



Sm³⁺ (reddish- orange) luminescence in NaMgSO₄F halosulphate Phosphor for solid state lightening devices

S.T.Taide

Department of Physics J.D. Institute of Engineering & Technology Yavatmal. (India)

Abstract: A new orange-red luminescent powder phosphor of NaMgSO₄F: Sm³⁺ has been developed by re-crystallization method to characterization them spectroscopically in order to identify the most suitable phosphor as solid state lightening devices. For this material X-ray diffraction, Fourier transform infrared spectroscopy (FTIR) characterization and SEM features have also been investigated to explore the structural details. Besides carrying out these essential measurements, we have also made an attempt to observe two intense emission band $^4G_{5/2} \rightarrow ^6H_{7/2}$ (orange) and $^4G_{5/2} \rightarrow ^6H_{9/2}$ (red) a strong reddish-orange emission band performance displayed by this phosphor under an excitation band $^6H_{5/2} \rightarrow ^4F_{7/2}$ (blue).

Key words: FTIR; Photoluminescence; Halosulphate; Phosphors

1. Introduction

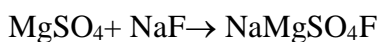
The emission of samarium is enough intense to find important applications in tricolor fluorescence lamps and display devices. The spectroscopic studied of samarium doped fluoride have been extensively investigated to characterize them for optical device application. The $^4G_{5/2}$ excited level of Sm³⁺ ions emits in visible region through different emission channels with high quantum efficiency Hence Sm³⁺ in an important case to analyze the energy transfer process. Samarium ions with 4f⁵ configuration exhibits a strong orange –red fluorescence in the visible region and finds applications in color display, visible solid state laser[1-4]

Special interest has been paid to the incorporation of Samarium as a Sm^{3+} ion into sodium based halosulphate phosphor by wet chemical method because presence of sodium ion gives Sm^{3+} emission in the halosulphate phosphor and they are technologically simple to obtain and conform at low cost even for large size. Among the different techniques employed to prepare these material, the re-crystallization process appears a promising route. Mohril et al.[5] and Dhoble et al.[6] reported phosphors on rare earth (RE) ions doped with Halosulphate –based materials. Klement[7] synthesized the halosulphate $\text{Na}_6\text{Ca}_4(\text{SO}_4)_6\text{F}_2$ and characterized this material by powder X-ray diffraction (XRD). Also, the compounds $\text{Na}_6\text{Cd}_4(\text{SO}_4)_6\text{Cl}_2$, $\text{Na}_6\text{Pb}_4(\text{SO}_4)_6\text{Cl}_2$ [8-9] have been synthesized and characterized.

In this paper we have reported synthesis and spectral characteristics of Sm^{3+} ions in NaMgSO_4F halosulphate using the wet chemical method. The XRD technique exhibits crystalline nature of the prepared material. Fourier transform infrared spectroscopy (FTIR) characterizations have been carried out to understand functional group analysis. The PL emission spectra of Sm^{3+} ions in the NaMgSO_4F phosphor under excitation 402 nm show a prominent Sm^{3+} emission peak due to $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ transition in the intense reddish –orange region of the visible spectrum in the host lattice are applicable for color displays and tricolor fluorescence lamps.

2. Synthesis and Experimental

The sample NaMgSO_4F (pure and Sm doped) were prepared by re-crystallization method .while preparing the raw materials NaF and MgSO_4 of analar grade were taken in stoichimetric ratio and dissolved separately in double distilled de-ionised water resulting solution of NaMgSO_4F . For $\text{NaMgSO}_4\text{F}:\text{Sm}$ we used samarium oxide (Sm_2O_3 Sigma, pure 99%) to obtain $\text{NaMgSO}_4\text{F}:\text{Sm}$, confirming that no undissolved constituents were left behind and that all the salts had completely dissolved in water and thus reacted.



The compound $\text{NaMgSO}_4\text{F}:\text{Sm}$ in powder form were obtained by evaporating at 80°C for 8hrs. The dried samples were then slowly cooled at room temperature. The resultant polycrystalline mass was crushed to fine particle in a crucible, then the dry powder was used for further study.

