

Synthesis and Characterization of BaSi₂O₂N₂:Eu Nitride based Phosphor

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Abstract— This paper discusses synthesis, photoluminescence and mechanoluminescence properties of Eu^{2+} activated $BaSi_2O_2N_2$ oxinitride phosphor. The material was synthesized through modified two step high temperature solid state diffusion technique. The prepared sample was confirmed by XRD technique. The Eu^{2+} activated $BaSi_2O_2N_2$ material shows efficient emission at 504nm due to $4f^6 5d^1 \rightarrow 4f^7$ transitions of Eu^{2+} ion under excitation at 355nm. The quenching of prepared sample occurred at 1mole%. This phosphor is potential phosphors that may be applicable in solid state lighting. The impulsive excitation of mechanoluminescence (ML) in Eu^{2+} doped barium based phosphor reports the shifting of peaks toward shorter time values with increasing impact velocity. It is also seen that the total ML intensity I_{Total} initially increases with impact velocity and then it attains a saturation value for higher values of impact velocity. The peak ML intensity I_m and total ML intensity I_T increase quardratically with the applied load and impact velocity. The present study may also be helpful in preparing ML-based light source by increasing trap-depth of shallow traps. If the ML emission in certain materials will be in ultraviolet range, then the ML pulses of short duration may be used to excite the phosphorescence and determining the decay time. This fundamental work might be applicable for ML sensors and dosimeter.

Keywords— $BaSi_2O_2N_2$, mechanoluminescence; phosphor; photoluminescence; solid state diffusion method;

1. INTRODUCTION

In recent years most of the researchers have concentrated on the era of white light-emitting-diodes (W-LEDs) due to their characteristics such as ecofriendly, longer life time, highly efficient, wide band gap etc[1-3]. The increasing demand for fossil fuels and the environmental impact of their use are continuing to exert stress on an already extended world energy infrastructure [4]. White LEDs which promises high brightness, high efficiency, low electrical power consumption is thus considered as the next-generation solid state lighting replacing traditional incandescent and fluorescent lamps [5]. In order to prevent deprivation with temperature and time that results in losing efficiency and causing changes in the produced light color is a matter of concern as far as the stability of phosphor with respect to both chemical and thermal stability is concerned [6]. Therefore the most probable requirement in lamp industry is better physical and chemical stability, water-resistant property to develop persistent phosphor. The demand and development for novel efficient inorganic luminescent materials is a outcome of recent developments in the field of solid state lighting (SSL). In this respect the special attention was attracted by europium doped materials. Based on near ultraviolet (UV) or blue emitting InGaN LEDs, Europium doped oxynitrides (MSi₂O₂N₂: Eu with M = Ba, Sr, Ca) have recently been proposed as excellent conversion phosphor materials for white-light-emitting LED applications. This can be attributed to their strong absorption in near UV to blue-light region of the light spectrum as well as to their high quantum efficiency and good thermal and chemical stability when compared to most of the oxide and sulfide phosphors [7–9]. In the electro-magnetic spectrum Eu^{2+} emits ultraviolet to red region and nature of the host lattice decides emission wavelength due to 5d \rightarrow 4f transition. The crystal field affects 5d excited state [10]. The present results reflect that $BaSi_2O_2N_2:Eu^{2+}$ is a promising blue-emitting phosphor for n-UV LED application.

Mechanoluminescence (ML) is photoemission from some materials due to an applied mechanical simulation. These mechanical actions could include friction, pressure, bending, erasing or rubbing, fracture and shocking etc. For a long time the interest in ML has been academic in nature with the majority of works either reporting new ML materials, detailing methods for quantitative generating and measuring ML, recording ML spectra and suggesting mechanisms underlying the deformation and fracture-induced excitation processes. Many efforts have been done to make the solar energy more available in recent years. One of the proposals is to use the longlasting phosphorescence (LLP) materials to absorb and store the sunlight energy in daytime and then emit slowly at night for illumination purposes [11]. As a category of ML materials, elastico mechanoluminescence (EML) materials present an accurate linearity of ML intensity against load in the elastic region, in addition to mechanooptical conversion [12].

