Mechanoluminesacence characterization of NaAlSiO$_4$:RE (RE=Tb,Eu and Dy) phosphors

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Abstract: This paper reports the impulsive excitation of Tb, Eu and Dy rare earth ions activated NaAlSiO$_4$ materials prepared by solid state diffusion technique. The mechanoluminescence(ML) intensity of NaAlSiO$_4$ enhances on addition Tb, Eu and Dy ions. Mechanoluminescence is attributed to realize of holes due to the load on the phosphors which then recombine with rare earth (Tb, Eu and Dy) emitting light. Rare earth ions centers reduces the trap depth and therefore, the detrapping of filled electron traps takes place, and subsequently the energy released non radiatively during electon-hole recombination excites rare earth (Tb, Eu and Dy) ions centers and de-excitation gives rise to ML. It seems that trapping and detrapping of charge carriers in such materials can be studied using ML. When the load is applied on to the sample, then the mechanoluminescence emission takes place in the form of light pulse lasting for duration of 2 ms. The prepared sample shows good storage capability due to lesser fading in ML intensity. The ML characterization exhibits simple glow curve with good linearity. Thus the prepared materials may be useful for radiation dosimetry purpose.

Keywords: Phosphor; solid state diffusion; mechanoluminescence; NaAlSiO$_4$; radiation dosimetry

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 is produced under different mechanical actions are sometime given specific names, such as triboluminescence, piezoluminescence, elastico and fracto luminescence, respectively.

Mechanoluminescence 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.

The Ba$_3$MgSi$_2$O$_8$:Eu$_2$C, Mn$_2$C phosphors are synthesized through combustion process with varying mixture ratio of citric acid and ethylene glycol used as a fuel to the used precursors[1]. Green light emitting (Ba,Sr)$_2$SiO$_4$:Eu phosphor particles with high photoluminescence intensity under long wavelength ultraviolet (UV) were prepared by spray pyrolysis from colloidal spray solution[2].The liquid-phase synthesis method for preparing Eu-doped alkaline-earth silicate phosphor particles, which is expected to be applied for lighting apparatuses, such as mercury-free fluorescent lamps and flat-plane displays, such as PDP, was investigated [3].CaMgSi$_2$O$_6$:Eublue phosphor was prepared by spray pyrolysis and the photoluminescence properties were optimized by controlling concentration of Si element and the activator content[4]. Luminescence efficiency of self-activated CaWO$_4$ under 147 nm vacuum ultraviolet (VUV) radiation excitation is about 90% of that of BaMgAl$_{10}$O$_{17}$:Eu^{2+}(BAM), the commercial blue plasma display panel (PDP) phosphor[5], investigated a novel green emitting phosphor of Eu^{2+}-doped Li$_2$Ca$_2$Si$_2$O$_7$ which can be excited by ultra-violet light[6].Aman et al[7] 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.

But no systematic studies have been made of mechanoluminescence of mixed silicate system. In this present paper Tb, Eu and Dy rare earth ions doped NaAlSiO$_4$ phosphors for mechonoluminescencedosimetry 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 -ray irradiated impurity Tb, Eu and Dy activated NaAlSiO$_4$ phosphors.

II. EXPERIMENTAL

The experimental setup used for impulsive excitation of ML in □ -ray irradiated impurity doped phosphate phosphors is as follows; sample was placed on the upper surface of a transparent Lucite plate. It will be covered with a thin aluminum foil and fixed with adhesive tape. The load of different masses was dropped from different heights and the impact velocity of the load was changed. For taking ML measurement the phosphor was placed on a transparent Lucite plate, inside a sampler holder below the guiding cylinder and the luminescence was monitored below the transparent plate using an RCA 931A photomultiplier tube connected to a storage oscilloscope (SCINTIFIC HM-205). The photomultiplier housing is made of thick soft iron to provide a shielding from light and magnetic field. The slit arrangement at the window is provided to adjust the size of the window according to the incident beam.