The formation of $\text{NaMgSO}_4\text{F}:\text{Sm}^{3+}$ compound was confirmed by powder XRD technique .X-ray diffraction of this compound was taken at room temperature in a wide range of Bragg angle 2θ using PAN analytical high resolution XRD-I, PW3040/60 at a scanning rate of 1.00 degree per minute. The FTIR Spectra were obtained on a

Nicolet IR-200 spectrophotometer using electron gun technique in the range of 400 cm^{-1} to 4000 cm^{-1} . The particle morphology and grain size of prepared materials were examined by FE-SEM, SEM micrograph shows regular elongated and trapezoidal rod like structure, disperse and densely agglomerates with typical diameter about $5\ \mu\text{m}$, which is suitable for coating and printing on display devices. Photoluminescence studies were made by using personal computer based fluorescence spectrometer (Hitachi, F-7000) with 150 W Xeon lamp light source. Emission and excitation spectra were recorded using a spectral slit width of 1nm.

3. Result and Discussion

The XRD pattern of $\text{NaMgSO}_4\text{F}:\text{Sm}^{3+}$ phosphor is displayed in **fig.1** to show its single phase nature. The XRD pattern was indexed with the monoclinic symmetry and it is in good agreement with the standard data available (JCDPS File No- 39-0320). The FTIR spectrum of the $\text{Sm}^{3+}:\text{NaMgSO}_4\text{F}$ phosphor is shown in fig.2 in order to understand the existence of various Sulfer –oxygen arrangement in sulphate phosphors. Normally sulphate contains two S=O and two S-O bands. The S=O asymmetric stretching vibration occurs at 1216 cm^{-1} and symmetric stretching vibration occurs at 1059 cm^{-1} . The S-O stretch vibration occurs at 755 cm^{-1} . The above assignment have been made for $\text{Sm}^{3+}:\text{NaMgSO}_4\text{F}$ phosphor and obtained result found quite well comparable with results in literature [10-13]. The assignment details are collected in Table.1

