Mechanoluminescence studies of 0.5BaO.0.5ZnO-Al₂O₃:xEu (x=0,0.02,0.05,0.1,0.2,0.3,0.4,0.5) Phosphor by impulsive deformation technique

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http://dx.doi.org/10.22147/jusps-B/291101

Acceptance Date 5th October, 2017, Online Publication Date 2nd November, 2017

Abstract

The undoped and Eu doped 0.5BaO.0.5ZnO-Al₂O₃:xEu phosphors were prepared by the method of high temperature solid state reaction in air atmosphere. The phase formations of the samples were confirmed by taking powder XRD. Monoclinic phases of barium zinc oxides were identified. The mechanoluminescence (ML) studies of the samples were carried out via impulsive deformation technique (impact method). The ML emissions observed during the deformation of samples consist of two peaks such that intensity of second peak is relatively lower than the first. A large difference in ML decay timings were observed in undoped and Eu doped samples. Significant increase in ML intensities were observed due to Eu doping up to 0.3mole % and beyond that concentration of Eu the ML emission intensity decreases considerably. The decay constant of 0.5BaO.0.5ZnO-Al₂O₃:0.3Eu is fairly good and also the sample showed a linear rise in intensity with impact velocity. All these suggest the suitability of the sample for stress sensing applications.

Key words: XRD, doping, mechanoluminescence (ML)

1. Introduction

Mechanoluminescence (ML) is the phenomenon of emission of light from certain materials when they are excited with any mechanical actions like bending, striking, cutting, scratching etc.1. Recently ML technique became an efficient tool for stress sensing purposes and sensors like damage sensors, impact sensors, were developed on this ground2. Also this phenomenon can be applied for the purposes of propagation of cracks3, ageing of bridges4, detection of earth quakes5 etc. The intense ML emissions from Eu doped strontium aluminate

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inspired the researches working in this field and as a result in the past few decades lots of works were reported to exploit the ML properties of strontium aluminates. But very limited researchs were conducted to understand about the ML emission properties of other aluminates. Sajan et al. have reported the ML emissions of 0.1 mole % Eu deped Zn Barium aluminates for various Zn/Ba ratios for the first time and identified Zn$_{0.5}$Ba$_{0.5}$ aluminate : 0.1 Eu as potential ML material in the series. In the present study the ML emissions of 0.5 ZnO.0.5 BaO-Al$_2$O$_3$ : Eu by varying Eu concentration was studied in detail and a comparison was made between the the ML emissions of undoped and Eu doped systems.

2. Experimental

2.1 Synthesis :
The samples of required composition were prepared via high temperature solid state reaction. Zinc oxide (ZnO), Barium carbonate (BaCO$_3$) alumina (Al$_2$O$_3$) & europium oxide (Eu$_2$O$_3$) all of having 99.9% purity were used as starting reagents. Stoichiometric weights of the samples were taken and thoroughly mixed using double distilled waste in an agate mortar for 2 hours and the mixture was dried in the hot air oven. The mixture was then calcined at 1100°C for 4 hours. The phase formations of the samples was carried out by x-ray diffraction analysis. (XRD) [Model D8 Antonn parr, TTK450 using Cu x-ray source (\(\lambda = 1.5406 \text{Å}\))].

2.2 Mechanoluminescence (ML) Studies :
The ML studies of the sample were carried out using the method of impulsive deformation (impact method). For each measurement 3mg of sample was used and after each impact the deformed samples were replaced with a fresh sample. In this method a load of 100gm was dropped from a height ‘h’ and ML emissions if any due to impact was captured by a photomultiplier tube (pmT 931A) whose output was interfaced with a storage oscilloscope. The signal appeared on the screen of the oscilloscope during impact is termed as ML glow curve.

3. Results and Discussions

Fig 1 indicates the XRD pattern of the 0.5 BaO.0.5 ZnO-Al$_2$O$_3$:0.3 Eu. The peaks are matched well with the standard peaks of the data of compounds of barium zinc oxides and aluminium oxides [ICDD card numbers 76-2158 and 80-0956]. Monoclinic phases of barium zinc oxides with space groups C2/c(15) was identified and the corresponding peaks were indexed. The ML glow curve of undoped 0.5BaO.0.5 ZnO-Al$_2$O$_3$ at 100 cm/s impact velocity is shown in fig. 2. The time taken by the signal to to attain maximum intensity (t$_{m}$) was found to be around 0.42 ms.

The variation of ML intensity of with Eu doping concentrations was depicted in fig. 3. Only slight variations in ML intensities were noticed when Eu concentration were below 0.1 mole %. Significant enhancement in ML emissions were observed as the concentration of Eu varies in the range 0.1 mole % to 0.3 mole % and highest ML emission were observed when Eu concentration become 0.3 mole %. Further increase in Eu concentration reduces the ML emission intensity. About 53% decrease in ML emission intensity was observed as the Eu concentration varies from 0.3 mole % to 0.5 mole %. Variations in ML intensities due to rare earth doping indicates the increase in density of electron-hole pairs there by increasing the possibility of recombination luminescence. But at higher concentrations of europium results in energy transfer between the free charge carriers,that decreases the luminescence.