The ML intensity was monitored by the photomultiplier tube whose output will be fed to one channel of storage oscilloscope. For determining the peak intensity, peak position, rise and decay time of ML, trace on the oscilloscope screen was recorded on tracing paper. Fig (1) shows the schematic diagram of experimental set-up used for deforming the sample and measuring the ML.
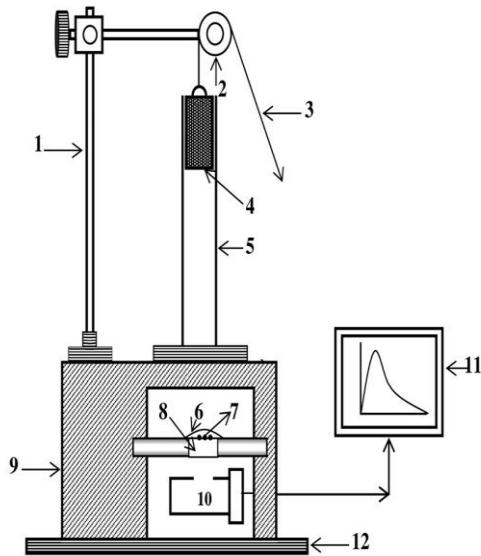
1. Stand	5. Guiding Cylinder	9. Wooden Block
2. Pulley	6. Aluminum foil	10. Photomultiplier tube
3. Metallic wire	7. Sample	11. Digital storage oscilloscope
4. Load	8. Transparent Lucite plate	12. Iron base mounted on table

Fig.1 Experimental set-up for ML

III. RESULTS AND DISCUSSION

Fig. 2 shows the XRD pattern of pure $NaAlSiO_4$ as prepared powder. This phosphor exhibit different diffraction peaks and most intense peak at $2\theta=29.86$, the XRD pattern of prepared $NaAlSiO_4$ sample is in accordance with standard ICDD File No. 88-1231.
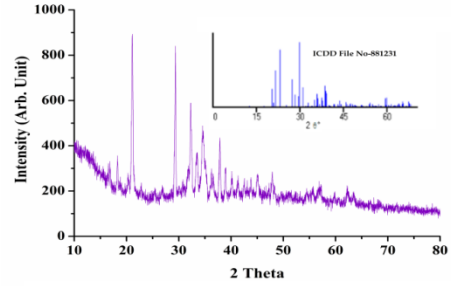
Fig. 2 X ray diffraction pattern of $NaAlSiO_4$ host.

No other impurity and allotropic forms are found, indicating that a pure crystalline compound with the same structure of $NaAlSiO_4$ could be formed.
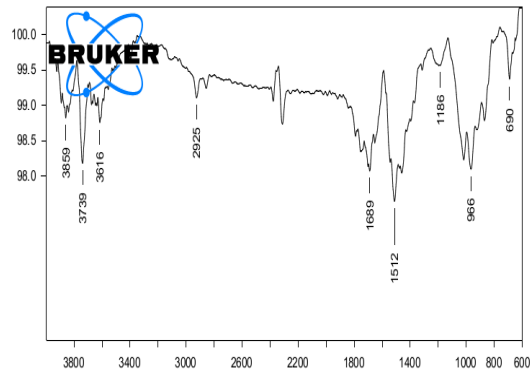
Fig. 3.FTIR spectrum of $NaAlSiO_4$ material

Fig. 3shows the FTIR spectrum of $NaAlSiO_4$. The absorptions from the main Si-O vibrations could be easily identified in the FTIR spectrum of $NaAlSiO_4$ (700-1200 cm^{-1}). Moreover, the bands in the range 1400-1600 cm^{-1} arising from Al-O vibrations and broad bands between $3400 – 3750$ cm^{-1} can be assigned to the adsorbed water (or water of crystallization).

