Tb$^{3+}$ Luminescence in NaMgSO$_4$Cl Halosulphate Phosphor for UV-LED Fluorescent Tubes

S. T. Taide$^*$, N. B. Ingle$^2$ and S. K. Omanwar$^3$

$^1$Department of Physics, Jawaharlal Darda Institute of Engineering and Technology, Yavatmal, India.
$^2$Department of Physics, PRMIET, College, Badnera, Amravati, India.
$^3$Department of Physics, SGB Amravati University, Amravati, India.

Authors’ contributions

This work was carried out in collaboration between all authors. Author STT designed the experiment synthesize samples and performed the spectroscopy study, and wrote the first draft of the manuscript. Author NBI analysis the results and author SKO finalized the draft. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/PSIJ/2015/18810

(1) Preeti Singh, Department of Physics, DIT, Greater Noida (U.P.), India.
(2) Mohd Rafatullah, Division of Environmental Technology, School of Industrial Technology, Universiti Sains Malaysia, Malaysia.
(3) Stefano Moretti, School of Physics & Astronomy, University of Southampton, UK.

Reviewers:
(1) Anonymous, University of Malaya, Malaysia.
(2) Anonymous, National Formosa University, Taiwan.

Complete Peer review History: http://sciencedomain.org/review-history/10340

ABSTRACT

Rare earth doped halosulphate specially fluoride based phosphor NaMg(SO$_4$)Cl:Tb$^{3+}$ have been synthesize by modified route of slow evaporation technique. Identification of crystal structure and particle morphology of synthesized material was done by using X-ray diffraction (XRD), scanning electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR) techniques. Iterations for photoluminescence properties of this material is of prime importance as absorption by the host material near the UV radiation edge have high excitation efficiency band at shorter wavelength than 230 nm wavelength which is characteristics of NaMg(SO$_4$)Cl:Tb$^{3+}$. This existence of excitation bands with high luminescence efficiency and deep green emission at 544 nm makes this material favorable as the phosphor for UV-LED fluorescent tubes.

Keywords: Halosulphate; Slow evaporation technique; Optical properties.
1. INTRODUCTION

The search for innovative materials with desirable optical properties attracts attention of material researchers towards recent developments and need of decade. In particular, a need has emerged for compounds that are candidates for luminescence study. Considerable improvement in the field of luminescent materials has been made by the introduction of the rare earth ions as activators. The optical value of these ions results from the electronics transitions occurring within the partially filled 4f energy levels of the lanthanide series. Traditionally, inorganic scintillators have played an important role in detection and visualization of high energy radiation. Applications in medical diagnostics are only few applications in inorganic scintillators are used. The most popular scintillators are sodium iodide doped with NaI: Ti+ and cesium iodide doped with thallium CsI: Ti+. The sulfates are an important mineral class and include some very interesting and attractive specimens. Some sulfate class minerals are soluble and several are fluorescent [1-10].

Recently Moharil and co-workers [11-16] have reported several phosphors on rare earth (RE) ions doped mix sulphate and they have shown how these ions can exist in different valence states as result to irradiation, which can induce valence changes conversion and the back conversion during heating, this change has been claimed to play an important role. It has been verified that under irradiation the doped ions in the crystal can cause defects easily and form colour centers, the doped ions in the crystal acts as trapping sites by capturing electrons or holes that are produced by irradiation, which change the chemical valence of doped ions. Other than sulphates and mixed sulphates, some investigators are going in progress on halosulphate based materials. Klement synthesized the halosulphate Na₀₆Ca₄(SO₄)₆F₂ and characterized this compound by X-ray powder diffraction [5,17-22]. Also Choubey reported luminescence properties in some halosulphate NaMgSO₄F:Ce³⁺, Na₃SO₄F:Ce³⁺ by solid state method [6]. In this paper we report the synthesis of NaMgSO₄Cl:Tb³⁺ material by slow evaporation technique and explain Tb³⁺ emission in present halosulphate phosphor which are favorable as the phosphor for UV-LED fluorescent tubes.

