

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 characteristics of NaMg(SO₄)Cl:Tb³⁺. 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.

Key Words- Halosulphate; Slow evaporation technique; Optical properties

1. Introduction

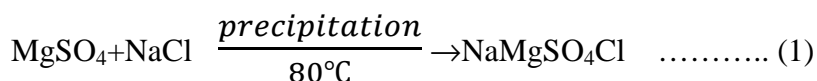
The search for innovative materials with desirable optical properties attracts attention of material researchers towards recent developments and need of decade. In particular, a need has emerged for compounds that are candidates for luminescence study. Considerable improvement in the field of luminescent 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

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.

Recently Moharil and co-workers [1-4] 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 $\text{Na}_6\text{Ca}_4(\text{SO}_4)_6\text{F}_2$ and characterized this compound by X-ray powder diffraction[5]. Also Chouby reported luminescence properties in some halosulphate $\text{NaMgSO}_4\text{F}:\text{Ce}^{3+}$, $\text{Na}_3\text{SO}_4\text{F}:\text{Ce}^{3+}$ by solid state method [6]. In this paper we report the synthesis of $\text{NaMgSO}_4\text{Cl}:\text{Tb}^{3+}$ material by slow evaporation technique and explain Tb^{3+} emission in present halosulphate phosphor which are favorable as the phosphor for UV-LED fluorescent tubes.

2. Experimental

Microcrystalline $\text{NaMgSO}_4\text{Cl:Tb}^{3+}$ sample was prepared by the method of slow evaporation technique. In this method MgSO_4 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 NaMgSO_4Cl (Eq.1) then water soluble salt of dysprosium sulfate was added to the solution to obtain $\text{NaMgSO}_4\text{Cl: Tb}^{3+}$. 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.



3. Characterizations of samples

The formation $\text{NaMgSO}_4\text{Cl:Tb}^{3+}$ compound was confirmed by powder XRD technique, X-ray diffractogram of this compound was taken at room temperature in a wide range of Bragg 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 –II 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 4000cm^{-1} to 450cm^{-1} . Photoluminescence studies were made by using personal computer based fluorescence spectrometer (Hitachi,F-7000) with 150W Xenon lamp light source.

4. Results and discussion

4.1 XRD Results

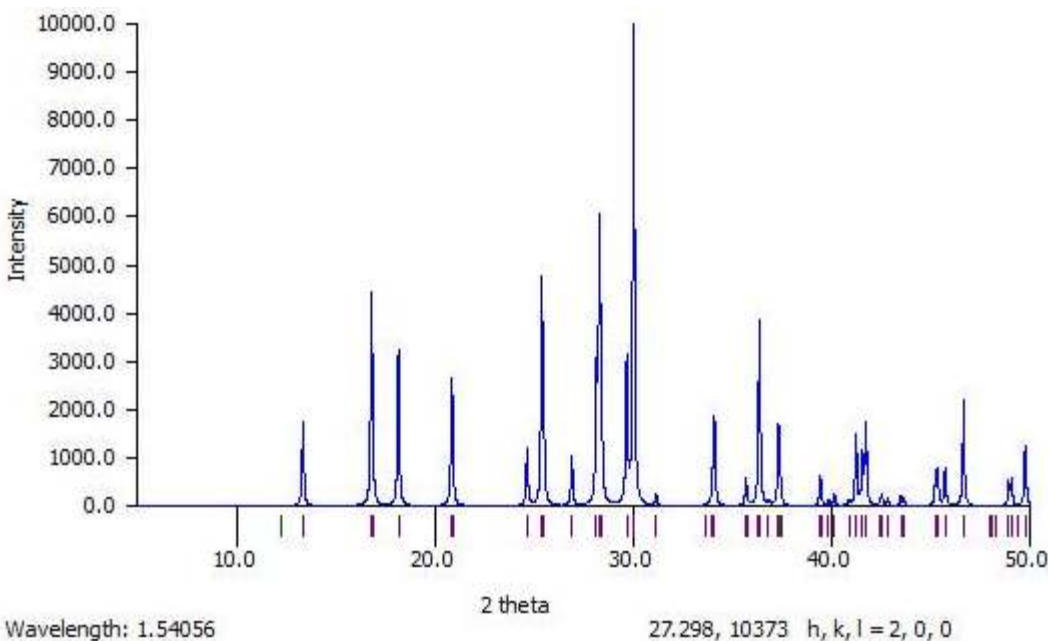


Fig.1. XRD Pattern of NaMgSO₄Cl

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 occur at 721 cm⁻¹. These bands are seen in the spectrum of NaMgSO₄Cl:Tb (Fig.2)