Fig. 4 (a,b and c) shows the time dependence of ML intensity of Tb, Eu and Dy doped $NaAlSiO_4$ sample for different concentration of impurity. It is clear that the ML intensity increases with increasing concentration of impurity, attains an optimum value for 0.5 mole %. However, there is no considerable change in t_m (i.e. the time corresponding to ML peak).
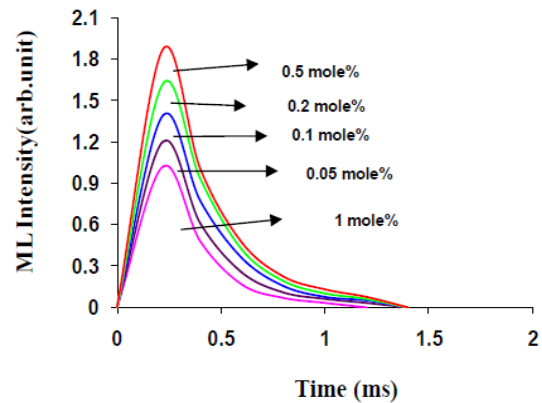
Fig.4(a) Time dependence of the ML intensity of γ - irradiated $NaAlSiO_4$:Tb sample for different concentration of Tb.
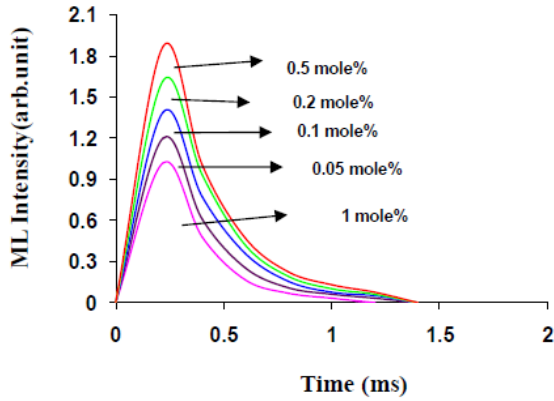
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Fig.4(b) Time dependence of ML intensity of γ - irradiated NaAlSiO$_4$:Eu sample for different concentration of Eu.

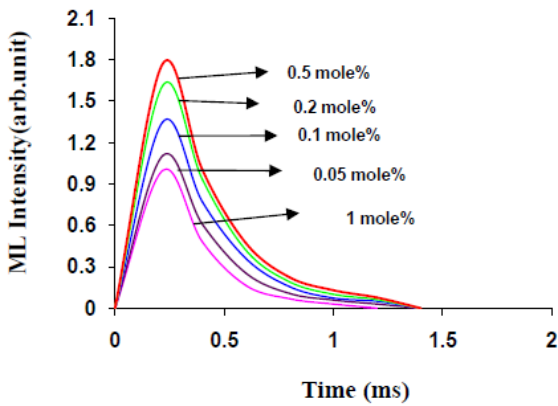**Fig.4(c)** Time dependence of ML intensity of γ- irradiated NaAlSiO$_4$:Dy sample for different concentration of Dy

Fig.5(a,b and c) shows the ML glow curves of γ – irradiated Tb, Eu and Dy doped NaAlSiO$_4$ (0.5 mole %) quenched samples for different impact velocities of the piston. It is seen that the ML intensityincreases with increasing impact velocity. However, the time corresponding to the ML peak(t$_m$) shifts towards shorter time values with increasing impact velocity.
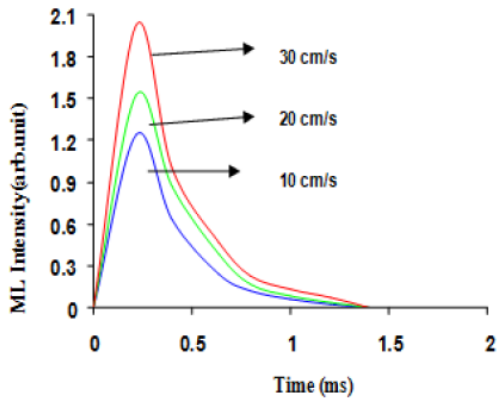

Fig. 5(a) ML glow curves of γ –irradiated NaAlSiO$_4$:Tb (0.5 mole %) quenched samples for different impact velocity.
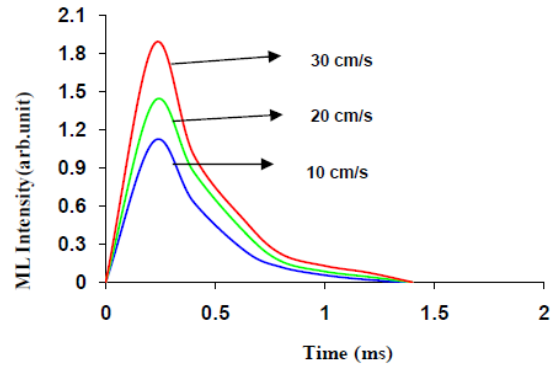

