

Original Research Article**Tb³⁺ luminescence in NaMgSO₄Cl Halosulphate phosphor for UV-LED****fluorescent tubes****Abstract**

Rare earth doped halosulphate specially fluoride based phosphor NaMg(SO₄)Cl:Tb³⁺ have been synthesized 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. Investigations 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 characteristic of NaMg(SO₄)Cl:Tb³⁺. This existence of excitation bands with high luminescence efficiency and deep green emission at 545 nm makes this material favorable as the phosphor for UV-LED fluorescent tubes.

Key Words- Halosulphate; Slow evaporation technique; Optical properties

1. Introduction

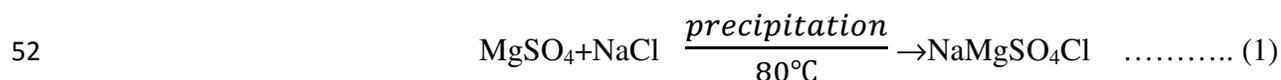
The search for innovative materials with desirable optical properties attracts attention of material researchers towards recent developments and need of decade. In particular, a need has emerged for compounds that are candidates for luminescence study. Considerable improvement in the field of luminescent materials has been made by the introduction of the rare earth ions as activators. The optical value of these ions results from the electronic transitions occurring within the partially filled 4f energy levels of the lanthanide series. Traditionally, inorganic

23 scintillators have played an important role in detection and visualization of high energy
24 radiation. Applications in medical diagnostics are only few applications in inorganic
25 scintillators are used. The most popular scintillators are sodium iodide doped with NaI: TI+ and
26 cesium iodide doped with thallium CsI: TI+. The sulfates are an important mineral class and
27 include some very interesting and attractive specimens. Some sulfate class minerals are soluble
28 and several are fluorescent.

29 Recently Moharil and co-workers [1-4] have reported several phosphors on rare earth (RE)
30 ions doped mix sulphate and they have shown how these ions can exist in different valence states
31 as result to irradiation, which can induce valence changes conversion and the back conversion
32 during heating, this change has been claimed to play an important role. It has been verified that
33 under irradiation the doped ions in the crystal can cause defects easily and form colour centers,
34 the doped ions in the crystal acts as trapping sites by capturing electrons or holes that are
35 produced by irradiation, which change the chemical valence of doped ions. Other than sulphates
36 and mixed sulphates, some investigators are going in progress on halosulphate based materials.
37 Klement synthesized the halosulphate $\text{Na}_6\text{Ca}_4(\text{SO}_4)_6\text{F}_2$ and characterized this compound by X-
38 ray powder diffraction[5]. Also Chouby reported luminescence properties in some halosulphate
39 $\text{NaMgSO}_4\text{F}:\text{Ce}^{3+}$, $\text{Na}_3\text{SO}_4\text{F}:\text{Ce}^{3+}$ by solid state method [6]. In this paper we report the synthesis
40 of $\text{NaMgSO}_4\text{Cl}:\text{Tb}^{3+}$ material by slow evaporation technique and explain Tb^{3+} emission in
41 present halosulphate phosphor which are favorable as the phosphor for UV-LED fluorescent
42 tubes.

43 2. Experimental

44 Microcrystalline NaMgSO₄Cl:Tb³⁺ sample was prepared by the method of slow
 45 evaporation technique. In this method MgSO₄ and NaCl of AR grade were taken in a
 46 stoichiometric ratio and dissolved separately in double distilled de-ionized water, resulting in a
 47 solution of NaMgSO₄Cl(Eq.1) then water soluble salt of dysprosium sulfate was added to the
 48 solution to obtain NaMgSO₄Cl: Tb³⁺. The compound in its powder form was obtained by
 49 evaporating on 80⁰C for 8h. The dried samples were then slowly cooled at room temperature.
 50 The resultant polycrystalline mass was crushed to fine particle in a crucible. Following is the
 51 proposed chemical equation.



