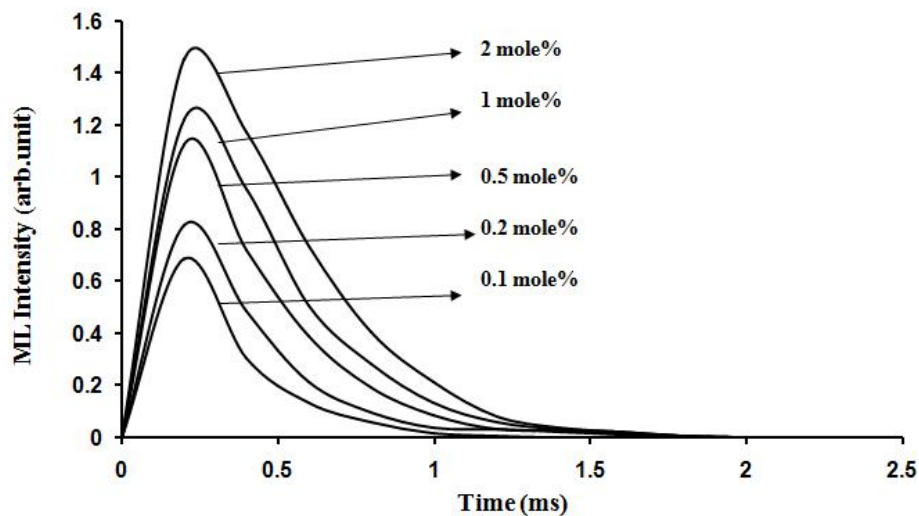


Fig.1a

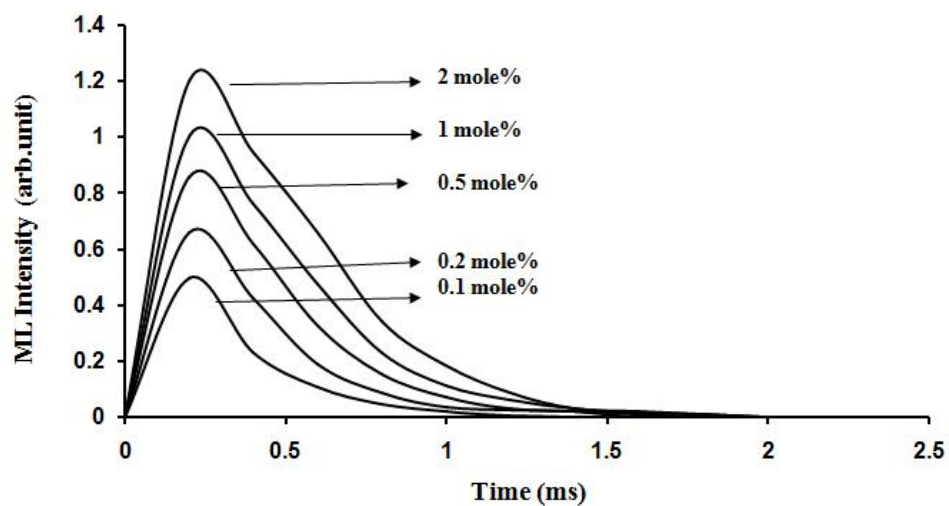


Fig.1b

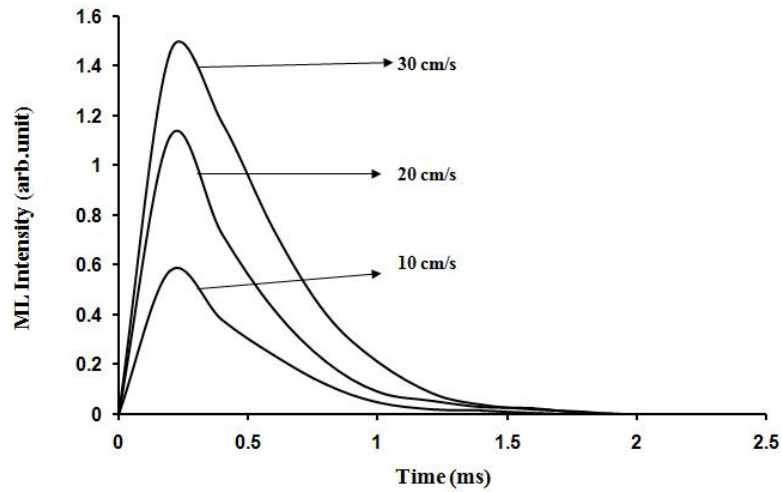


Fig.2a

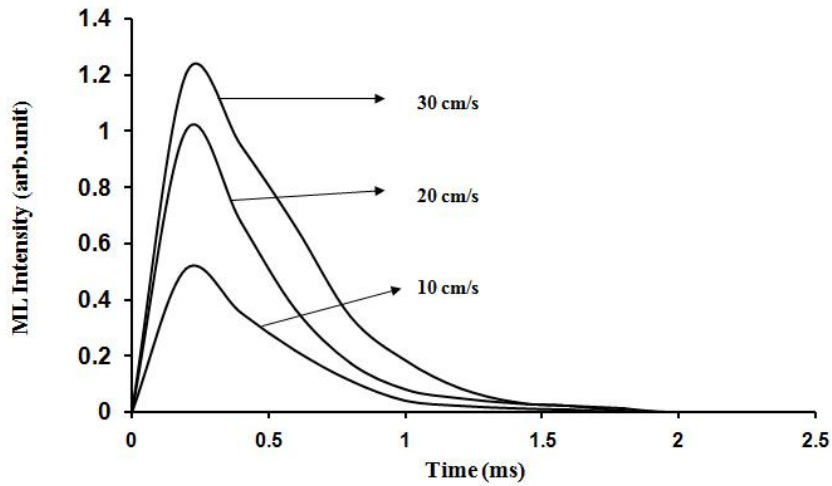


Fig.2b

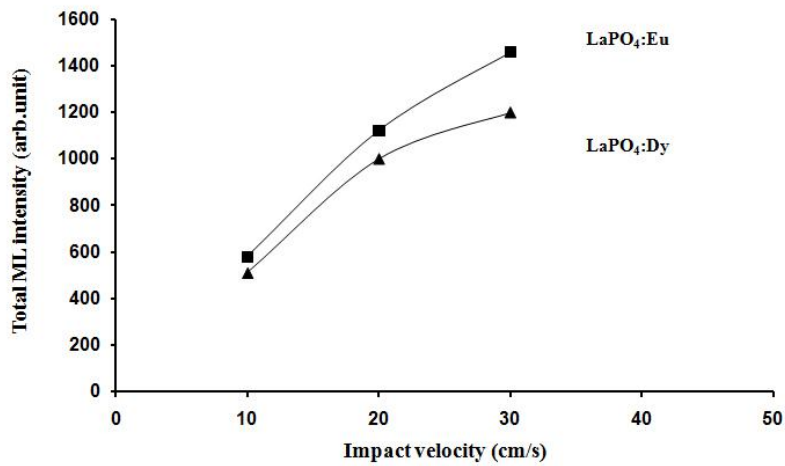


Fig.3

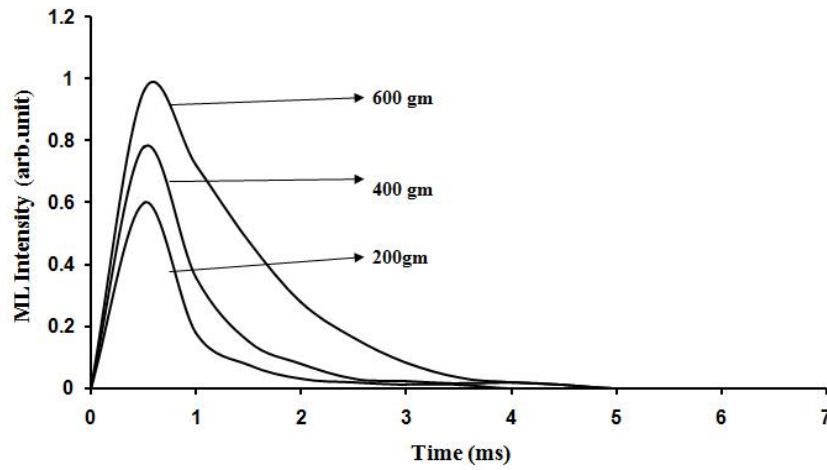


Fig.4a

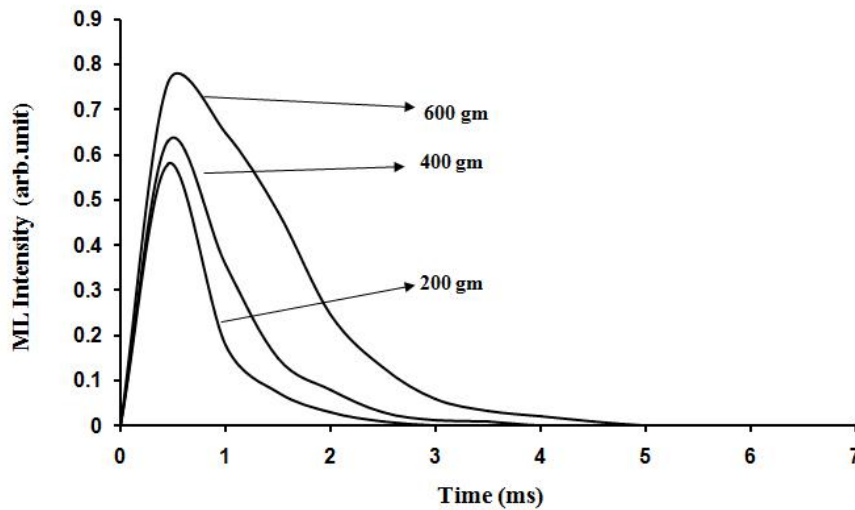


Fig.4b

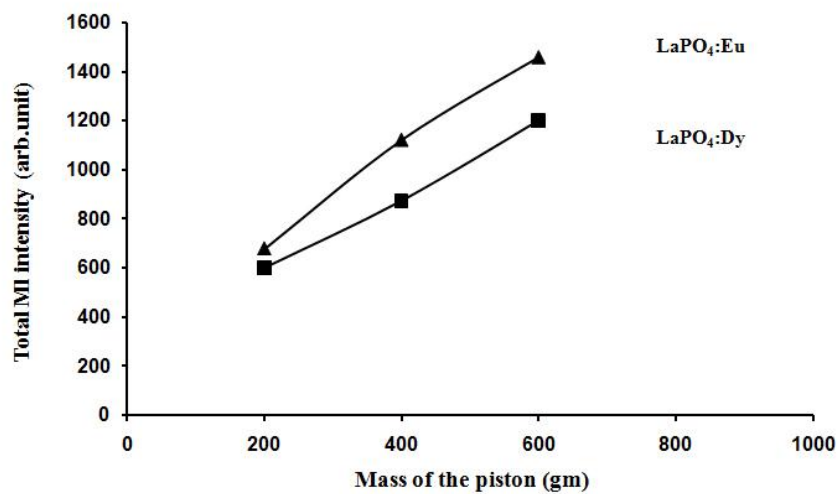


Fig.5

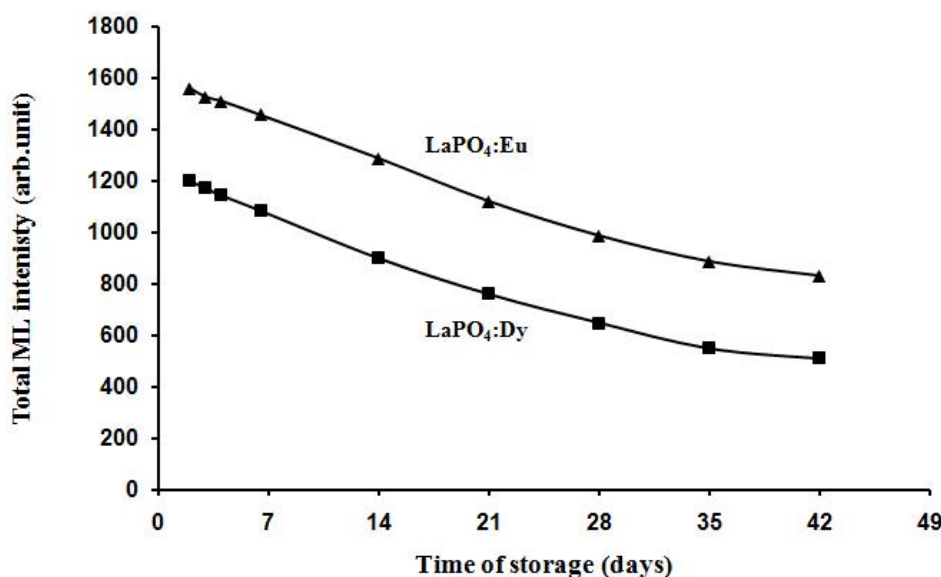


Fig.6

REFERENCES

- [1]. C.T.Buttler, Phys.Rev.141,750(1996).