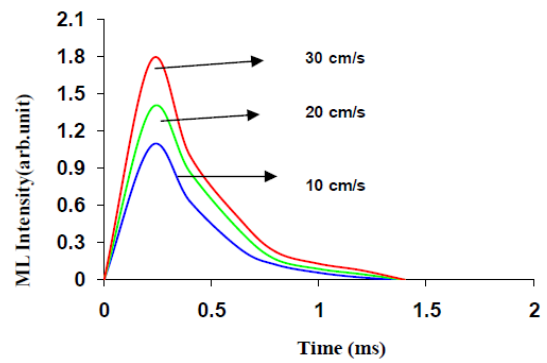**Fig. 5(b)** ML glow curves of γ – irradiated NaAlSiO$_4$:Eu (0.5 mole %) quenched samples for different impact velocity.

Fig. 5(c) ML glow curves of γ –ray irradiated NaAlSiO$_4$:Dy (0.5 mole %) quenched samples for different impact velocity.

Fig 6 shows that the total ML intensity of γ –ray irradiated impurity doped NaAlSiO$_4$ increases linearly with increasing impact velocity of the piston, then it attains a value for higher value of impact velocity.
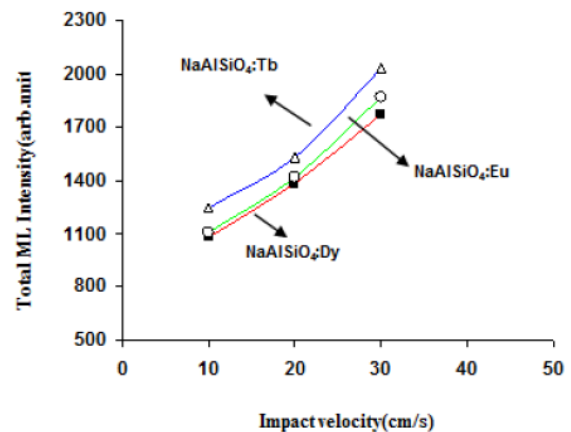

Fig. 6 Dependence of total ML intensity of γ - irradiated NaAlSiO$_4$ sample s on the impact of the piston.

Fig.7 (a,b and c) shows the dependence of time corresponding to ML peak for Tb, Eu and Dy doped NaAlSiO$_4$ (0.5 mole%) sample for different mass. It is

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clear that the time corresponding to the ML peak decreases with increasing impact velocity.
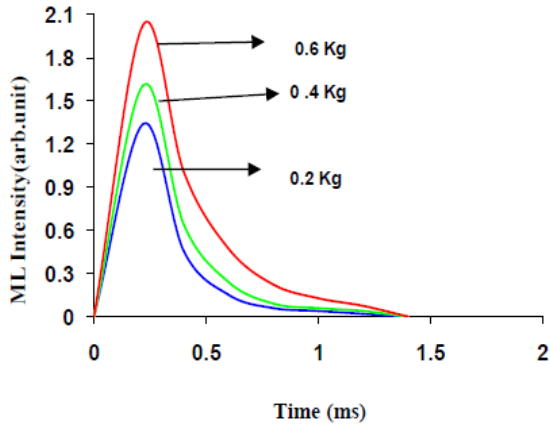

Fig.7(a) Time dependence ML intensity of γ - irradiated NaAlSiO₄:Tb sample for impact of piston of different mass.
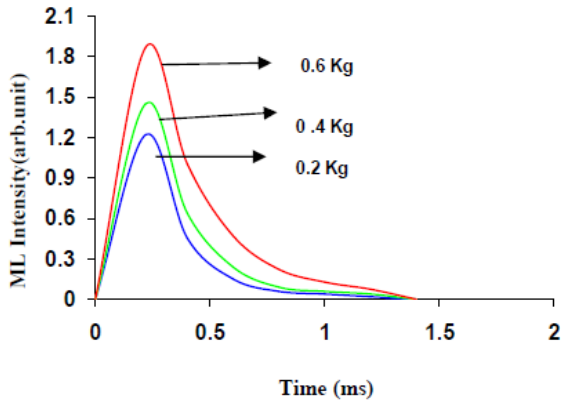