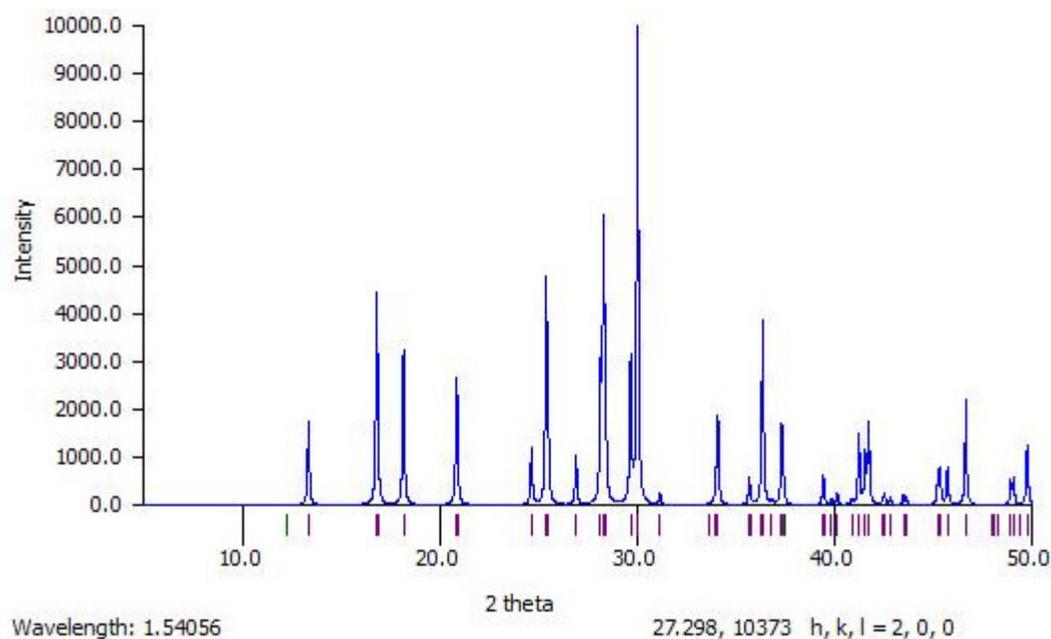
53 **3. Characterizations of samples**

54 The formation NaMgSO₄Cl:Tb³⁺ compound was confirmed by powder XRD technique, X-
 55 ray diffractogram of this compound was taken at room temperature in a wide range of Bragg angle
 56 2θ using Panalytical High Resolution XRD-I, PW3040/60 at a scanning rate of 1.00 degree per
 57 minute. The morphology of the phosphor particles was observed by using Hitachi –II Model No-
 58 S4800 scanning electron microscope. For SEM studied, the sample was gold coated using a
 59 sputter coater polaron SC7610 system. The FTIR studies carried out on FTIR spectrometer with
 60 electron gun technique from 4000cm⁻¹ to 450cm⁻¹. Photoluminescence studies were made by
 61 using personal computer based fluorescence spectrometer (Hitachi,F-7000) with 150W Xenon
 62 lamp light source.

63 **4. Results and discussion**

64 **4.1 XRD Results**

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Fig.1. XRD Pattern of NaMgSO₄F

