Journal of Luminescence 143 (2013) 337–342

Contents lists available at SciVerse ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Photoluminescence and thermoluminescence properties of Dy^{3+}/Eu^{2+} activated $Na_{21}Mg(SO_4)_{10}Cl_3$ phosphors

Bhushan P. Kore [a], N.S. Dhoble [b], K. Park [c], S.J. Dhoble [a,*]

[a] Department of Physics, RTM Nagpur University, Nagpur 440033, India
[b] Department of Chemistry, Sevadal Mahila Mahavidyalaya, Nagpur 440009, India
[c] Faculty of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul 143-747, Korea

ARTICLE INFO

Article history:
Received 16 December 2012
Received in revised form
20 April 2013
Accepted 26 April 2013
Available online 17 May 2013

Keywords:
Phosphors
Thermoluminescence (TL)
Photoluminescence (PL)
Deconvolution
$Na_{21}Mg(SO_4)_{10}Cl_3$

ABSTRACT

In the present work luminescence properties of rare earth (RE) doped $Na_{21}Mg(SO_4)_{10}Cl_3$ were studied. Modified solid state method was employed to synthesize the phosphors. The influence of RE (RE = Dy and Eu) doping on the luminescence properties of as prepared phosphor were investigated in detail. PL emission spectra of the $Na_{21}Mg(SO_4)_{10}Cl_3$:Dy phosphor exhibits the characteristic emission of Dy. The characteristic Dy^{3+} emission in the form of peaks around 482 and 576 nm corresponding to transitions $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ was seen when excited by excitation wavelength 351 nm. However, interesting thermoluminescence results are observed in case of Dy as well as Eu doped $Na_{21}Mg(SO_4)_{10}Cl_3$. The TL glow curves for $Na_{21}Mg(SO_4)_{10}Cl_3$:Dy exhibit broad peak composed of three overlapping peaks, these peaks were deconvoluted using deconvolution program. The peaks at different temperatures indicate that different sets of traps are being activated within the particular temperature range each with its own value of activation energy (E) and frequency factor (s). The peaks observed were due to formation of trap levels by γ-rays irradiation and subsequently activation of traps on thermal stimulation. The trapping parameters for both the samples were calculated using Chen's peak shape method and reported in this paper.

1. Introduction

Thermoluminescence (TL) is a very important technique due to its applications in various fields such as radiation therapy, dosimetry, geology, space research and other research related areas [1–4]. Studies on radiation induced defects in insulating and semiconducting materials have been interesting over the last few decades [5]. Several materials such as LiF:Ti, Mg and α-Al_2O_3:C, $CaSO_4$:Dy due to their excellent thermoluminescent properties such as high TL efficiency, dose response, thermal stability, high sensitivity and reproducibility, are now commonly used as thermoluminescent dosimeters (TLD) in a great diversity fields of applications. The main applications of these materials are in radiation dosimetry, for personnel and environmental monitoring [6,7]. Many sensitive synthetic materials are developed for fulfilling the above mentioned properties [8,9]. Different preparative methods [10,11] and thermoluminescent properties of several materials have been studied so far [12] and it is found that mixed alkali/alkaline sulfate constitute a class of thermoluminescence phosphors with good performances, especially when doped with appropriate activators [13]. Sulfate based TL materials are synthesized and studied because of their well desired characteristics like a high temperature glow peak, linear response with ionizing radiation exposure, negligible fading and an easy methods of preparation [14]. There are several thermoluminescent materials such as $CaSO_4$:Eu, Ag, $K_2Ca_2(SO_4)_3$:Eu, $KMgSO_4Cl$ doped with Dy, Ce and Mn etc. of which almost all has been studied for improvement in the thermoluminescence characteristics and the trapping parameters [15–17]. The study of the luminescence as a function of the temperature, the so called glow curve, is used to determine the trapping parameters and its integral is proportional to the radiation dose absorbed by the irradiated sample. The position, shape and intensities of the glow peaks are related to the properties of traps responsible for the TL. The shape and position of the resultant TL glow curves can be analyzed to extract information about the various parameters of the trapping process such as activation energy which is the thermal energy required to liberate the trapped electrons and holes, frequency factor, trap depth, trapping and retrapping rates etc. A popular method of analyzing a TL glow curve in order to ascertain the kinetic parameters E, s, and b is by considering the shape or geometrical properties of the peak. TL glow peaks corresponding to second-order kinetics are characterized by an almost symmetrical shape, whereas first-order peaks are asymmetrical. Grossweiner was the first to use the shape of the glow peak to calculate the trap depth E [18].