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Previous researches have indicated that the developed EML materials belong to the defect controlled type piezoelectric materials and the EML mechanism has been explained using the piezoelectrically induced carrier detrapping model [13-18]. Consequently the EML performance mentioned above should be closely related to the concentration and depth of trap levels. On one hand the EML intensity is mainly influenced by the concentration of trap levels. If the concentration of trap levels whose depths are suitable for EML is relatively higher, more trapped carriers will be released which will recombine with the luminescence centers under the applied stress resulting into an intense EML e.g. In cases of $Sr_{n+1}Sn_nO_{3n+1}:Sm^{3+}$ (n = 1, 2, ∞) and $(Ca,Sr,Ba)Si_2O_2N_2:Eu^{2+}$ [16,17]. On the other hand the depth of trap levels is responsible for the load threshold and measurement range of dynamic load. For example SrAl₂O₄:Eu²⁺ exhibits an intense EML even under the application of a weak mechanical force, such as that generated by scratching the material with a finger. The shallow trap levels $(0.2 \pm 0.1 \text{ eV})$ are one of the most important reasons for its sensitivity to the weak load [15]. Nevertheless it should be also pointed out that if there are only shallow (accessible) or less deep trap levels, the carriers in traps can be released and then be emptied under the weak load, which results in absence or weakness of EML under the strong load. On the contrary, if there are only deep or less shallow trap levels, the energy necessary for carriers to release from the traps is so high that the trapped carriers cannot be excited by weak load, resulting in a high load threshold for EML. Therefore to search and design novel EML materials with suitable multiple trap levels is an effective and promising method to obtain the excellent EML performance.

2. EXPERIMENTAL

BaSi₂O₂N₂:Eu²⁺ phosphors were synthesized by a high temperature solid-state diffusion method. The starting materials were high purity BaCO₃ (Merck, >99.0%), α -Si₃N₄ powder, SiO₂ and Eu₂O₃ of AR grade. The appropriate amounts of starting materials were weighed out separately on an analytical balance and subsequently mixed and ground together in an agate mortar. The powder mixtures were then transferred into crucibles. Subsequently those powder mixtures were fired in a furnace at 400°C for 1 hr. The powder mixture was again crushed together in an agate mortar for one hour and fired in a horizontal tube furnace (muffle furnace) at 800°C for 24 hr in open air atmosphere. The samples were gradually cooled down to room temperature in the furnace. The prepared material was then heated at 1200°C for 2 hours in a carbon based reducing atmosphere and was then annealed and pulverized for further measurements.

All measurements were performed on finely ground samples, which were analyzed by X-ray powder diffraction. All the XRD measurements were performed at room temperature in air. The composition and phase purity of products were measured by powder X-ray diffraction (XRD) analysis with an X'Pert PRO diffractometer with Cu-Ka radiation (λ = 1.54060Å) operated at 45 kV and 40 mA. The XRD data were collected in a 2θ range from 10^{0} to 80^{0} . The photoluminescence (PL) emission spectra of the sample were recorded using fluorescence spectrometer (Hitachi F-4000). The same amount of sample was used in each case. The emission and excitation spectra were recorded using spectral slit width of 1.5 nm. The experimental setup used for impulsive excitation of mechanoluminescence (ML) in y- irradiated Eu doped BaSi₂O₂N₂ phosphors is as follows- The sample was placed on the upper surface of a transparent Lucite plate. It was 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 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 was 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.

3. RESULT AND DISCUSSION

3.1 XRD Analysis

The powder XRD pattern of the sample was analyzed for structure confirmation. The XRD of the prepared sample



Fig. 1: XRD of BaSi₂O₂N₂:Eu²⁺

is shown in Fig.1. The JCPDS file of the sample is not available. So the XRD of prepared sample is compared with papers data. The XRD of prepared sample matched well with the XRD reported by Jonas Botterman et al.[19]



3.2 Photoluminescence Study of BaSi₂O₂N₂:Eu²⁺

Fig. 2: Photoluminescence excitation spectrum of BaSi₂O₂N₂:Eu²⁺

A series of BaSi₂O₂N₂:Eu²⁺ phosphor was prepared with different Eu²⁺ concentrations (Eu = 0.5, 1, 2 mol %) and the effect of Eu²⁺ ion concentration on the emission spectra were investigated. The excitation spectra are shown in fig.2. The PL emission spectrum under 355 nm excitation exhibits a well-known characteristic Eu²⁺ emission (Fig.3).