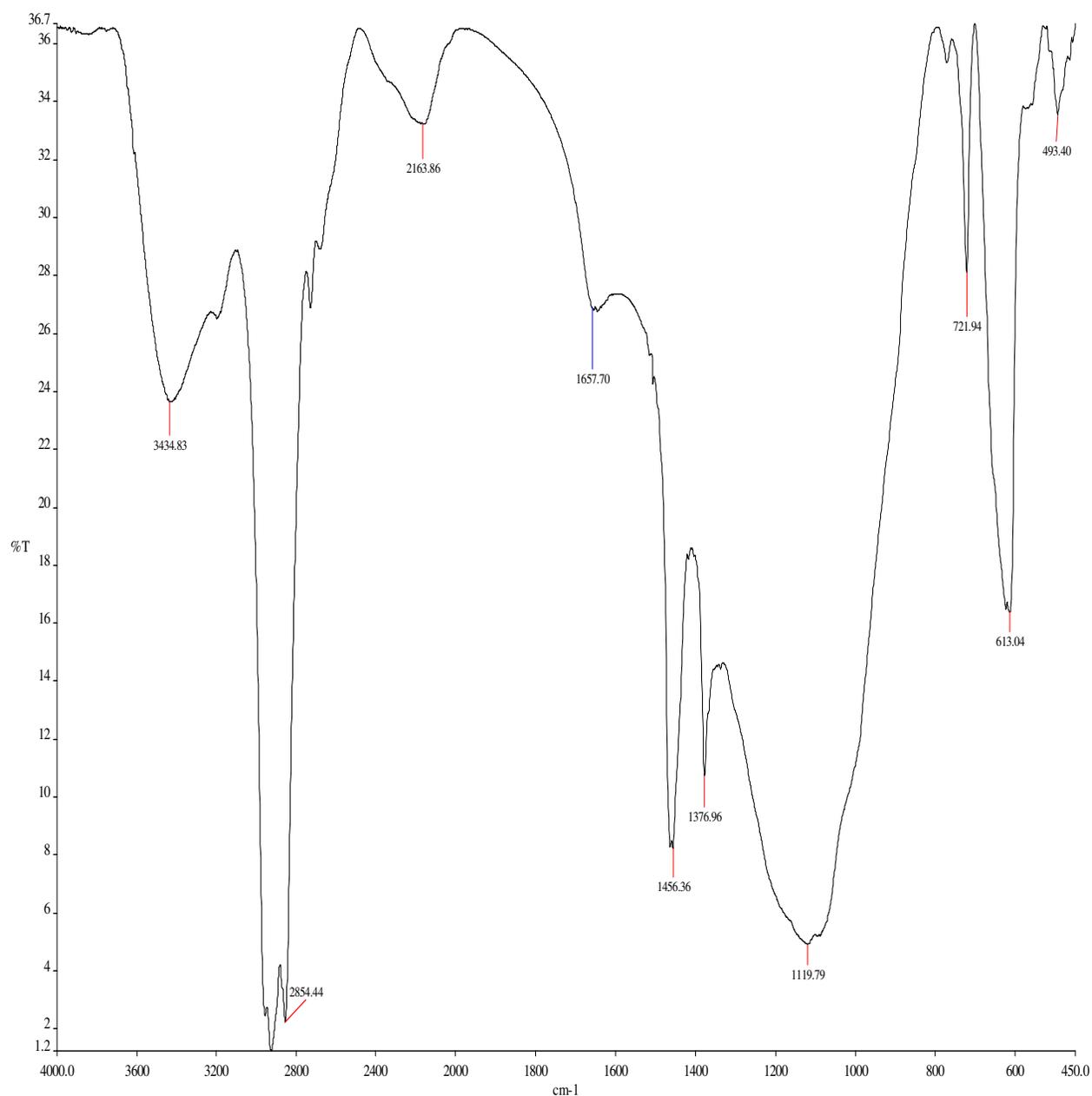
68 The X-ray diffraction of Tb doped NaMgSO₄Cl sample was taken at room temperature and is
 69 shown in fig.1. The sharp and single peaks of the XRD pattern suggest the formation of single
 70 phase new NaMgSO₄Cl:Tb compound and that matched with the standard data available (JCPDS
 71 file number 39-0320)

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73 4.2 Fourier Transform Infrared Spectroscopy (FTIR)

74 The 'FTIR' structure of Tb doped NaMgSO₄Cl as observed experimentally is
 75 shown in fig.3. Normally, sulfate contains two S=O and two S-O bonds. The S=O asymmetric
 76 stretch occurs at 1376.96 cm⁻¹ and symmetric stretch at 1119 cm⁻¹. The S-O stretch bands occur
 77 at 721 cm⁻¹. These bands are seen in the spectrum of NaMgSO₄Cl:Tb (Fig.2)

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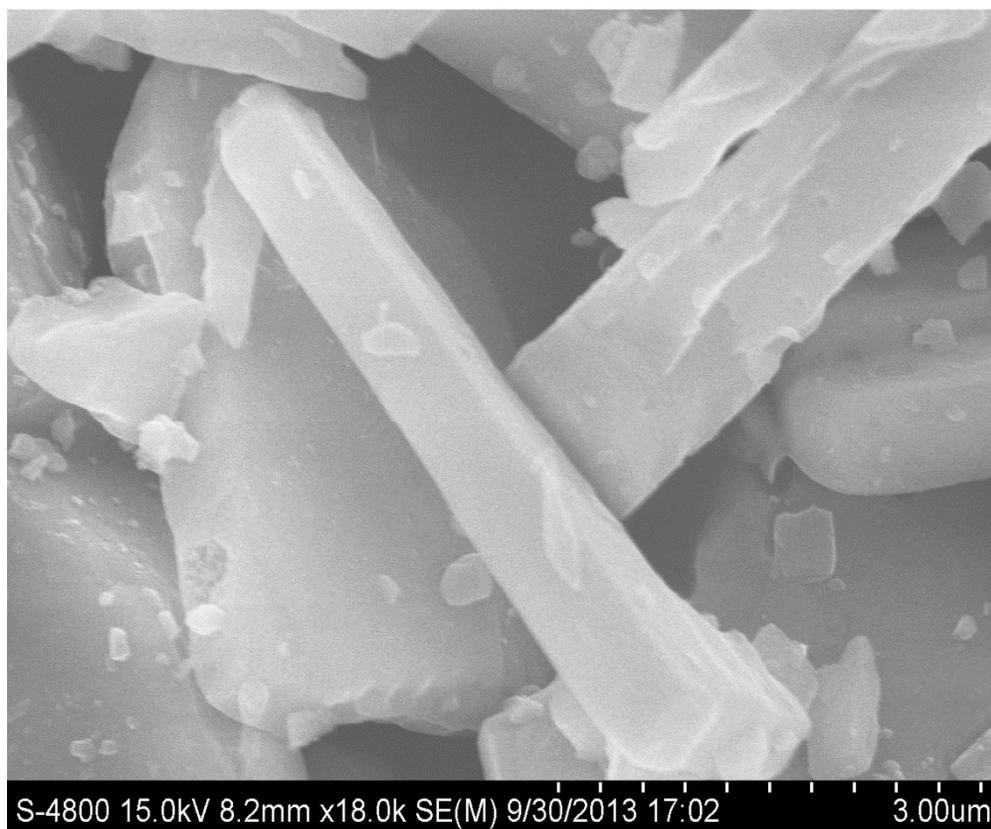
Fig.2 FTIR spectra of NaMgSO₄Cl: Tb sample