2. EXPERIMENTAL

Microcrystalline NaMgSO₄Cl:Tb³⁺ sample was prepared by the method of slow evaporation technique. In this method MgSO₄ and NaCl of AR grade were taken in a stoichiometric ratio and dissolved separately in double distilled de-ionized water, resulting in a solution of NaMgSO₄Cl(Eq.1) then water soluble salt of dysprosium sulfate was added to the solution to obtain NaMgSO₄Cl: Tb³⁺. The compound in its powder form was obtained by evaporating on 80°C for 8h. The dried samples were then slowly cooled at room temperature. The resultant polycrystalline mass was crushed to fine particle in a crucible. Following is the proposed chemical equation.

\[ \text{MgSO}_4 + \text{NaCl} \xrightarrow{\text{precipitation at 80°C}} \text{NaMgSO}_4\text{Cl} \]

3. CHARACTERIZATIONS OF SAMPLES

The formation NaMgSO₄Cl:Tb³⁺ compound was confirmed by powder XRD technique, X-ray diffractogram of this compound was taken at room temperature in a wide range of Brag angle 2θ using Panalytical High Resolution XRD-I, PW3040/60 at a scanning rate of 1.00 degree per minute. The morphology of the phosphor particles was observed by using Hitachi –I Model No-S4800 scanning electron microscope. For SEM studied, the sample was gold coated using a sputter coater polaron SC7610 system. The FTIR studies carried out on FTIR spectrometer with electron gun technique from 4000 cm⁻¹ to 450 cm⁻¹. Phololuminescence studies were made by using personal computer based fluorescence spectrometer (Hitachi, F-7000) with 150 W Xenon lamp light source.

4. RESULTS AND DISCUSSION

4.1 XRD Results

The X-ray diffraction of Tb doped NaMgSO₄Cl sample was taken at room temperature and is shown in Fig. 1. The sharp and single peaks of the XRD pattern suggest the formation of single phase new NaMgSO₄Cl:Tb compound and that matched with the standard data available (JCPDS file number 39-0320).
4.2 Fourier Transform Infrared Spectroscopy (FTIR)

The 'FTIR' structure of Tb doped NaMgSO₄Cl as observed experimentally is shown in Fig. 2. Normally, sulfate contains two S=O and two S-O bonds. The S=O asymmetric stretch occurs at 1376.96 cm⁻¹ and symmetric stretch at 1119 cm⁻¹. The S-O stretch bands occurs at 721 cm⁻¹. These bands are seen in the spectrum of NaMgSO₄Cl:Tb (Fig. 2).

4.3 Scanning Electron Microscopy (SEM)

The microstructure of the prepared Tb doped NaMgSO₄Cl powder sample is studied by SEM and is shown in Fig. 3. The SEM Photograph shows regular morphology with different particle size. The particle size can be categorized in to three types, one that shows particle with particle size 1 μm. The second kind of particle has a size of about 3 μm and third one has a particle size 5μm and this non uniform particle size is caused due to the non-uniform particle size is caused due to the non-uniform distribution of temperature and mass flow rate during the synthesis. Luminescence efficiencies are related to the phosphor crystalline size with optimum size being in the 1.0 to 5 μm range. This powder sample can easily be termed an ultra fine phosphor because the particle size is less than 5 μm.

