Recent Research in Science and Technology 2012, 4(8): 64-66
ISSN: 2076-5061
Available Online: http://recent-science.com/

Luminescence induced by elastic deformation of $BaSi_2O_2N_2$:Eu crystals

P. Jha[1], V.K.Vhandra[2] and B. P. Chandra[3]

[1]Department of Applied Physics, Raipur Institute of Technology, Mandir Hausad, Raipur, 492101(C.G.), India.
[2]Department of Electrical and Electronics Engineering, Chhatrapati Shivaji Institute of Technology, Shivaji Nagar, Kolihapuri, Durg 491001 (C.G.), India.
[3]Deparment of Postgraduate Studies and Research in Physics, Rani Durgavati University, Jabalpur 482001(M.P.), India.

Abstract

$BaSi_2O_2N_2$:Eu is a very intense elastico-mechanoluminescent and photoluminescent materials. The microcrystalline $BaSi_2O_2N_2$:Eu can be prepared using solid state reaction technique in reduced atmosphere. Then the microcrystalline phosphor was mixed epoxy and the samples of desired dimension size were prepared. For the ML excitation the sample was pressed using a material testing machine. When a compressive load is applied on the $BaSi_2O_2N_2$:Eu sample, mixed in epoxy, then initially the elastico-mechanoluminescence (EML) intensity increases linearly with time, attains a peak value and later on it decreases with time. The recovery of EML intensity of previously to compressed crystals with ultraviolet light reveals non-destructive phenomenon of EML. The EML of $BaSi_2O_2N_2$:Eu crystals can be understood on the basis of the piezoelectrically induced electron detrapping model.

Keywords: Luminescence, crystals, $BaSi_2O_2N_2$:Eu

INTRODUCTION

Mechanoluminescence (ML) is a type of luminescence induced by any mechanical action on solids. The light emissions induced by elastic deformation, plastic deformation and fracture of solids are called elastico-ML, plastico-ML and fracto-ML, respectively. The ML induced by rubbing of solids or separation of two solids in contact is known as tribo-ML or triboluminescence [1]. In recent years, ML materials exhibiting intense ML during their elastic deformation and fracture have been reported to be useful for stress sensors [2, 3], fracture sensors [4, 5], safety management monitoring system [6], damage sensors [7] and in the fuse systems for army warheads [8]. ML has also been reported to be useful in online monitoring of the grinding process in milling machines [9] and in radiation dosimetry [1].

Persistent luminescent materials are phosphors which are able to emit light for a long time after excitation [9]. This remarkable ‘afterglow’ of persistent luminescence originates in energy storage in the phosphor by trapping of charge carriers in long-lived energy levels inside the band gap. This stored energy can then be released by emission of light after thermal de-trapping of the charge carriers. Many details concerning persistent luminescence, such as the origin of the traps or the transfer pathway from the traps to the luminescent centers remain unclear [10].

This paper reports the strong non-destructive elastico ML of $BaSi_2O_2N_2$:Eu phosphors.

Theory

For the measurement of EML of persistent mechanoluminescent materials, the microcrystals or nanocrystals are mixed in epoxy resin and then the samples of suitable dimension are made using a mold. The EML in the sample is excited by applying a load. If Ω is the activation volume near an activator ion at which the piezoelectric constant is high, N_c is the number of crystallites in the sample, N_l is the number of activators in a crystallite and N_t is the concentration of traps, then the total number of traps in the sample is given by, $N_0 = \Omega N_c N_l N_t$. Considering the exponential distribution of traps in the activation volume near the activator ions in the crystallites, the number of traps $N_c(E_i)$ of energy E_i is given by the following Boltzmann statistical formula [11-13]

$$N(E_i) = ZN_0 \exp(-ZE_i) \quad \ldots(1)$$

where N_0 is the total number of traps in the activation volume of the crystallites and Z=1/kT is the distribution coefficient, in which k is the Boltzmann constant and T is the absolute temperature of the crystals.