In this paper, the kinetic parameters of Rare Earth (RE)-doped $Na_{21}Mg(SO_4)_{10}Cl_3$ phosphor, synthesized by the modified solid state diffusion technique, are reported. In irradiated phosphor

* Corresponding author.
E-mail address: sjdhoble@rediffmail.com (S.J. Dhoble).

0022-2313/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jlumin.2013.04.053

$Na_{21}Mg(SO_4)_{10}Cl_3$:Dy peak consisting of three overlapping (unresolved) peaks was observed whereas in $Na_{21}Mg(SO_4)_{10}Cl_3$:Eu single peak peaking at 136.5 °C was observed. For the first time the kinetic parameters of these materials were calculated by peak shape method and the results are presented in this paper.

2. Experimental

The samples $Na_{21}Mg(SO_4)_{10}Cl_3$ (pure); $Na_{21}Mg(SO_4)_{10}Cl_3$:Dy and $Na_{21}Mg(SO_4)_{10}Cl_3$:Eu were prepared by a modified solid state diffusion method. While preparing the samples, the constituents Na_2SO_4(Loba, 99% pure), NaCl(Loba, 99% pure), $MgSO_4$(Loba, 99% pure), Dy_2O_3(Merck 99.9% pure) and Eu_2O_3(Merck 99.9% pure) were taken in a stoichiometric ratio and crushed in a mortar pestle for 1 h. Then this material was heated at 350 °C for 3 h; after 3 h heating the material was again crushed for an hour and finally heated at 650 °C for 18 h resulting in the compounds of $Na_{21}Mg(SO_4)_{10}Cl_3$:Dy and $Na_{21}Mg(SO_4)_{10}Cl_3$:Eu in powder form according to the following chemical reaction.

$$Na_2SO_4+3NaCl+MgSO_4 \rightarrow Na_{21}Mg(SO_4)_{10}Cl_3$$

The samples were then slowly cooled at room temperature, at cooling rate of 0.5 °C/min. The resultant polycrystalline material was crushed to fine powder in a mortar pestle, the resultant powder formed was used for further study.

SEM micrographs were obtained using a HITACHI S-4800 scanning electron microscope. The SEM micrographs were taken at 5000 V accelerating voltage, 8300 μm working distance, 7800 nA emission current, at high lens mode with fast scan speed and gray scale color mode. The prepared host lattice was characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using a X'pert-PRO PANalytical diffractometer (Cu-Kα radiation) at a scanning step of 0.001, in the 2θ range from 10 to 80°. The photoluminescence (PL) emission spectra of the samples were recorded using a Fluorescence spectrometer (Shimadzu, RF 5301 PC). Excitation and emission spectra were recorded using a spectral slit width of 1.5 nm.

For TL studies, samples were exposed to gamma rays from a ^{60}Co source at room temperature at the rate of 0.58 kGy/hr. After the desired exposure, TL glow curves were recorded with the help of Nucleonix 1009I TL reader, at a heating rate of 5 °C s^{-1}. All the measurements were carried out in an open atmosphere. The Nucleonix 1009I TL reader consists of photomultiplier tube (931B), DC Amplifier, IR filters and milivolt recorder. For TL measurement, each time 5 mg of phosphor is used which is in powder form, having particle size as specified in Section (3.2). For comparison TL glow curve of standard thermoluminescence dosimeter (TLD) $CaSO_4$:Dy was recorded, under identical conditions. For measurement of dose response and fading three aliquot of the same sample were used for taking each measurement. Therefore, single point in these plots corresponds to average of three readings.