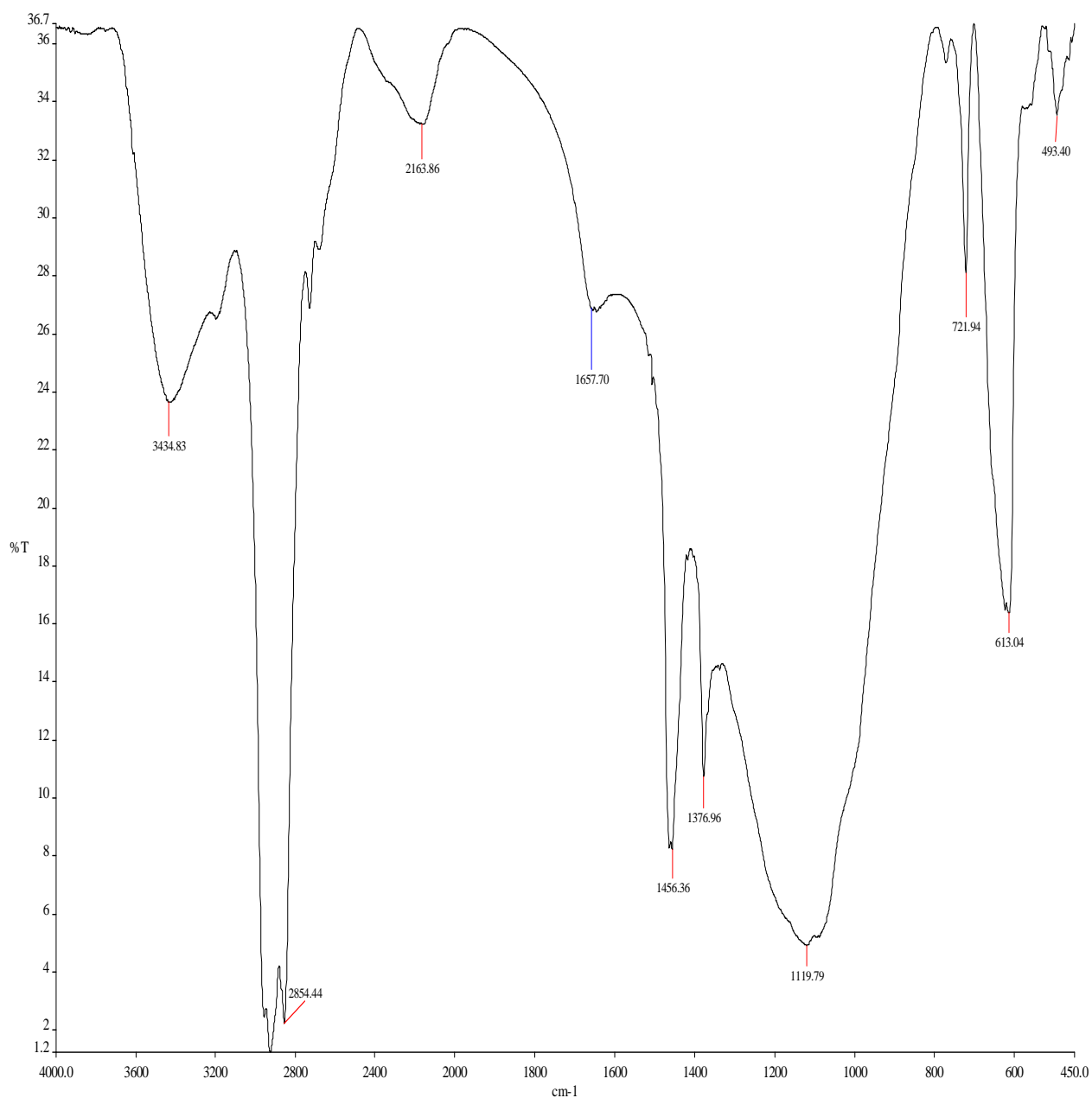


Fig.2 FTIR spectra of NaMgSO₄Cl: Tb sample

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 1μm. The second kind of particle has a size of about 3μm and third one has a particle size

5 μ m 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 μ m range. This powder sample can easily be termed an ultra fine phosphor because the particle size is less than 5 μ m.