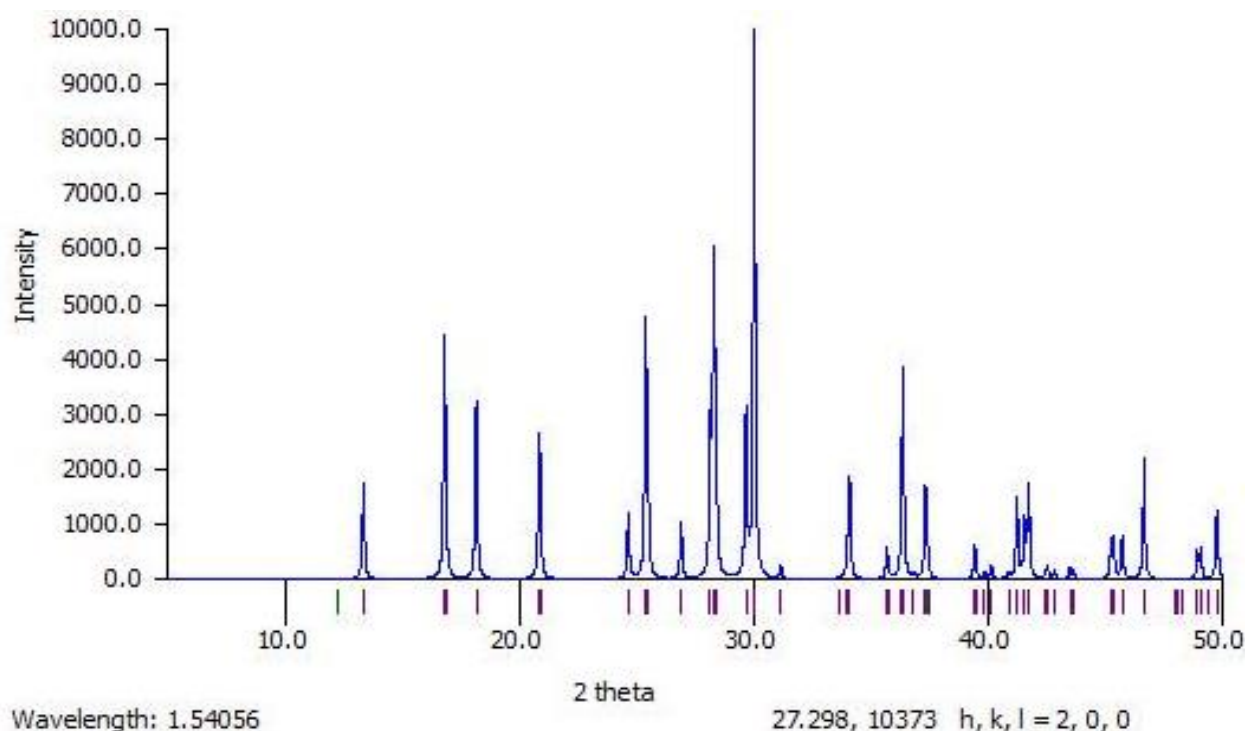


Fig.1. XRD Pattern of $\text{NaMgSO}_4\text{F}:\text{Sm}^{3+}$

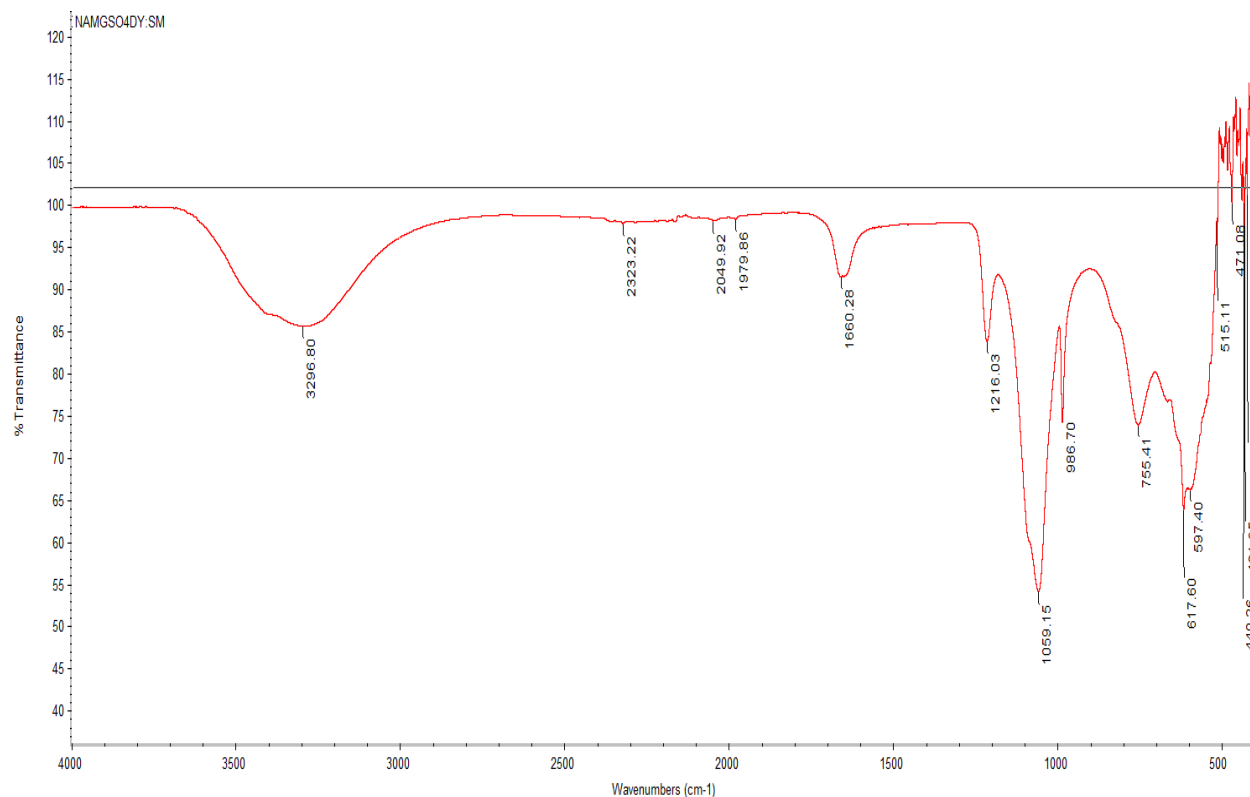


Fig.2.FIIR Spectrum of NaMgSO₄F: Sm³⁺ Powder Phosphor.