Fig.7(b) Time dependence ML intensity of γ - irradiated NaAlSiO₄:Eu sample for impact of piston of different mass.
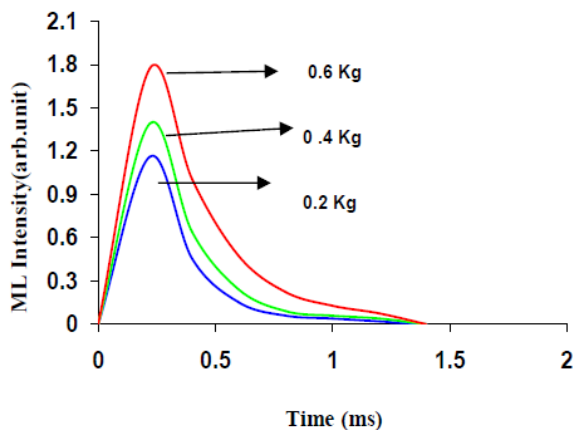

Fig.7(c) Time dependence ML intensity of γ - irradiated NaAlSiO₄:Dy sample for impact of piston of different mass.

Fig.8 shows that the total ML intensity of γ - irradiated impurity doped NaAlSiO₄ increases linearly with increasing mass of the piston.
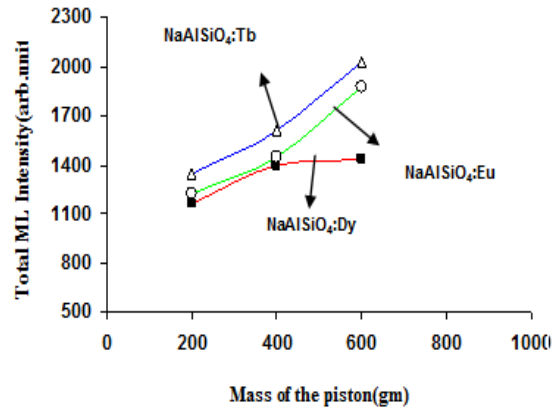
Fig.8 Dependence of total ML intensity of γ - irradiated NaAlSiO₄ sample on the mass of the piston.

Therotical proof for factors affecting onmechanoluminescence:

The velocity of moving piston with initial velocity V_0 can be expressed as ;

$$\mathbf{dv}/dt = -\beta v \qquad (1)$$

where,

β = coefficient of attrition.

v = velocity of moving piston.

For $v = v_0$ at t = 0 eqns(1) becomes

$$v = v_0 \exp(-\beta t) \qquad (2)$$

The rate of generation of new surface is directly proportional to the strain rateβ and volume v of the sample [8].

Thus eqns can be written as ;

$$dS/dt = Av\,\beta \qquad (3)$$

But, $\beta = v/H_0'$

$$dS/dt = [\, Av_0 v / H_0 \,]\exp(-\beta t) \qquad (4)$$
(from eqns 2 and 3)

On integrating, eqns (4) becomes ;

$$S = -1/\beta \;[\, Av_0 v / H_0 \,]\exp(-\beta t) + C \qquad (5)$$

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where, A = proportionality constant. H_0 = thickness of the sample volume of the mixed phosphate sample. C= integration constant.

When there is no new surface is created at t=0 , then we can take S=0 , t=0 .

Thus $C = Av_0v / H_0 \beta$.

On substituting the value of C in eqns (5), we get ;

$S = 1/\beta \ Av_0v / H_0 [1- \exp(-\beta t)]$ (6)

The surface charge density σ is defined as the total charge q per unit area S.i.e. Q = σS.