- [2]. A.AL-Hasimi, A.M.Eid, K.V. Ettinger and J.R. Mallard: Radiat Prot.Dosim.6,203,(1984).
- [3]. K.Copty-Wergles, R.Nowotay and P.Hilley., Radiat. Prot.Dosim.33,339(1990).
- [4]. A.V.Shul Dinner and V.A.Zakrevskii: Rad.Prot. Dosim,65,113(1996).
- [5]. B.P.Chandra, R.P. Patela, Anubha S.Gourb, V.K.Chandra, R.K.Guptaa, J.Lum.104, 35(2003).
- [6]. Sergej Aman and Jorgen Tomas, Powder Technology ,146, 147(2004).
- [7]. Jun-Cheng Zhang, Xusheng Wang, Xi Yao, Chao-Nan Xu and Hiroshi Yamada Strong Elastico-Mechanoluminescence in Diphas (Ba , Ca) TiO₃ : Pr³⁺ with Self-Assembled Sandwich Architectures J. Electrochem. Soc. 2010 volume 157, issue 12, G269-G273.
- [8]. Lin Zhang, Chao-Nan Xu, Hiroshi Yamada and Nan Bu. Enhancement of Mechanoluminescence in CaAl₂Si₂O₈ : Eu²⁺ by Partial Sr²⁺ Substitution for Ca²⁺ . J. Electrochem. Soc. 2010 volume 157, issue 3, J50-J53.
- [9]. Wanyuan Li, Rong-Jun Xie, Tianliang Zhou, Lihong Liu and Yuejin Zhu . Synthesis of the phase pure Ba₃Si₆O₁₂N₂:Eu²⁺ green phosphor and its application in high color rendition white LEDs . The international journal for inorganic, organometallic and bioinorganic chemistry. Dalton Transactions , Issue 16, 43, 2014.
- [10]. A.K.Sahu, Bhusan P.Kore, P.S.Chowdhary, V.Nayar, S.J.Dhoble .The journal of biological & chemical luminescence.29, (2014) 58-64.
- [11]. Pushpraj Kumar Pathak and Rajnish Kurchania, Radiation physics and chemistry 117, (2015)48-53.
- [12]. Zhenhua Chen , Xinxin Qin , Qinghong Zhang , Yaogang Li, Hongzhi Wang , Journal of Colloid and Interface Science 459 (2015) 44–52.