Peak Position (cm ⁻¹)	Assignment	
597	S-O (Stretching vibrations)	
617		
755		
986		
1059		S=O(symmetric stretching vibrations)
1216		S=O(Asymmetric stretching vibrations)
1660		

Table 1. FTIR spectrum and energy level assignments for Sm³⁺ : NaMgSO₄F powder phosphor from 4000 to 400 cm⁻¹

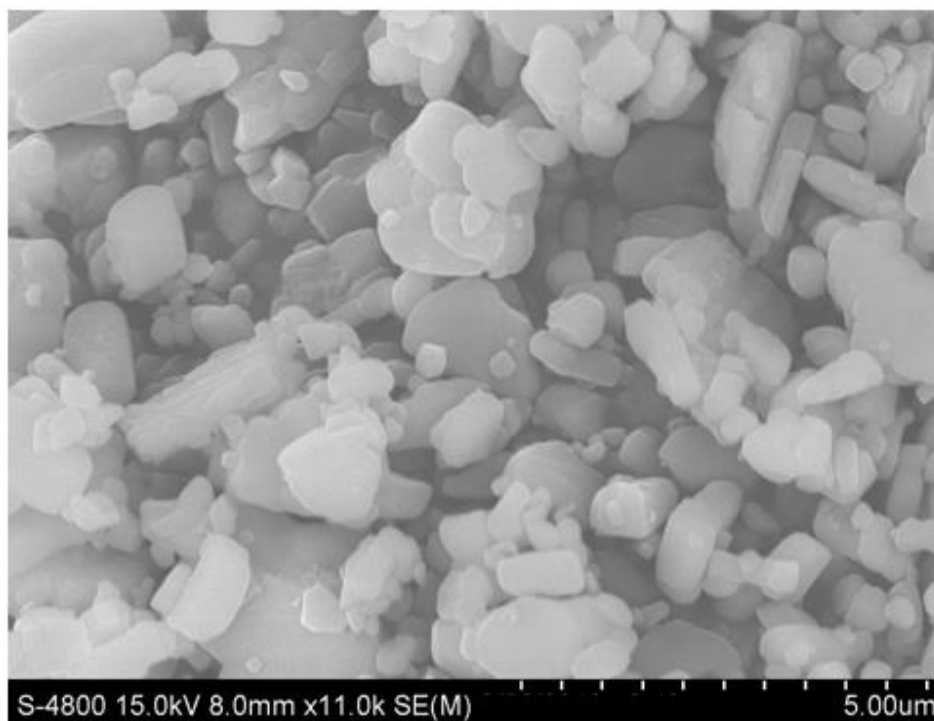


Fig.3.SEM image of $\text{NaMgSO}_4\text{F: Sm}^{3+}$ Powder Phosphor.