A comparison of ML emission of 0.5BaO.0.5ZnO-Al$_2$O$_3$ :xEu :undoped and 0.5BaO.0.5 ZnO-Al$_2$O$_3$ :xEu: 0.3 mole% was made in fig. 4. After doping with Eu the ML emission intensity increased to about 46 %and
photon emission time increases from 1.3 ms to 2.4 ms. Also a shift of less than 1 ms in $t_m$ was noticed after doping with Eu. In all cases two peaks are visualized in the ML glow curve where the first peak is more intense than second peak. During impact of a load electrons are excited to the conduction band due to the influence of electric field developed between the fractured surfaces. The excited electrons combines with holes present in luminescence centres and gives out light which is visualized as first peak. In the mean time a portion of excited electrons again get trapped in trap levels lying close to the conduction band for short interval of time and later gets detrapped which also gives out light which is seen as second peak\textsuperscript{10}.

Time taken to attain ML peak intensity ($t_m$) of 0.5BaO.0.5 ZnO-Al\textsubscript{2}O\textsubscript{3}: undoped and 0.5 BaO.0.5 ZnO-Al\textsubscript{2}O\textsubscript{3}:0.3 Eu for different impact velocities are shown in fig 5. The $t_m$ values were 0.42 ms and 0.5 ms respectively and also only insignificant variations were found in $t_m$ with variations in impact velocities. This indicates that only insignificant variations in compressions of powder samples are taking place with increasing impact velocity\textsuperscript{11}.

A semilog plot between log I version ($t - t_m$) for 0.5 BaO.0.5 ZnO-Al\textsubscript{2}O\textsubscript{3}: undoped and 0.5BaO.0.5ZnO-Al\textsubscript{2}O\textsubscript{3}:0.3 Eu was shown in fig 6. The data points were fitted with straight line and corresponding shapes of each lines were calculated and the reciprocals of slopes gives the values decay constant ($\tau$) in each case. It was found that the decay time increases to about 2.8 times due to Eu doping. The decay constants of 0.5BaO.0.5 ZnO-Al\textsubscript{2}O\textsubscript{3}:0.3 Eu corresponding to each impact velocities was calculated & tabulated in table 1 and only insignificant variations are found with change in value of impact velocities.

| Impact velocity (cm/s) | 100 cm/s | 141 cm/s | 178 m/s | 200 cm/s |
|------------------------|----------|----------|---------|----------|
| Decay constant ($\tau$) | 890 $\mu$s | 850 $\mu$s | 879 $\mu$s | 883 $\mu$s |

Table 1: Variations of decay constant ($\tau$) of 0.5 BaO.0.5 ZnO-Al\textsubscript{2}O\textsubscript{3}:0.3 Eu with impact velocities.

Fig 7a-b shows the variations of ML intensities of 0.5BaO.0.5 ZnO-Al\textsubscript{2}O\textsubscript{3}:0.3 Eu with impact velocities in the range 100 cm/s to 245 cm/s a found a good linear rise up to 200 cm/s. As impact velocity increases rate of creation of new surfaces due to fracture also increases with impact velocity. Linear rise in total ML intensity indicates the linear rise of total area of newly created surfaces. Beyond 200 cm/s impact velocity only insignificant variations in ML intensities was observed. This can be due to strain hardening at higher impact velocities\textsuperscript{12}. The intense ML response with appreciable decay timings and linear rise of ML intensity with impact increases the possibility of the phosphor for stress sensing applications.
Fig 3: ML intensity variation of 0.5 BaO:0.5 ZnO-Al₂O₃:xEu (x=0, 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5) (Impact velocity=100 cm/s)

Fig 4: Comparison of ML glow curves of 0.5BaO:0.5 ZnO-Al₂O₃: undoped and 0.5BaO:0.5ZnO-Al₂O₃:0.3 Eu

Fig 5: Comparison time taken to ML peak ($t_m$) of (a)0.5 BaO:0.5 ZnO-Al₂O₃:undoped and (b) 0.5BaO:0.5 ZnO-Al₂O₃:0.3 Eu with impact velocities (mass of load=100 gm)

Fig 6: Semi-log plot between logI versus ($t-t_m$) of (a) 0.5BaO:0.5 ZnO-Al₂O₃:undoped and (b) 0.5BaO:0.5ZnO-Al₂O₃:0.3 Eu (Impact velocity=100 cm/s)
4. Conclusion

The undoped and Eu doped samples of 0.5BaO.0.5 ZnO-Al\(_2\)O\(_3\) were successfully synthesized via high temperature solid state reaction. ML studies of 0.5BaO.0.5 ZnO-Al\(_2\)O\(_3\); undoped were conducted and found two ML emission peaks in the ML glow curve. The ML emission intensities of both emission peaks became intense after doping with europium and highest ML emission intensity was found at 0.3 mole % of europium beyond
which quenching of luminescence was noticed. A comparison was made between ML emissions of undoped and 0.3 Eu doped 0.5BaO.0.5 ZnO-Al₂O₃ phosphors and significant rise in ML intensity, photon emission time and decay constants due to Eu doping was observed.

Acknowledgements

The authors are thankful to the University Grants Commission (UGC), New Delhi for the financial support, Sophisticated Analytical Instruments Facility (SAIF), STIC, Cochin for providing XRD.

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