81 4.3 Scanning Electron Microscopy (SEM)

82 The microstructure of the prepared Tb doped NaMgSO₄Cl powder sample is studied by SEM
83 and is shown in fig.3 The SEM Photograph shows regular morphology with different particle
84 size. The particle size can be categorized in to three types, one that shows particle with particle
85 size 1 μ m. The second kind of particle has assize of about 3 μ m and third one has a particle

86 size $5\mu\text{m}$ and this non uniform particle size is caused due to the non- uniform particle size is
87 caused due to the non-uniform distribution of temperature and mass flow rate during the
88 synthesis. Luminescence efficiencies are related to the phosphor crystalline size with optimum
89 size being in the 1.0 to $5\mu\text{m}$ range. This powder sample can easily be termed an ultra fine
90 phosphor because the particle size is less than $5\mu\text{m}$.

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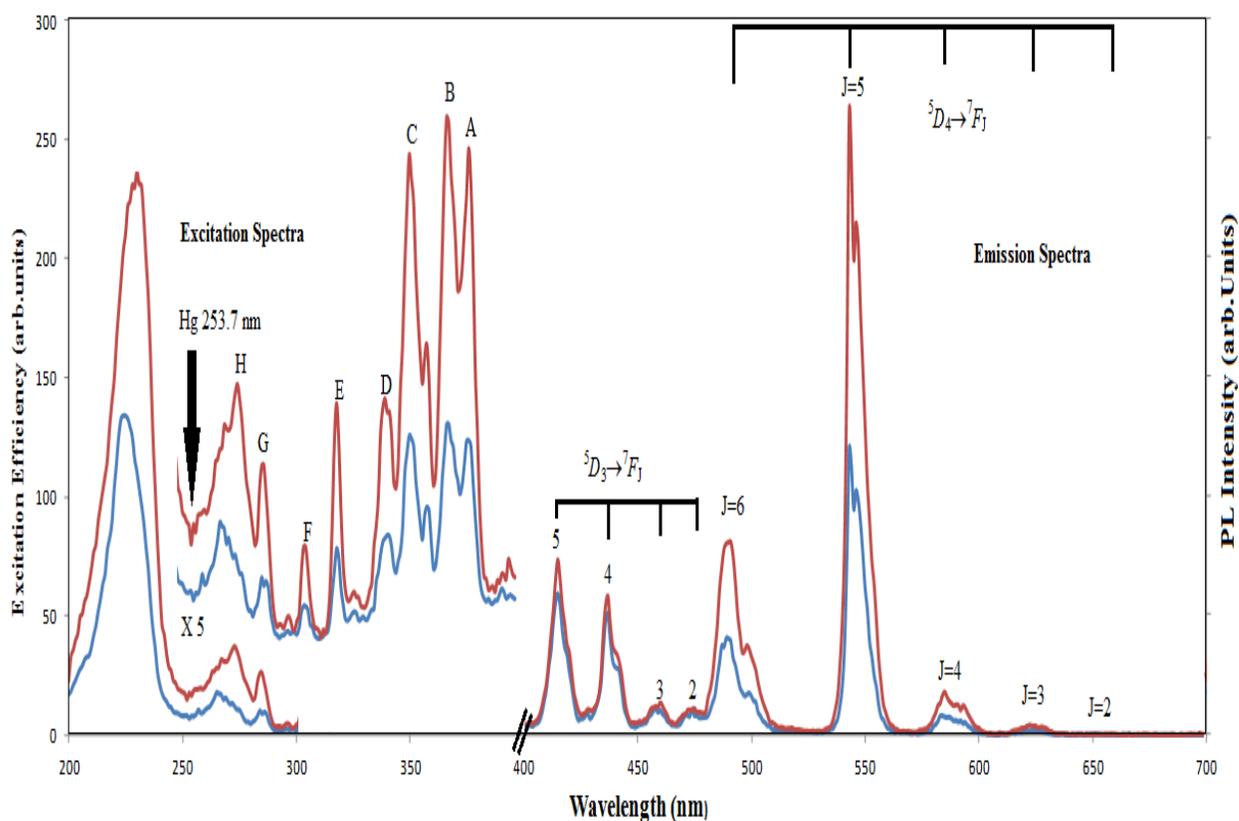
94 **Fig.3 SEM photograph of Tb^{3+} doped NaMgSO_4F**