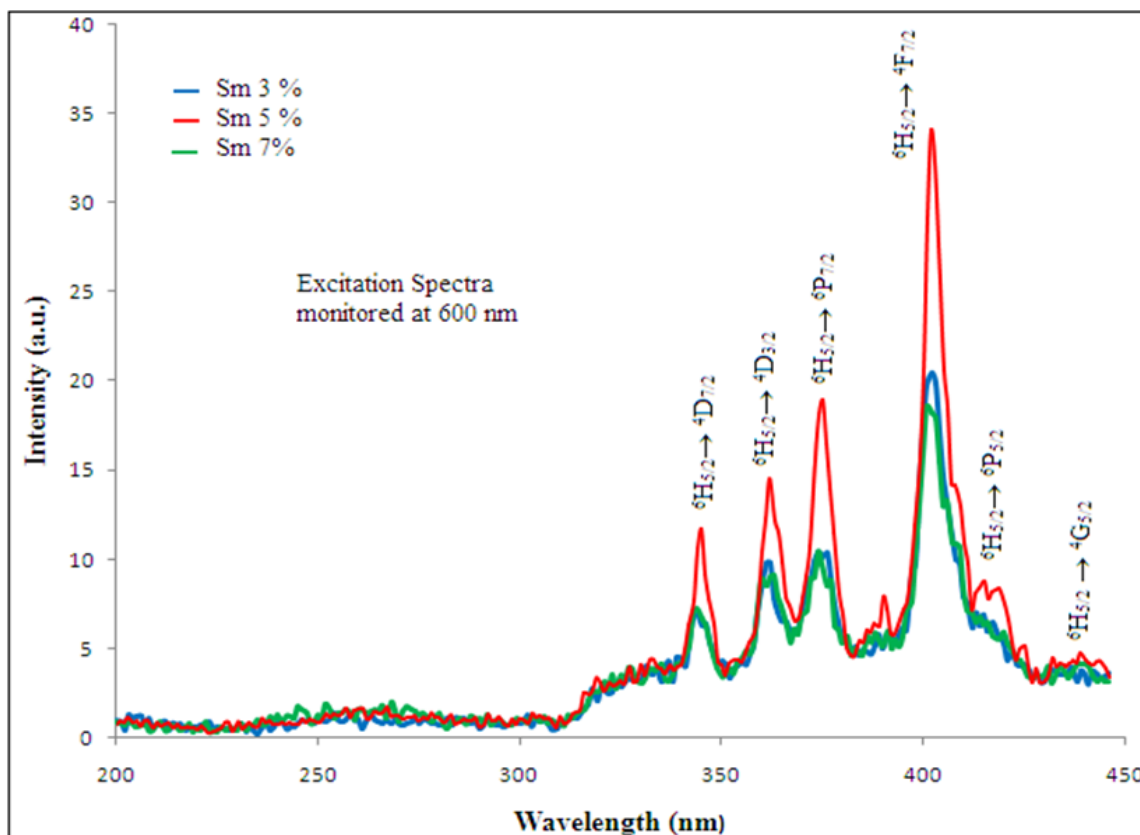


Fig.4. Excitation spectrum of $\text{NaMgSO}_4\text{F: Sm}^{3+}$ Powder Phosphor.

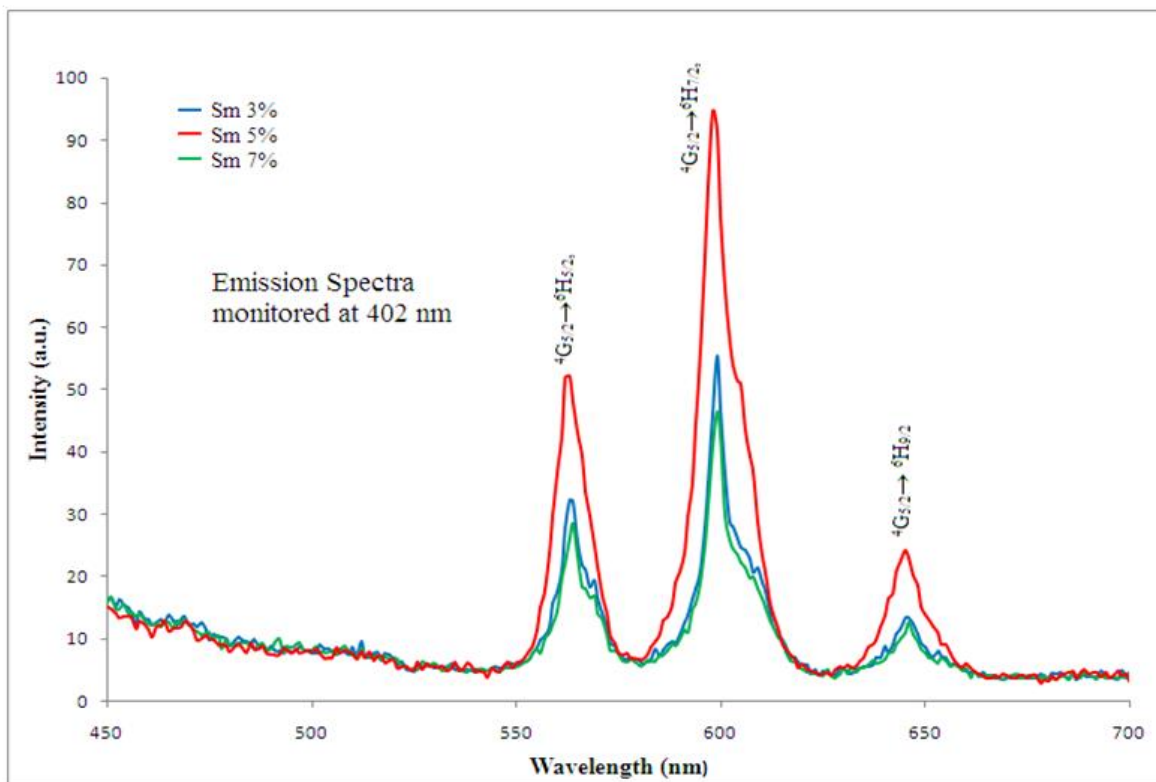


Fig.5. Emission spectrum of NaMgSO₄F: Sm³⁺ Powder Phosphor.