BaSi₂O₂N₂:Eu²⁺

The emission spectra of $BaSi_2O_2N_2:Eu^{2+}$ phosphor excited at 355 nm wavelength gives emission at 504 nm in bluegreen region of electromagnetic spectrum corresponding to $4f^65d^1 \rightarrow 4f^{7}$ transition of Eu^{2+} ion. The emission and excitation band of $BaSi_2O_2N_2:Eu^{2+}$ phosphor is broad which the characteristics of Eu^{2+} are. The emission band spread in the range 450 - 570 nm in a blue-green region peaking at 480-520 nm where as excitation band (Fig.2) spread in the range 300 – 440 nm with shoulder at 400 nm. The symmetrical emission spectra indicated that the Eu^{2+} ions had one emission centre in the BaSi₂O₂N₂ host. No emission beyond 600 nm was observed indicating that Eu^{3+} ions have been effectively reduced to Eu^{2+} ions when heated in charcoal atmosphere. The broad luminescence of Eu^{2+} is due to $4f^{6}5d^{1} \rightarrow 4f^{7}$ transition of Eu^{2+} ion which is an allowed electrostatic dipole transition. Surrounding ligands of host material affect the luminescence spectrum of Eu^{2+} ion because the redistribution of electrons takes place in inner 4f sub-shell of Eu²⁺. No change was observed in shifting of positions of emission bands with increasing Eu²⁺ concentration. The emission intensity increases with increasing concentration of Eu²⁺ and the maximum luminescence intensity is observed for 1 mole % of Eu²⁺ ion in BaSi₂O₂N₂ host lattice. Generally emission intensity gets enhanced with increased concentration of rare earth ions in a host. The decrease in emission intensity beyond critical concentration can be explained by concentration quenching. Concentration quenching results due to energy transfer among Eu²⁺ ions in the lattice of $BaSi_2O_2N_2$. This non radiative energy transfer increases with Eu^{2+} content[20]. Concentration quenching occurs when the Eu²⁺ concentration is more than 1mole %. The luminescence characteristics indicate that the phosphor can be effectively excited by near UV light and can exhibit a satisfactory blue emission. The results reveal that BaSi₂O₂N₂:Eu²⁺ is a promising candidate as a blue component for fabrication of NUVbased white light emitting diodes [6].

3.3 CIE and Color Purity



Fig. 4: CIE chromaticity coordinates of BaSi₂O₂N₂:Eu²⁺ phosphors

purity The emitted blue color of the BaSi₂O₂N₂:Eu²⁺phosphors can be found bv the Commission Internationale de l'Eclairage (CIE) coordinates. The values of x and y coordinates are 0,142 and 0.441 respectively which fall into blue region of CIE chromaticity diagram as shown in Fig. 4.

3.4 Mechanoluminescence Study of BaSi₂O₂N₂:Eu²⁺ Phosphors

Fig.5 shows the time dependence of ML intensity of $BaSi_2O_2N_2$:Eu sample for different concentration of impurity. It is clear that the ML intensity increases with increasing concentration of impurity and attains an optimum value for 1 mole %. However there is no considerable change in t_m (i.e. the time corresponding to ML peak). For recording ML the sample were irradiated with gamma ray dose of 0.037kGy/hr.



Fig. 5: Variation of ML intensity of BaSi₂O₂N₂:Eu sample with Time for different concentration of impurity



Fig. 6: Variation of ML intensity of γ – irradiated BaSi₂O₂N₂:Eu samples, (1mole %) with Time for different impact velocities of the piston



Fig. 6: (a) MI glow curve of γ – irradiated BaSi₂O₂N₂:Eu samples, (1 mole %) for different impact velocities of the piston

For the study of variation of ML intensity with different impact velocities of the piston, 1 mole% of BaSi₂O₂N₂:Eu sample was selected. Fig.2 shows that ML intensity initially increases with time attain maximum value and then decrease for different impact velocities of the piston. It is seen that the ML intensity increases with increasing impact velocity. However the time corresponding to ML peak(t_m) shifts towards shorter time values with increasing impact velocity. From Fig 6a it is clear that the total ML intensity initially increases linearly with increasing impact velocity of the piston and then it attains a saturation value for higher value of impact velocity.



Fig. 7: Variation of ML intensity of γ – irradiated BaSi₂O₂N₂:Eu samples, (1 mole %) with time for different mass



Fig.7: (a) MI glow curve of γ – irradiated BaSi₂O₂N₂:Eu samples, (1 mole %) for different mass of the piston

Fig.7 shows that ML has been excited impulsively by dropping a various loads from height of 30 cm on to the phosphors. 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 and finally disappeared for all the samples. Total ML intensity increases with mass of the piston (Fig.7a).