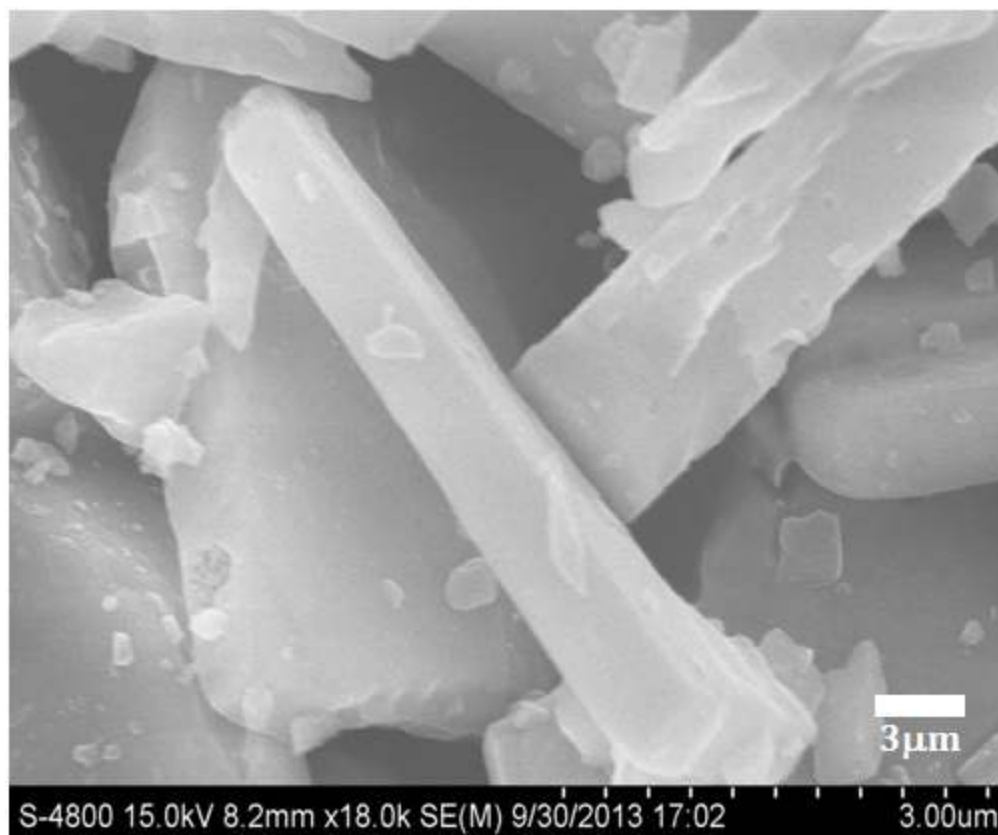


Fig.3 SEM photograph of Tb³⁺ doped NaMgSO₄F

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 (5D_3 series) between 380 and 480 nm and a prominent series (5D_4 series) between 480 and 680 nm. They are identified with the electronic transitions from 5D_3 and 5D_4 respectively to 7F_J ($J= 2$ to 6) within the $4f^8$ configuration of Tb^{3+} (Fig. 5). Yamashita and Hamada [8] and Yamashita et al. [9] observed the PL and TL spectra of the $MgSO_4:Tb^{3+},Na^+$, $CaSO_4:Tb^{3+},Na^+$, $SrSO_4:Tb^{3+},Na^+$ and $BaSO_4:Tb^{3+},Na^+$ powder phosphors. The PL spectra of these phosphors consist of the very weak 5D_3 and the prominent 5D_4 series. Trivalent Tb^{3+} ion is generally used as a green emitting center in a variety of commercial phosphors. The electronic configuration of Tb^{3+} ion is $4f^8$. In case of Tb^{3+} ion, the absorption is usually due to allowed f-d transition from excited state of $4f^75d^1$ configuration, the electron loses energy to lattice and comes to 5D_j . $^5D_3 \rightarrow ^7F_j$ emission is in UV and blue region while $^5D_4 \rightarrow ^7F_j$ emission is pre-dominantly green. At lower concentrations of Tb^{3+} , blue emission is observed, but at higher concentration, there is an energy transfer between 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 which the blue emission gets quenched increasing the green emission at the same time. The intensity ratios of the 5D_3 to 5D_4 series in the PL spectra at 300K 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 $NaMgSO_4F:Tb^{3+}$ at 300K (Fig. 4 (right)) was approximately 0.2. According to here results of the halo sulfates activated with Tb^{3+} , we might observe different ratios in the TL and CL spectra of $NaMgSO_4Cl:Tb^{3+}$. 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, 253.7nm).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.

