

## Characterization and photoluminescence studies of Dy<sup>3+</sup> doped Na<sub>2</sub>SO<sub>4</sub> phosphor prepared by re-crystallization method.

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**Abstract:** Dy<sup>3+</sup> doped Na<sub>2</sub>SO<sub>4</sub> was prepared by the recrystallization method and characterization of material was done by using X-ray diffraction (XRD), scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR) techniques. From the XRD pattern of Dy doped Na<sub>2</sub>SO<sub>4</sub> compound, it was found that the prominent phase formed was Na<sub>2</sub>SO<sub>4</sub> and the result of FTIR spectrum of Na<sub>2</sub>SO<sub>4</sub>:Dy shows that the Sulfur-oxygen stretch was found at around 1376 cm<sup>-1</sup>. Narrow bands observed in PL and excitation spectra of Na<sub>2</sub>SO<sub>4</sub>:Dy<sup>3+</sup> phosphors were well identified with the electronic transitions within the 4f<sup>9</sup> configurations of Dy<sup>3+</sup>. The existence of excitation bands with high luminescence efficiency at wavelength shorter than 230 nm is characteristics of Na<sub>2</sub>SO<sub>4</sub>:Dy<sup>3+</sup> phosphor. The obtained results suggest that these phosphor is unfavorable as the phosphor for usual fluorescence tubes, i.e., mercury discharge tubes, but may be favorable as the phosphor for UV-LED fluorescent tubes and as cathodoluminescence, X-ray luminescence and thermo luminescence phosphors.

### I. Introduction

Sodium sulphate (thenardite), though very simple in chemical composition, has been the subject of various applications. It is used for the production of glasses and paints and for thermal energy storage techniques [1, 2]. Na<sub>2</sub>SO<sub>4</sub> exhibits a variety of phase transitions between its five anhydrous polymorphs (labelled I–V). The phase transformation sequence among the Na<sub>2</sub>SO<sub>4</sub> polymorphs can be described as V ↔<sup>473K</sup> III ↔<sup>503K</sup> II ↔<sup>510K</sup> I ← melt --- (1). Na<sub>2</sub>SO<sub>4</sub> forms two naturally occurring minerals mirabilite (Na<sub>2</sub>SO<sub>4</sub> : 10H<sub>2</sub>O) and thenardite (Na<sub>2</sub>SO<sub>4</sub>). Both are in thermodynamic equilibrium at 32<sup>o</sup>C which maybe lowered to 18<sup>o</sup>C in the presence of foreign ions [3]. At room temperature phase V (thenardite) is reported to be stable while phase III is meta stable. Phase I, and II are high-temperature polymorphs however, phase II is reported to have a narrow stability zone. Phase IV is considered to be metastable and its phase relation and structure have yet to be well established [4–7]. Also thenardite is fluorescent material showing white luminescence under short-wave ultra violet (UV) light (253.17 nm Hg line), and long phosphorescence. Reliable studies on the photoluminescence (PL) properties of thenardite or synthetic Na<sub>2</sub>SO<sub>4</sub> activated with rare-earth (RE) ions are few to the best of our knowledge. Bykovskii and Pisarenko [3] observed the PL spectra of Sm<sup>2+</sup> in synthetic Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>. The PL properties of alkali sulfates activated with Eu have been reported by some investigators [2-4,7]. He et al. [8] reported the PL properties of Na<sub>2</sub>SO<sub>4</sub>:TbF<sub>3</sub> under vacuum UV-UV light excitation. The object of this investigation is to prepare Na<sub>2</sub>SO<sub>4</sub> phosphors activated with rare earth ion Dy<sup>3+</sup>, and to obtain the PL and excitation spectra of the prepared phosphors.

### II. Sample preparation

Microcrystalline Na<sub>2</sub>SO<sub>4</sub>:Tb<sup>3+</sup> sample was prepared by the method of recrystallization. In this method Na<sub>2</sub>SO<sub>4</sub> of AR grade were taken in a stoichiometric ratio and dissolved in double distilled de-ionized water, then water soluble salt of dysprosium sulfate was added to the solution to obtain Na<sub>2</sub>SO<sub>4</sub>:Dy<sup>3+</sup>. The compound Na<sub>2</sub>SO<sub>4</sub>:Dy<sup>3+</sup> in its powder form was obtained by evaporating on 80<sup>o</sup>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. Preparation of sample was done in the Luminescence laboratory of the department of Physics Sant Gadge Baba Amravati University Amravati (M.S.). The formation of Dy doped Na<sub>2</sub>SO<sub>4</sub> compound was confirmed by XRD, SEM and FTIR studies. 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 powder phosphor 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<sup>-1</sup> to 450cm<sup>-1</sup>. Photoluminescence studies were made by using personal computer based fluorescence spectrometer (Hitachi, F-7000) with 150W Xenon lamp light source.