The stability of stored signal at normal temperatures is an important characteristic of ML materials in ML dosimetry. Any appreciable decay in stored signal at room temperature will invalidate the relationship between ML emitted and radiation exposure that may have been delivered some considerable time before readout. The fading of glow curves of BaSi₂O₂N₂:Eu for storage period of 20 days are shown in Fig. 8. ML fading studies have shown that at room temperature ML peak fades to 20%

after storage for 10 days which may be related to shallow trap recombination. As seen from this figure, the peak intensity of glow peaks is not sufficiently influenced by storage period at room temperature. The ML yield was reduced to 30% of its original value after 20 days storage at room temperature.



Fig. 8: Show the effect of storage at room temperature on total ML intensity of γ –irradiated BaSi₂O₂N₂:Eu sample.

It is observed that ML intensity of γ – irradiated Eu activated BaSi₂O₂N₂ sample initially increases with increasing concentration of impurity doped and then 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 for 1 mole % of sample. It is believed that the factors leading to an increase in 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.

4. CONCLUSIONS

BaSi₂O₂N₂:Eu_x phosphor powder was successfully prepared by two step solid state diffusion technique. The emission spectra of BaSi₂O₂N₂:Eu_x doped with different concentration of Eu shows a single broad blue emission band with maximum at 504 nm under UV excitation at 355 nm. The quenching occurs at 1 mole%. ML intensity varied with dopant concentration and has been obtained optimum for the sample having 1 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 ions.

REFERENCES

- W. B. Im, Y. I. Kim, N. N. Fellows, H. Masui, G. A. Hirata, S. P. DenBaars and R. Seshadri, Appl. Phys. Lett., 93(2008), 091905.
- [2] T. Nishida, T. Ban and N. Kobayashi, Appl. Phys. Lett., 82 (2003), 3817
- [3] J. S. Kim, P. E. Jeon, J. C. Choi, H. L. Park, S. I. Mho and G. C. Kim, Appl. Phys. Lett., 84(2004), 2931.
- [4] S. Ye, F. Xiao, Y.X. Pan, Y.Y. Ma, Q.Y. Zhang Materials Science and Engineering R 71 (2010) 1
- [5] Rong-Jun Xie Naoto Hirosaki, Yuanqiang Li and Takashi Takeda Materials 3 (2010) 3777
- [6] Ashwini Kumar, S.J. Dhoble, D.R. Peshwe, Jatin Bhatt Journal of Alloys and Compounds 578 (2013) 389
- [7] R. Mueller-Mach, G. Mueller, M. R. Krames, H. A. Höppe, F. Stadler, W. Schnick, T. Juestel, and P. Schmidt, Phys. Status Solidi A 202(9), (2005) 1727
- [8] R. J. Xie, N. Hirosaki, K. Sakuma, and N. Kimura, J. Phys. D Appl. Phys. 41(14), (2008).144013
- [9] P. F. Smet, A. B. Parmentier, and D. Poelman J. Electrochem. Soc. 158(6), R37–R54 (2011).
- [10] K.S. Bartwal, H. Ryu, J. Semicond. Display Equip. Technol. 6 (2007) 65
- [11] S. Lian, Y. Qi, C. Rong, L. Yu, A. Zhu, D. Yin, and S. Liu, J. Phys. Chem. C 114(15), (2010) 7196.
- [12] B. P. Chandra, edited by D. R. Vij (Plenum Press, 1988), 361.
- [13] C. N. Xu, T. Watanabe, M. Akiyama, and X. G. ZhengAppl. Phys. Lett. 74(9), (1999).1236
- [14] X. Wang, C. N. Xu, H. Yamada, K. Nishikubo, and X. G. Zheng, Adv. Mater. 17(10), (2005) 1254
- [15] C. N. Xu, T. Watanabe, M. Akiyama, and X. G. ZhengAppl. Phys. Lett. 74(17), (1999).2414
- [16] S. Kamimura, H. Yamada, and C. N. Xu, Appl. Phys. Lett. 101(9) (2012) 091113.
- [17] J. Botterman, K. V. Eeckhout, I. D. Baere, D. Poelman, and P. F. Smet, Acta Mater. 60(15), (2012).5494
- [18] J. C. Zhang, X. Wang, X. Yao, C. N. Xu, and H. Yamada, J. Electrochem. Soc. 157(12), (2010) G269.
- [19] Jonas Botterman, Koen Van den Eeckhout, Adrie J. J. Bos, Pieter Dorenbos, and Philippe F. Smet Optical Materials Express 2(3) (2012) 341-349
- [20] Chau-Chyun Chung,Jau-Ho JeanJ of material Chemistry and Physics 123(2010) 13