95 **4.4 Photoluminescence Properties**

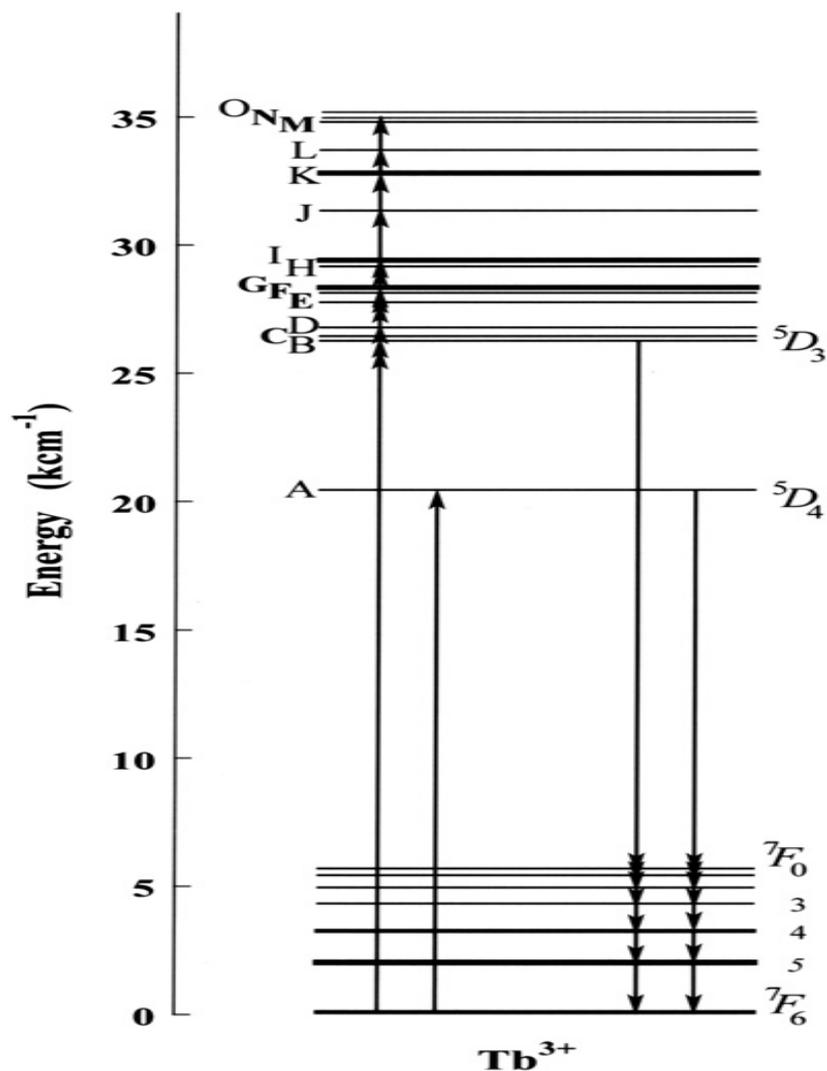
96 Fig. 4 shows the PL and excitation spectra of $\text{NaMgSO}_4\text{Cl}:\text{Tb}^{3+}$ at 300 K. The PL spectrum,
97 shown in Fig.4 (right) was obtained under the G-band excitation at 352 nm (Fig. 4 (left)). The PL