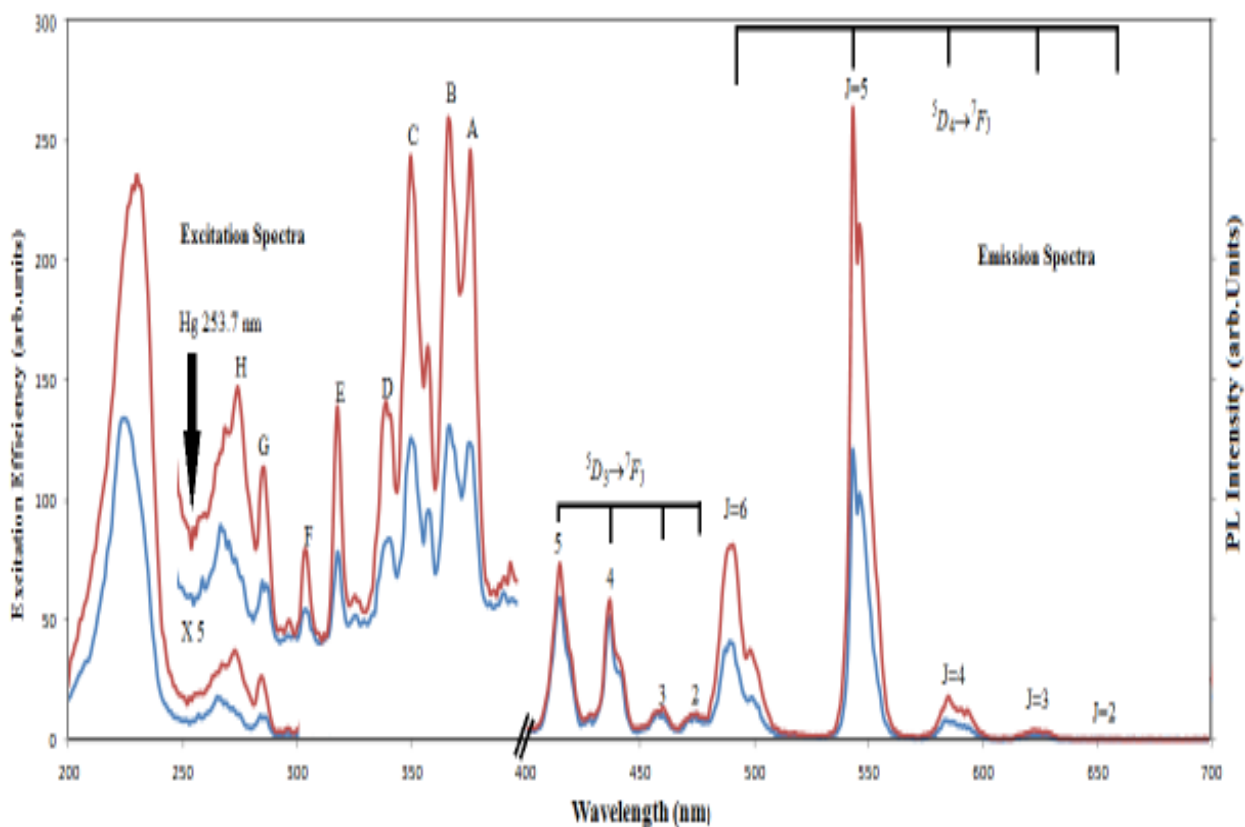


Fig.4. Optical excitation spectrum (left) and PL spectrum (right) of $NaMgSO_4Cl:Tb^{3+}$
Excitation spectrum (left) was obtained by monitoring the green luminescence at 544 nm,
and PL spectrum (right) was obtained under 352 nm excitation .Excitation spectrum at
long wavelengths is magnified 5. Vertical arrow shows the wavelength of Hg line at
253.7nm

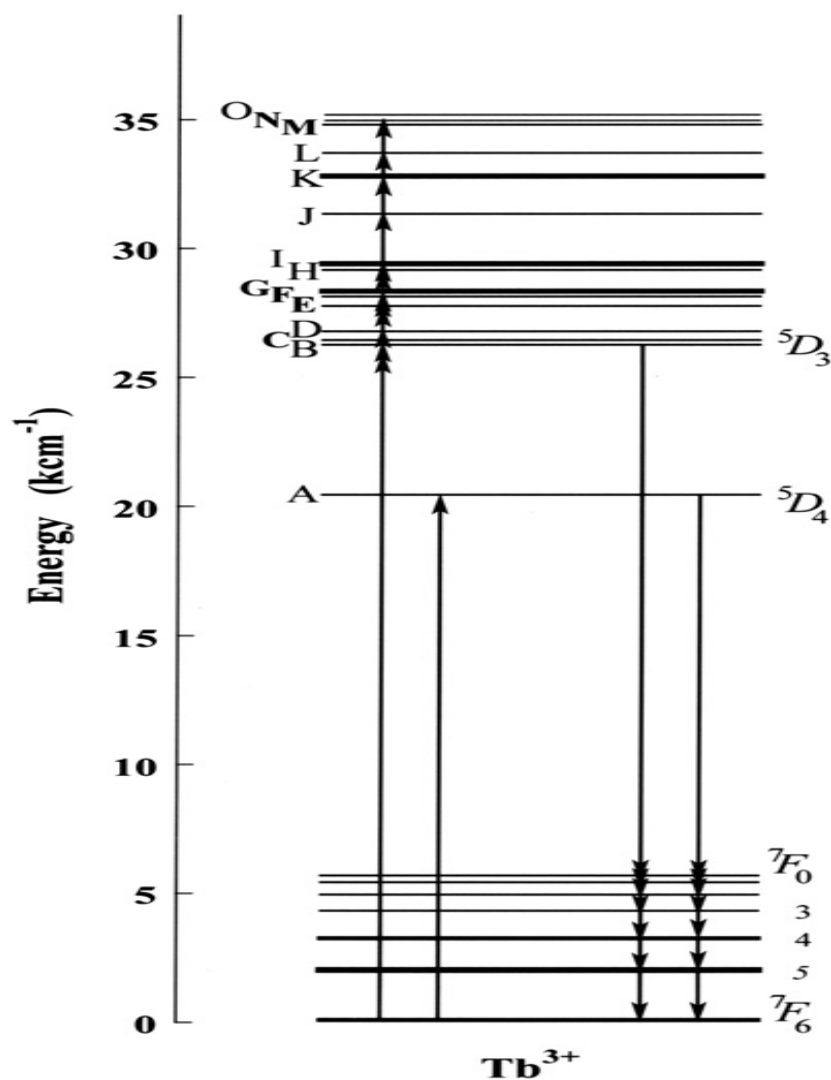


Fig. 5. Schematic energy levels of Tb^{3+} in the NaMgSO_4Cl

5. Conclusions

The PL and excitation spectra of NaMgSO_4Cl 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 $\text{NaMgSO}_4\text{Cl}:\text{Tb}^{3+}$ phosphor. These results suggest that $\text{NaMgSO}_4\text{Cl}:\text{Tb}^{3+}$ phosphor may be favorable as the phosphor for UV-LED fluorescent tubes.

6. References

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