$Q = \sigma/\beta \ Av_0v / H_0 [1- \exp(-\beta t)]$ (7)

There are some defects can be seen in γ-irradiated impurity activated sulphate based phosphatesamples, that create the electron trapping centers whose energy levels lie close to the conduction band and the holes trapping centers whose energy levels lie close to the valence band. The oppositely charge surfaces are created when the sample is fractured. The electric field generated at the crack may cause bending of the conduction band, valence band and the energy levels of electron / holes trapping centers. Therefore these bands bended downwords near the positively charge surface of the crack. Similarly, these bands are bended upwords near the negatively charge surface of the crack [9].In the phosphate based phosphor, the difference between the hole trapping levels and valence band is less, this may cause tunneling of holes from the hole trapping levels to the valence band.

All the trapped holes may be released and may be transferred to the valence band. The tunneling of holes will takes place , within a certain width will depends on surface charge density σ and start beyond a critical value of surface charge density σ_c[10]. Therefore due to the tunneling process the number of electrons reaching to the conduction band may be neglected as compared to the number of holes reaching the valence band . If χ is the maximum width within which tunneling occure, the value of χ will depend on σ then the volume V_s near the surface from where the trapped holes can tunnel may give by

$V_s = S\chi$ (8)

As the tunneling takes place beyond a particular value of the electric field, density σ_c as the electric field ($E_0 = \sigma/\epsilon_0$) χ may be assumed to be directly proportional to ($\sigma - \sigma_c$) and it can be written as;

$\chi = B(\sigma - \sigma_c)$ ----(9)

By using eqns(8) and (9) we can write

$V_s = S B (\sigma - \sigma_c)$------(10)

The powder luminophor the microcrystalline particle of smaller dimensions then the number of holes (N_h) transferred due to the tunneling process may be expressed as;

$N_h = S B N_c P_t \rho_d(\sigma - \sigma_c)$ ---(11)

Where

N_c=number of crystallites in the phosphor

ρ_d=density of the defect centre in the phosphor

P_t= average probability of the tunnelling of hole from hole trap to valence band

B = proportionality constant

From eqns (6) and (11)

$N_h = \dfrac{Av_0v \ B \ N_c \ P_t \ \rho_d \ (\sigma - \sigma_c)}{\beta \ H_0}[1- \exp(-\beta t)]$ (12)

On differentiating eqns (12) the rate of generation of holes near the surface may be written as;

$g = \dfrac{Av_0v \ B \ N_c \ P_t \ \rho_d \ (\sigma - \sigma_c)}{H_0}\exp(-\beta t)]$or

$g = g_0\exp(-\beta t)$ ---(13)

If p is the number of moving holes near the surface at any time 't' and if β_r and β_n be the rate constants for radiative and non-radiative recombination respectively then the above eqns (13) may be written as in the form of rate equation as fallows;

$dp/dt = g_0\exp(-\beta t) - \beta_r p - \beta_n p$

or

$dp/dt = g_0\exp(-\beta t) - p(\beta_r + \beta_n)$ (14)

at p=0 and t=0 eqns (14) written as

$p = \dfrac{g_0}{\beta_r + \beta_n - \beta} [\exp(-\beta t) - \exp\{-(\beta_r + \beta_n) t\}]$ (15)

The radiative recombination of the holes will be $\beta_r\, p$, the ML intensity may be calculated by

$I = \dfrac{\beta_r g_0}{\beta_r + \beta_n - \beta}[\exp(-\beta t) - \exp\{-(\beta_r + \beta_n) t\}$ ---(16)

The total ML intensity (I_T) is given by

$I_T = \int_0^{\infty} I\, dt$

$I_T = \int_0^{\infty} \dfrac{\beta_r g_0}{\beta_r + \beta_n - \beta} [\exp(-\beta t) - \exp\{-(\beta_r + \beta_n) t\}]\, dt$

$= \dfrac{\beta_r g_0}{\beta_r + \beta_n - \beta}\dfrac{1}{\beta} - \dfrac{1}{\beta_r + \beta_n}$

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$$= \frac{\beta r g_0}{\beta \, (\, \beta r \, + \, \beta n}$$

substituting the value of g_0 ,we get

$$I_T = \frac{\beta r}{\beta \, (\, \beta r + \beta n} \quad \frac{Av\,0v\,B\,Nc\,Pt\,\rho d\,(\sigma - \sigma c)}{H_0} \text{----(16)}$$

eqns (16) represent the total mechanoluminescence intensity ,from the above discussion the total ML intensity depends on the following factors.