3. Results and discussion

3.1. XRD study

Fig. 1 shows the XRD patterns from pure $Na_{21}Mg(SO_4)_{10}Cl_3$ powder. X-ray diffraction pattern indicates the presence of crystalline $Na_{21}Mg(SO_4)_{10}Cl_3$ host lattices. The XRD-pattern of the as prepared phosphor powder shows good agreement with standard ICDD file no. 41-1473.The final product was formed in homogeneous form, the XRD pattern of $Na_{21}Mg(SO_4)_{10}Cl_3$ did not show the presence of the phases of starting materials like Na_2SO_4, NaCl, $MgSO_4$ and other likely phases which indicates the formation of the desired compound. The mineralogical name of $Na_{21}Mg(SO_4)_{10}Cl_3$ is D'ansite. $Na_{21}Mg(SO_4)_{10}Cl_3$ has a cubic crystal structure with space group of I-43m and the cell parameters are $a=b=c=15.95$ Å, $V=4029.55$, and $Z=4$. It has been found that the crystal structure of $Na_{21}Mg(SO_4)_{10}Cl_3$ is Isometric of class Hextetrahedral type. Point group: −43m. As tetrahedral {211} crystals, modified by {211} and{110}[19].

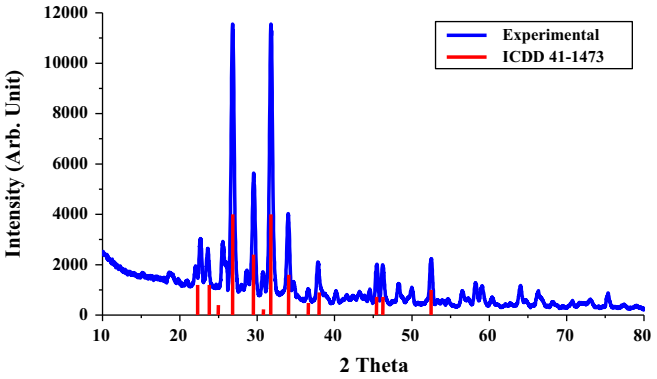

Fig. 1. X-ray diffraction pattern of the $Na_{21}Mg(SO_4)_{10}Cl_3$ host lattice.

3.2. SEM study

The morphology of the $Na_{21}Mg(SO_4)_{10}Cl_3$ phosphor was analyzed using SEM as shown in Fig. 2.The SEM micrographs in (a) and (b) shows the agglomerated particles of oval shapes, whereas from micrographs (c) and (d) the spherical agglomerated particles can be observed. From SEM observation the estimation of particle size is uncertain since the particles are agglomerated; approximately the particle size varies from 0.2 μm to 0.6 μm.

3.3. PL Studies

3.3.1. PL study of $Na_{21}Mg(SO_4)_{10}Cl_3$:Dy

A series of $Na_{21}Mg(SO_4)_{10}Cl_3$:Dy samples has been synthesized with Dy concentration ranging from 0.05 to 1 mol%. Fig. 3 shows the excitation spectrum in the range 250–400 nm consisting of four peaks, arising due to ($^6H_{15/2} \rightarrow {}^4M_{17/2}$), ($^6H_{15/2} \rightarrow {}^6P_{7/2}$), ($^6H_{15/2} \rightarrow {}^4I_{11/2}$) and ($^6H_{15/2} \rightarrow {}^4I_{13/2}$) transitions which are located at 325 nm, 351 nm, 365 nm, 388 nm respectively. The photoluminescence emission spectra of Dy^{3+} doped $Na_{21}Mg(SO_4)_{10}Cl_3$:Dy sample under excitation at 351 nm is shown in Fig. 4. The emission spectrum of Dy^{3+} has two groups of emissions located at 482 and 576 nm, which correspond to the transitions of $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (blue), $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow) respectively. Among the two emission peaks, the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ emission belongs to hypersensitive transition with $\Delta J=2$, which is strongly influenced by outside environments of Dy^{3+} [20]. In the excitation spectrum of 1 mol% Dy^{3+} doped $Na_{21}Mg(SO_4)_{10}Cl_3$, the peaks which range from 250 to 400 nm are due to 4f–4f transitions of Dy^{3+} [21]. For the lower concentration of Dy there is no photoluminescence observed.

3.3.2. PL study of $Na_{21}Mg(SO_4)_{10}Cl_3$:Eu

The PL spectra of $Na_{21}Mg(SO_4)_{10}Cl_3$:Eu ($x=0.2$ mol%, 0.5 mol%, and 1 mol%) phosphors are presented in Fig. 5, monitored at 370 nm (as shown in inset of Fig. 5.). It can be seen that the phosphors exhibit a broad blue emission band with a peak at around 450 nm, which is corresponding to the 5d→4f allowed transition of Eu^{2+}. From the spectra it is clear that the PL intensity increases with increasing Eu^{2+}