Up to the threshold energy E_{th} the trap-depths are comparable to kT, and therefore, the shallow traps lying between zero and E_{th} are thermally detrapped. Thus, the detrappable traps will be present only from E_{th} to E and using Eq. (1), the total number N_t of detrappable traps from E_{th} to E can be expressed as

$$N_t = \int_{E_{th}}^{E} ZN_0 \exp(-ZE)dE$$

or,

$$N_t = N_0[\exp(-ZE_{th}) - \exp(-ZE)] \quad \ldots(2)$$

When an external pressure is applied, then the piezoelectric field F is produced. If α is the decrease in the trap-depth per unit electric field, then the decrease in trap-depth for the field F will be αF. Due to the decrease in trap-depth detrapping of electrons will take place and consequently the total number of filled traps will decrease. If N_d is the total number of detrapped traps after change in the trap-depth αF, then from Eq. (2), we get

$$N_d = N_0\left[\{\exp(-Z\alpha F_{th}) - \exp(-Z\alpha F)\}\right] \quad ...(3)$$

where F_{th} is the threshold piezoelectric field for the EML.

Differentiating Eq. (3), we get

$$\frac{dN_d}{dF} = N_0 Z\alpha[\exp(-Z\alpha F)] \quad ...(4)$$

Equation (4) can be expressed as

$$\frac{dN_d}{dt} = N_0 Z\alpha\dot{F}[\exp(-Z\alpha\dot{F}t)] \quad ...(5)$$

where $\dot{F} = dF/dt$

As the detrapped electrons are transferred to the conduction band the rate of generation of electrons in the conduction band is given by

$$g = \frac{dN_d}{dt} = N_0 Z\alpha\dot{F}[\exp(-Z\alpha\dot{F}t)] \quad ...(6)$$

It is evident from Eq.(6) that, for significant value of $Z\alpha\dot{F}$, the value of g will decrease with increasing deformation time of the crystals.

If τ is the lifetime of electrons in the conduction band, then for 1/τ>>α, the change in the number of electrons in the conduction band, that is, the change in the carrier density can be expressed as

$$\Delta n = g\tau = N_0 Z\alpha\dot{F}[\exp(-Z\alpha\dot{F}t)]\tau \quad ...(7)$$

If σ is the capture cross-section of the electrons, v_d is the drift velocity of electrons and n_r is the concentration of the energy states for the excited Eu^{2+} ions, then the rate of generation of the excited Eu^{2+} ions can be expressed as

$$R = \sigma v_d n_r \Delta n = \sigma v_d n_r N_0 Z\alpha\dot{F}[\exp(-Z\alpha\dot{F}t)]\tau \quad ...(8)$$

If μ is the mobility of electrons in the crystals, then $v_d = \mu F$, and Eq. (8) can be expressed as

$$R = \sigma\mu F n_r N_0 Z\alpha\dot{F}[\exp(-Z\alpha\dot{F}t)]\tau \quad ...(9)$$

It is to be noted that up to F_{th} there are no detrapping of charge carriers because the trap-depths up to this energy are comparable with kT and consequently traps are thermally detrapped. Thus, the detrapping takes place from the trap-depth E_{th} to E or for the piezoelectric field F_{th} to F. If η is the efficiency for the radiative decay of excited Eu^{2+} ions, then using Eq.(9) the EML intensity can be expressed as

$$I = \eta R = \eta\sigma\mu n_r N_0 Z\alpha\tau\dot{F}(F - F_{th})[\exp(-Z\alpha\dot{F}t)] \quad ...(10)$$

If B is the correlating factor between F and the piezoelectric charge Q, then F = BQ. For the piezoelectric constant d_0 near the localized piezoelectric region in the crystal, applied pressure P and pressing rate $\dot{P}$, $\dot{F} = B\dot{Q} = Bd_0\dot{P}$ and $F = BQ = Bd_0P$, and therefore, Eq. (10) can be expressed as

In the elastic region, P is low, and therefore, $Z\alpha Bd_0P$ <<1,and Eq.(11)can be written as

$$I = \eta\sigma\mu n_r N_0 Z\alpha\tau B^2 d_0^2\dot{P}(P - P_{th})[1 - (Z\alpha Bd_0P)] \quad ...(12)$$

$$I = \eta\sigma\mu n_r N_0 Z\alpha\tau B^2 d_0^2\dot{P}(P - P_{th})[\exp(-Z\alpha Bd_0P)]$$

where P_{th} is the threshold pressure for the EML emission.