Mechanoluminescence intensity depends on mass of the sample:

On the volume of the sample, the number of crystallites (N_c) in the sample increases and therefore the total ML intensity (I_T) increase .This fact is justified with eqns (16).

Mechanoluminescence intensity depends on the γ-dose:

Defect centers such as cation vacancies and sulphoxyredicals are created when the phosphate based sample is exposed to ionizing radiation. when we increase the γ -dose applied to the sample, the density of the defect centers (ρ_d) increases. eqns (16) indicate that I_T should increase with the density of defect centres. It is observed that the ML intensity of γ-ray irradiated impurity activated $NaAlSiO_4$ 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. The critical concentration of impurity for which the ML intensity attains an optimum value is higher (0.5 mole %) for the sample, it is observed that the ML intensity of γ-ray 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. The critical concentration of impurity for which the ML intensity attains an optimum value is higher (0.5 mole %) for the sample $NaAlSiO_4$ .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.

IV . CONCLUSION

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. When the silicate based sample is exposed to ionizing radiation the defect centres like cation vacancies and sulphoxy radicals are created. On increasing the γ – rays dose, the density of defect centres (ρ_d) increases.

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REFERENCES

[1] J.S. Kim , S.W. Mho, Y.H. Park, J.C. Choi, H.L. Park, G.S. Kim, White - light emitting Eu^{2+} and Mn^{2+}-codoped silicate phosphors synthesized throught combustion process, Solid State Communications 136 (2005) 504–507.

[2] Hee Sang Kang, Seung Kwon Hong, Yun Chan Kang, KyeongYoulJung,Yong Gun Shul , Seung Bin Park, The enhancement of photoluminescence chercteristics of Eu–doped barium strontium silicate phosphor particle by co-doping materials. Journal of Alloys and Compounds 402 (2005) 246–250.

[3] Yoshihiro Nishisu, Mikio Kobayashi, Hitoshi Ohya, Toshiyuki Akiya, Preparation of Eu-doped alkaline-earth silicate phosphor particle by using liquid–phase synthesis method. Journal of Alloys and Compounds 408–412 (2006) 898–902.

[4] KyeongYoul Jung , Joo Hyun Kim , Yun Chan Kanopeg, Luminescence enhancement of Eu-doped calcium magnesium silicate blue phosphor for UV- LED application. Journal of Luminescence 129 (2009) 615–619.

[5] Seon-Bae Kim , ByungGonKum, Hyun Myug Jang , ArunachalamLakshmanan, Bong koo Kang ,Luminescence efficiencies of self and Tm^{3+} activated $CaWO_4$ under vacuum ultraviolet radiation excitation.Journal of Luminescence 131 (2011) 1625–1628.

[6] JuSeongKim ,Hee Jo Song , Hee-Suk Roh , Dong KyunYim , Jun Hong Noh, Kug Sun Hong . Luminescence chercteristics of green emitting $Li_2Ca_2Si_2O_7$: Eu^{2+} phosphors. Materials Letters 79 (2012) 112–115.

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[7] SergejAman and Jorgen Tomas, Mechanoluminescence of quartz particles during grinding in a stirred media mill, Powder Technology ,146 (2004) 147.

[8] B.P.Chandra, A.S.Gaur, V.K. Chandra, D.S.Raghuwanshi, A.K.Luka, R.N.Baghel Mechanoluminescence induced by elastic and plastic deformation of coloured alkali halide crystals at fixed strain rates. Radiation Effects Defects Solids.12(2010)165.

[9] G. Ahnstrom, Physical and chemical processes accompanying the dissolution of irradiated substances, studied by means of luminescence measurements. ActaChemScand 19(1965)12-300.

[10] G. Ahnstrom, G.vEhrenstein and R.Nilsson, The study of horoeradish peroxidase catalyzed oxidations by means of chemiluminescence, ActaChemScand 15(6)(1961) 1417-1419.

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