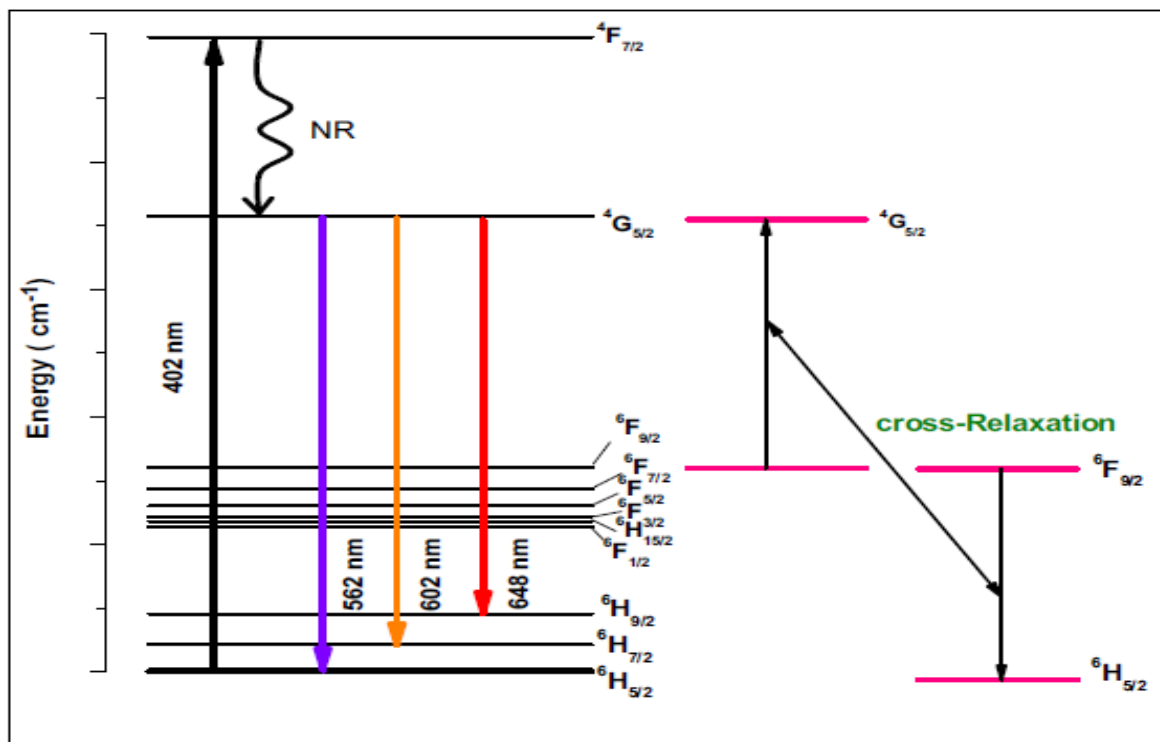


Fig.6. Energy level depicting the various lasing transitions of Sm³⁺ ions

Fig 4.shows excitation spectrum of Sm³⁺: NaMgSO₄F powder phosphor reveals the presence of Sm³⁺ examined.

The excitation spectrum monitored with emission band at 600nm shows totally six bands are observed at