For the crystals having low value of Z, α and d_0, the product $Z\alpha Bd_0P$ is much less than 1,and therefore, Eq.(12) can be written as

$$I = \eta\sigma\mu n_r N_0 Z\alpha\tau B^2 d_0^2\dot{P}(P - P_{th}) \quad ...(13)$$

The number N_t of trapped electrons is given by, $N_t=(N_0-N_d)=[N_0-N_0\{1-\exp(-Z\alpha Bd_0P)\}] =N_0\exp(-Z\alpha Bd_0P) =N_0\exp(-\beta P)$, where $\beta=Z\alpha Bd_0$. Thus, $\beta=Z\alpha Bd_0$is the rate constant for deformation detrapping or coefficient of deformation detrapping. Substituting the value of N_0, Eq. (13) can be written as

$$I = \eta\sigma\mu n_e\Omega N_c N_l N_t Z\alpha\tau B^2 d_0^2\dot{P}(P - P_{th}) \quad ...(14)$$

Equation (14) can be written as

$$I = \eta\sigma\mu n_e\Omega N_c N_l N_t Z\alpha\tau B^2 d_0^2\dot{P}^2(t - t_0) \quad ...(15)$$

Equation (15) can also be expressed as

$$I = \eta\sigma\mu n_e\Omega N_c N_l N_t Z\alpha\tau B^2 d_0^2 Y^2\dot{\varepsilon}^2(t - t_0) \quad ...(16)$$

where $t_0 = P_{th}/\dot{P}$, that is, the time at which the EML emission starts after pressing the sample at a fixed pressing rate, Y is the Young's modulus of elasticity and $\dot{\varepsilon}$ is the strain rate.

Equation (14) indicates that for a given pressing rate or strain rate, after the threshold pressure P_{th} ,the EML intensity should increase linearly with pressure P. Equation (16) indicates that for a given strain rate the EML intensity should increase linearly with the deformation time t.

Using the Eq. (14), equations of I_m, total ML intensity (I_T) , fast decay (I_{df}) and slow decay (I_{ds}) of ML intensity,

$$I_m = \eta\,\sigma\,\mu n_e\Omega\,N_l N_t\,N_c Z\alpha\tau\,B^2 d_0^2 Y(P_m - P_{th})\dot{\varepsilon} \quad ...(17)$$

$$I_m = \eta\,\sigma\mu n_e\,\Omega\,N_l N_t\,N_c Z\alpha\tau\,B^2 d_0^2(P_m - P_{th})\frac{dP}{dt}$$

$$I_T = \frac{\eta\sigma\mu n_e\,\Omega N_l N_t N_c n_e Z\alpha\tau B^2 d_0^2 P_m^2}{2}\left(1 + \frac{2\tau_m}{t_m}\right) \quad ...(18)$$

$$I_{df} = \eta\sigma\mu n_e\,\Omega N_l N_t N_c n_e Z\alpha\tau B^2 d_0^2 P_m Y\dot{\varepsilon}_0 \exp[-\phi(t - t_m)] \quad ...(19)$$

$$I_{ds} = I_{0s}\exp\left[-\frac{(t - t_c)}{\tau_s}\right] = I_{0s}\exp[-\chi(t - t_c)] \quad ...(20)$$

EXPERIMENTAL

$BaSi_2O_2N_2$:Eu powders were synthesized by (Botterman et al. 2012 [13]) using a high temperature solid state reaction. Stoichiometric amounts of starting materials $BaCO_3$ (99.95%) and Si_3N_4 (α-phase, 99.5%) were weighed and thoroughly mixed in a mortar. In order to dope with Eu, appropriate amounts of $BaCO_3$ were substituted by EuF_3 (99.5%). The powders were prepared with 2 mol% of Eu. The obtained mixtures were put in zirconia crucibles and fired at 1425°C for 4 hours in a horizontal tube furnace under a flowing atmosphere of forming gas (90% N_2 , 10% H_2).