4.4 Photoluminescence Properties

Fig. 4 shows the PL and excitation spectra of NaMgSO₄Cl:Tb³⁺ at 300 K. The PL spectrum, shown in Fig. 4 (right) was obtained under the G-band excitation at 352 nm (Fig. 4 (left). The PL spectra consist of narrow bands that correspond to two series: a weak series (⁵D₃) between 380 and 480 nm and a prominent series (⁷F_J) between 480 and 680 nm. They are identified with the electronic transitions from ⁵D₃ and ⁵D₄ respectively to ⁷F_J (J= 2 to 6) within the ⁴f configuration of Tb³⁺ (Fig. 5). Yamashita and Hama [8] and Yamashita et al. [9] observed the PL and TL spectra of the MgSO₄:Tb³⁺,Na⁺, CaSO₄:Tb³⁺,Na⁺, SrSO₄:Tb³⁺Na⁺ and BaSO₄:Tb³⁺,Na⁺ powder phosphors. The PL spectra of these phosphors consist of the very weak ⁵D₃ and the prominent ⁷D₄ series. Trivalent Tb³⁺ ion is generally used as a green emitting center in a variety of commercial phosphors. The electronic configuration of Tb³⁺ ion is ⁴f⁸. In case of Tb³⁺ ion, the absorption is usually due to allowed f-d transition from excited state of ⁴f ⁵d₁ configuration, the electron loses energy to lattice and comes to ⁵D₃, ⁵D₄ → ⁷F₁ emission is in UV and blue region while ⁵D₄ → ⁷F₁ emission is predominantly green. At lower concentrations of Tb³⁺, blue emission is observed, but at higher concentration, there is an energy transfer between Tb³⁺ ions, e.g. the cross relaxation- Tb³⁺ (⁵D₃) + Tb³⁺ (⁷F₁) → Tb³⁺ (⁷D₄) + Tb³⁺ (⁷F₀), due to...
to which the blue emission gets quenched increasing the green emission at the same time [23-25]. The intensity ratios of the $^5D_3$ to $^5D_4$ series in the PL spectra at 300 K was found to be 0.2, these results are consistence crystals structure of host and concentrations of Tb$^{3+}$ shown in Fig. 4. The intensity ratio of the $^5D_3$ to $^5D_4$ series in the PL spectra of NaMgSO$_4$F:Tb$^{3+}$ at 300 K (Fig. 4 (right)) was approximately 0.2. According to here results of the halo sulfates activated with Tb$^{3+}$, it might observe different ratios in the TL and CL spectra of NaMgSO$_4$Cl:Tb$^{3+}$. The excitation spectrum, shown in Fig. 4 (left), was obtained by monitoring the prominent green luminescence at 544 nm, which corresponds to the $^5D_4 \rightarrow ^7F_5$ transition within Tb$^{3+}$ (Figs.4–5). The excitation bands labeled as A–N correspond well to the electronic transitions from $^7F_6$ to the upper levels within Tb$^{3+}$. The wavelength of Hg 253.7 nm fits the shoulder of the excitation band at 260 nm. This results in the bright yellow–green luminescence from this phosphor under short –UV light irradiation from a handy Hg lamp (11W, 253.7 nm). At 300K, the relative luminescence efficiency of the high-energy band at 220 nm is approximately 50 times those of B–N bands corresponding to transitions within Tb$^{3+}$. The PL spectrum obtained under 220 nm excitation was the same as that shown in Fig. 5 (right). The prominent excitation band at 220 nm attributed to Tb$^{3+}$ charge-transfer band.
Fig. 3. SEM photograph of Tb$^{3+}$ doped NaMgSO$_4$F

Fig. 4. Optical excitation spectrum (left) and PL spectrum (right) of NaMgSO$_4$Cl: Tb$^{3+}$ Excitation spectrum (left) was obtained by monitoring the green luminescence at 544 nm, and PL spectrum (right) was obtained under 352 nm excitation. Excitation spectrum at long wavelengths is magnified 5. Vertical arrow shows the wavelength of Hg line at 253.7 nm
CONCLUSIONS