wavelength approximately 344nm, 360nm, 374nm, 402nm, 411nm, 436nm corresponding to transitions ${}^6\text{H}_{5/2} \rightarrow {}^4\text{D}_{7/2}$, ${}^4\text{D}_{3/2}$, ${}^6\text{P}_{7/2}$, ${}^4\text{F}_{7/2}$, ${}^6\text{P}_{5/2}$, ${}^4\text{G}_{5/2}$ respectively. In general the Sm^{3+} ion will exhibit several overlapping excitation bands due to closely spaced energy levels. For this reason we measured excitation of Sm^{3+} from 200 to 450 nm by fixing the emission at 600nm. The sharpness of emission bands depends on host matrix phonon energies. Sometimes the stark splitting may cause broadening of these observed bands. It is well known that the wavelength corresponding to intense excitation band can give intense emissions. Among all excitation bands, a band corresponding to transition ${}^6\text{H}_{5/2} \rightarrow {}^4\text{F}_{7/2}$ at 402 nm is more intense and is used as an excitation wavelength to record the emission spectra. **Fig.5.** shows emission spectra Sm^{3+} : NaMgSO_4F powder phosphor. The emission spectrum monitored with excitation band at 402nm shows totally three peaks centered at 563nm, 600 nm, 643nm corresponding to transitions ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$, ${}^6\text{H}_{7/2}$, ${}^6\text{H}_{9/2}$ respectively. Among the three transitions ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$ is more intense when compared with remaining two transitions. Upon the excitation at 402nm, the intense reddish-orange luminescence is observed in visible region. The energy level depicting the various lasing transitions of Sm^{3+} ions as shown in **fig.6.** Reveals when Sm^{3+} ions are excited to any level above ${}^4\text{G}_{5/2}$, a fast non-radiative decay takes place due to closely spaced energy level above ${}^4\text{G}_{5/2}$. The excited Sm^{3+} ions thus reaching to ${}^4\text{G}_{5/2}$ relax radiatively through ${}^4\text{G}_{5/2}$ transition. The large energy separation ($\sim 7600 \text{ cm}^{-1}$) between ${}^4\text{G}_{5/2}$ emission level and its lower lying ${}^6\text{F}_{11/2}$ prevents the possibility of multi phonon relaxation. Because according to Judd-Ofelt theory the measured life time are significantly smaller than the radiative lifetimes hence the energy transfer through cross-relaxation but not due to multi phonon relaxation because energy gap existing between ${}^4\text{G}_{5/2}$ energy level to the next lower level ${}^6\text{F}_{11/2}$ is very large ($\sim 7600 \text{ cm}^{-1}$).

4. Conclusions

In summary we have developed and carried out an optical analysis on halosulphate phosphor NaMgSO_4F doped with Sm^{3+} ions. From the characterization, it is clear that Sm^{3+} (reddish-orange) emission was obtained due to ${}^6\text{H}_{5/2} \rightarrow {}^4\text{F}_{7/2}$ transition of Sm^{3+} ion in the sodium based halosulphate phosphor. The presence of Sodium ion gives Sm^{3+} emission in the halosulphate phosphor by re-crystallization method because they are technologically simple to obtain at low cost, even for large sizes. This prepared material may be applicable for orange/red emission in solid state lightening devices.

5. References

- [1] M. Peng, L. Wondraczek, Optics letters, 2010;35,2544.
- [2] A.Mohan Babu,B.C.Jamalaiah,J.Suresh Kumar,T.Sasikala,L.Rama Moorthy, J.Alloys and compounds; 2011,509,457
- [3] J.T. Ingle, A.B.Gawande, R.P.Sonekar, S.K.Omanwar, Y. Wang, L. Zhao, J. Alloys and Compounds Vol.no.585, (2014),633–636.
- [4] J. T. Ingle, R.P.Sonekar, S.K.Omanwar, Yuhua Wang and Lei Zhao, Combust.Sci.Technol. Vol.no.186, (2014),83–89.
- [5] S.V.Moharil,P.D.Sahare,Phys.Stat.Sol.a1990;118,K55.
- [6] S.J.Dhoble,S.V.Moharil,S.M.Dhopte,P.L.Muthal,V.K.Kondwar,Phys.Stat.Sol.a 2003;198(2),322.
- [7] R.Klement, Naturwiss enschaften 1939;27,568.
- [8] W.Schneider,N.Jahrb,F.MinerMonatsch.1967;284.
- [9] W.Schneider,N.Jahrb,F.MinerMonatsch.1969;58.
- [10] L.P.Donald,G.M.Lampman, G.S.Kriz,Int.to spectrometer 3rd edition; Saunders college publishing.
- [11] S.C.Gedam,S.J.Dhoble, S.K.Omawar ,S.V.Moharil,Eur.Phys.J.Appl.Phys;2007,39.
- [12] S.Shanmuka,Sundari,K.Marimuthu,M.Shivraman,S.SurendraBabu,J.lumin.2010;47,1313.
- [13] K. Maheshvaran,K.Lingana,K.marimuthu, J.lumin.2011;131,2746.