98 spectra consist of narrow bands that correspond to two series: a weak series (5D_3 series) between
 99 380 and 480 nm and a prominent series (5D_4 series) between 480 and 680 nm. They are identified
 100 with the electronic transitions from 5D_3 and 5D_4 , respectively, to 7F_J ($J= 2$ to 6) within the $4f^8$
 101 configuration of Tb^{3+} (Fig. 5). Yamashita and Hamada [8] and Yamashita et al. [9] observed the
 102 PL and TL spectra of the $MgSO_4:Tb^{3+},Na^+$, $CaSO_4:Tb^{3+},Na^+$, $SrSO_4:Tb^{3+},Na^+$ and
 103 $BaSO_4:Tb^{3+},Na^+$ powder phosphors. The PL spectra of these phosphors consist of the very weak
 104 5D_3 and the prominent 5D_4 series. Trivalent Tb^{3+} ion is generally used as a green emitting center
 105 in a variety of commercial phosphors. The electronic configuration of Tb^{3+} ion is $4f^8$. In case of
 106 Tb^{3+} ion, the absorption is usually due to allowed f-d transition from excited state of $4f^75d^1$
 107 configuration, the electron loses energy to lattice and comes to 5D_j . $^5D_3 \rightarrow ^7F_j$ emission is in UV
 108 and blue region while $^5D_4 \rightarrow ^7F_j$ emission is pre-dominantly green. At lower concentrations of
 109 Tb^{3+} , blue emission is observed, but at higher concentration, there is an energy transfer between
 110 Tb^{3+} ions, e.g. the cross relaxation- $Tb^{3+} (^5D_3) + Tb^{3+} (^7F_j) \rightarrow Tb^{3+} (^5D_4) + Tb^{3+} (^7F_0)$, due to
 111 which the blue emission gets quenched increasing the green emission at the same time. The
 112 intensity ratios of the 5D_3 to 5D_4 series in the PL spectra at 300K was found to be 0.2, these
 113 results are consistence crystals structure of host and concentrations of Tb^{3+} shown in Fig.4. The
 114 intensity ratio of the 5D_3 to 5D_4 series in the PL spectra of $NaMgSO_4F:Tb^{3+}$ at 300K (Fig. 4
 115 (right)) was approximately 0.2. According to here results of the halo sulfates activated with Tb^{3+} ,
 116 we might observe different ratios in the TL and CL spectra of $NaMgSO_4Cl:Tb^{3+}$. The excitation
 117 spectrum, shown in Fig. 4 (left), was obtained by monitoring the prominent green luminescence
 118 at 544 nm, which corresponds to the $^5D_4 \rightarrow ^7F_5$ transition within Tb^{3+} (Figs.4-5). The excitation
 119 bands labeled as A-N correspond well to the electronic transitions from 7F_6 to the upper levels
 120 within Tb^{3+} . The wavelength of Hg 253.7 nm fits the shoulder of the excitation band at 260 nm.

121 This results in the bright yellow- green luminescence from this phosphor under short –UV light
 122 irradiation from a handy Hg lamp (11W, 253.7nm).At 300K, the relative luminescence efficiency
 123 of the high-energy band at 220 nm is approximately 50 times those of B–N bands corresponding
 124 to transitions within Tb^{3+} . The PL spectrum obtained under 220 nm excitation was the same as
 125 that shown in Fig. 5 (right). The prominent excitation band at 220 nm may be attributed to
 126 aligand-to- Tb^{3+} charge-transfer transition .



127
 128 **Fig.4. Optical excitation spectrum (left) and PL spectrum (right) of NaMgSO4Cl:Tb³⁺**
 129 **Excitation spectrum(left) was obtained by monitoring the green luminescence at 544 nm,**
 130 **and PL spectrum (right) was obtained under 352 nm excitation .Excitation spectrum at**
 131 **long wavelengths is magnified 5. Vertical arrow shows the wavelength of Hg line at**
 132 **253.7nm**



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Fig. 5. Schematic energy levels of Tb³⁺ in the NaMgSO₄Cl

135 **5. Conclusions**

136 The PL and excitation spectra of NaMgSO₄Cl activated with Tb³⁺ ions were well identified with
 137 the electronic transitions within rare-earth ions. The existence of excitation bands with high
 138 luminescence efficiency at wavelength shorter than 230 nm is characteristic of NaMgSO₄Cl:Tb³⁺
 139 phosphor. These results suggest that NaMgSO₄Cl:Tb³⁺ phosphor may be favorable as the
 140 phosphor for UV-LED fluorescent tubes.

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