The PL and excitation spectra of NaMgSO$_4$Cl activated with Tb$^{3+}$ ions were well identified with the electronic transitions within rare-earth ions. The existence of excitation bands with high luminescence efficiency at wavelength shorter than 230 nm is characteristic of NaMgSO$_4$Cl:Tb$^{3+}$ phosphor. These results suggest that NaMgSO$_4$Cl:Tb$^{3+}$ phosphor may be favorable as the phosphor for UV-LED fluorescent tubes.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Upadeo SV, Moharil SV. Redox reactions and thermo-luminescence in some europium-doped phosphates. J. Cond. Matter 7,957(1995).
2. Upadeo SV, Gundurao TK, Moharil SV, Luminescence in Ce$^{3+}$ doped mixed sulphate fluoride phosphor. J. Phys. Cond. Matter 6, 9459(1994).
3. Nair SR, Kondawar VK, Upadeo SV, Moharil SV, Gundurao TK. Luminescence in Ce$^{3+}$ doped mixed sulphate fluoride phosphor NaMgSO$_4$F and Na$_3$SO$_4$F. J. Phys. cond. Matter 9, 8307(1997).
4. Dhoble SJ, Moharil SV, Gundurao TK, J.Lumin. Site Selective luminescence of Eu$^{3+}$ ions in K$_2$Mg(SO$_4$)$_2$. 2.6H$_2$O crystal. 2001;93:43.
5. Klement R. Naturwiss enchaften 27,568 natrium-calcium-sulfatapatite Na$_6$Ca$_4$(SO$_4$)$_6$F$_2$. 1939.
6. Choubey SR, Gedam SC, Dhoble SJ, Lumin J. PL and TL study of NaMgSO$_4$F:X(X=Dy or Ce) fluoride Phosphor by SSD Method. 2013;142:48-51.
7. Sabelli C, Bull. Mineral Uklonskovite NaMg (SO₄) F₂H₂O. 1985;108:150.
8. Yamashita N, Hamada T. Preparation of Eu doped Y₂O₃ luminescent nanoparticle in nonionic reverse microemulsion. Jpn. J. Appl. Phys. 1999;38:1326.
9. Yamashita N, Hamada T, Takada M, Katsuki M, Nakagawa M. Photoluminescence and thermoluminescence of MgSO₄,SrSO₄, and BaSO₄ powder phosphor activated with Tb3+. Jpn. J. Appl. Phys. 2001;40:6732.
10. Gedam SC, Dholbe SJ, Moharil SV, lumen. J. Dy3+ and Mn2+ emission in KMgSO₄ Cl Phosphor. 2006;121(2):450.
11. Gedam SC, Dholbe SJ, Moharil SV, lumen J. Dy3+ and Mn2+ emission in KMgSO₄ Cl phosphor. 2007;124(1):120.
12. Nagpure IM, Dholbe SJ, Godbole SV., Bhide MK, Pode RB, Eu³⁺ luminescence in Na₃SO₄F and NaMgSO₄F halosulphate phosphor for mercury-free lamps. Indian Journal of Engg. Material Sciences. 2009;16:181-184.
13. Dholbe SJ, Gedam SC,. Nagpure IM, Godbole SV, Bhide MK, Photoluminescence and thermoluminescence characteristics of KXSO₄Cl : Eu (X = Zn or Mg) halosulfate phosphor. J. Phys. D: Appl. Phys. 2007:40.
14. Dhope SM, Muthal PL, Kondawar VK, Moharil SV, Sahare PD, Characterization of K₂Ca₂(SO₄)_3:Eu phosphor. J. Phys D; Appl. Phys. 1991;24:1869.
15. Urvashi Manik, Gedam SC, Dholbe SJ, Lumin J. The characterization and mechanism of energy transfer in Na₂Mg(SO₄)₂: Ce phosphor co-doped by Dy, Mn and Tb. 2013;136:47.
16. Thakre PS, Gedam SC, Dholbe SJ, Atram RG, Lumin J. Lumininescence of KCaSO₄Cl:X, Y (X=Eu or Ce; Y=Dy or Mn) halosulfate material. 2011;31:3132.
17. Blasse G, Lumin. Inorg. Solids 475 (1978)215. Electronic and vibrational spectra of ordered perovskites.
18. Atone MS, Dholbe SJ, Dhole SM, Muthal PL, Kondawar VK, Moharil SV. Sensitization of Luminescence of CaSO₄: Dy. Phy Status Solidi A. 1993;135:299.
19. Pandey A, Sahare PD, Bakhare JS, Lochab SP, Singh F, Kanjilal D. Thermoluminescence and photo-luminescence characteristics of nanocrystalline LiNaSO₄: Eu phosphor. J. Phys. D. Appl. Phys. 2003;36:2400.
20. Nambi KSV. Thermoliminescence dating of burnt clay from an upper paleolithic occupation level cave site in south India. Sci. Today India Dec. 1981;12.
21. Wiedemann HG, Thermochimica Acta, Thermal Studies on thenardite. 1981;17:50.
22. He JY, Yusupu T, Ablai A, Aierken Sidike, Gong LK, Chin. Photoluminescence properties of Na₂SO₄:TbF₃+ under VUV-UV light excitation. J. lumlin. 2010;31:176.
23. Gong X, Wu P, Chan WK, Effect of γ-ray irradiation on structures and luminescence properties of nanocrystalline MSO₄:xEu³⁺ (M=Ca, Sr, Ba; x=0.001–0.005) J. Phys. Chem. Solids. 2000;61:115.
24. Rowlands AP, Tyagi AK, Karali T, Townsend PD.) SpectrallyResolved Luminescence of Undoped and Dy³⁺ Doped Na₂SO₄. Radiat. Prot. Dosim. 2002;55:100.
25. Rabindro Singh L, Ningthoujam RS.Critical view on energy transfer, site symmetry, improvement in luminescence of Eu 3+, Dy 3+ doped YVO 4 by core-shell formation. J. Appl. Phys. 2010; 107:104304.