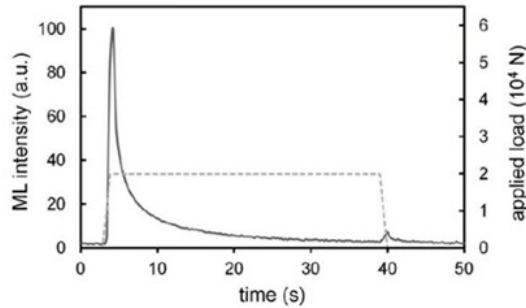

Fig 1. Typical mechanoluminescence (ML) behavior of stress-stimulated $BaSi_2O_2N_2$:Eu during application of a force of 20 kN (64 MPa). The solid line shows the ML intensity (on a linear scale) and the dashed line shows the force profile (after Botterman et al. 2012, ref [13]).

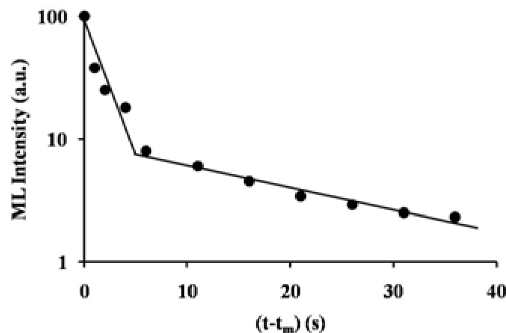

Fig 2. Semilog plot of ML intensity *I* versus ($t - t_m$).

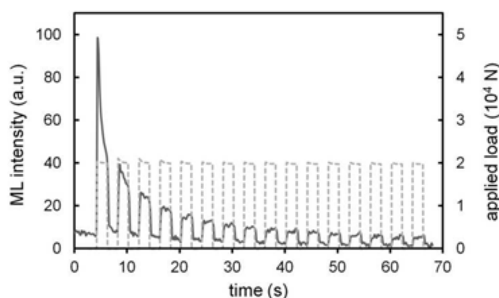

Fig 3. Mechanoluminescence (ML) of $BaSi_2O_2N_2$:Eu, stimulated by a periodically applied external force of 20 kN (64 MPa). The ML intensity on a linear scale (solid line) follows the ¼ Hz square wave profile of the external force (dashed line) (after Botterman et al. 2012, ref [13]).).

Correlation between theoretical and experimental results

Fig.1 shows typical mechanoluminescence behavior of stress-stimulated $BaSi_2O_2N_2$:Eu during application of a force of 20 kN (64 MPa). Such time dependence of EML can be understood using Eq. (13).

Fig.2 shows the semilog plot of *I* versus ($t - t_m$). It is seen that initially the ML intensity decreases at a fast rate and then decreases at a slow rate.This results is in accord with Eq.(17). The fast decay time 2.33 ms and slow decay time is 36 ms.

Fig.3 Mechanoluminescence (ML) of $BaSi_2O_2N_2$:Eu, stimulated by a periodically applied external force of 20 kN (64 MPa).

CONCLUSIONS

The ML intensity decreases with the number of applied stress stimulations, but after irradiating the sample with UV light, the recovery of ML intensity occurs completely, indicating that the ML process is non-destructive. On the basis of the piezoelectrically induced detrapping model of elastico ML, expressions are derived for the peak ML intensity, total ML intensity, fast decay of ML intensity and slow decay of ML intensity, in which a good agreement is found in theoretical and experimental results.

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