### III. Result and discussions

#### 3.1 XRD Results

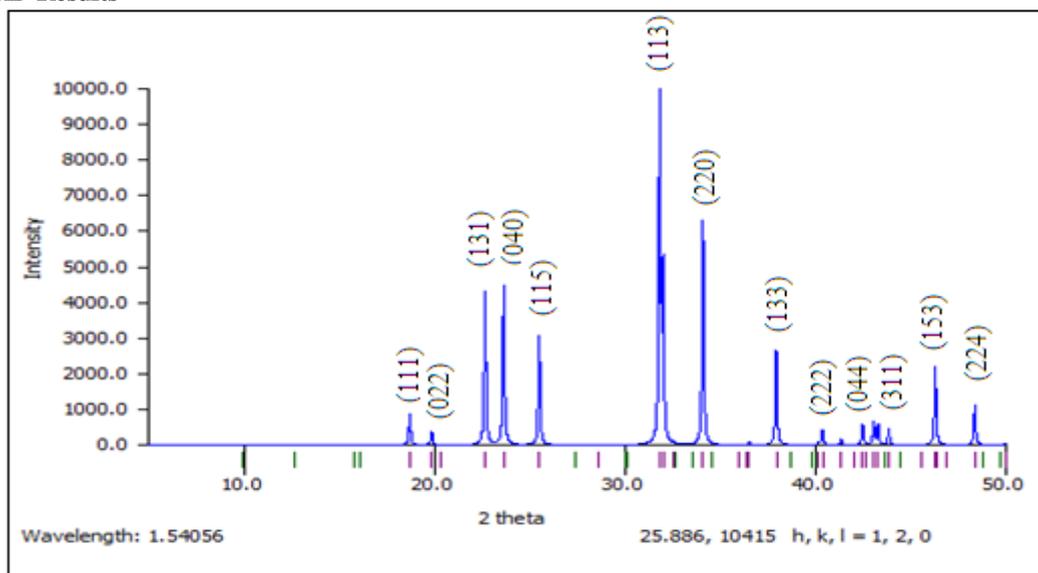


Fig.1 XRD pattern of Dy<sup>3+</sup> doped Na<sub>2</sub>SO<sub>4</sub> sample

Figure 1. shows the XRD pattern of Na<sub>2</sub>SO<sub>4</sub> at room temperature. The reflections pattern were indexed to phase V thenardite (ICDD card 37–1465). It is well known that the calcinations can improve the crystallinity of the sample. The increase of calcinations temperature results in the grain growth of sample due to nucleation in interaction between small crystallite which fuses to form larger particles.

#### 3.2 Crystal Structure of Na<sub>2</sub>SO<sub>4</sub>

The crystal structure of thenardite is shown in Figure 2. Thenardite belongs to *F* ddd space group with octahedral structure of nearly regular SO tetrahedral and distorted NaO<sub>6</sub> octahedral. The sodium atoms are each surrounded by 6 oxygen atoms each at 2.334 Å<sup>0</sup>, 2.426 Å<sup>0</sup>, and 2.534 Å<sup>0</sup> forming distorted NaO<sub>6</sub> octahedra with a two fold axis parallel to *c*-axis. The O–Na–O angles, 56.15°–134.93°, are greatly distorted from octahedral symmetry [11, 12]. All the sulphate ions are separated from each other by distances >3 Å for two oxygen atoms belonging to different sulphate groups. All S–O distances are equal (1.476 ± 0.001 Å); thus the sulphur atom is fixed in a special point position with 222 point symmetry. Each SO<sub>4</sub> tetrahedron shares two of its edges with two different 2.534 Å<sup>0</sup> representing the distances to oxygen's forming the shared tetrahedral edge. The remaining corners of the NaO<sub>6</sub> octahedron are shared with another four SO<sub>4</sub> tetrahedron there giving a 3D framework [11, 12]. Mirabilite (phase III) also has an orthorhombic crystal structure with space group *Cmcm*. Its cell parameters are *a* = 7.038 Å,

*b* = 9.043 Å, *c* = 5.785 Å, and  $\alpha = \beta = \gamma = 90^\circ$  [9]. The average calculated S–O band length is 1.478 Å<sup>0</sup>. There are two different types of sodium atoms in the phase III bulk structure, giving five different Na–O distances, which are found to be 2.46, 2.37, 2.29, 2.54, and 2.86 Å<sup>0</sup> [10]. The relative lattice energies of phases III and V are –548.91 eV and –1097.97 eV, respectively. Due to the lower lattice energy, Na<sub>2</sub>SO<sub>4</sub> nucleates in thenardite form predominantly in solution phase attributed to thermodynamic constraints.

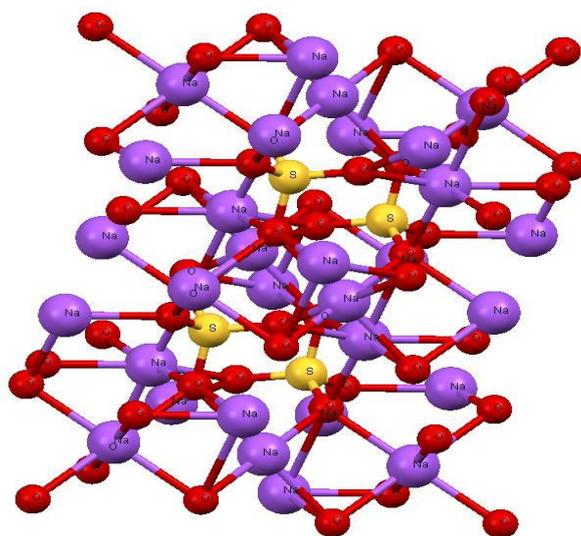


Fig. 2: Crystal structure of Na<sub>2</sub>SO<sub>4</sub>

### 3.3 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR structure of Dy doped Na<sub>2</sub>SO<sub>4</sub> as observed experimentally is shown in Fig. 3. Normally, sulfate contains two S=O and two S-O bonds. Actually, the four S-O bonds are equivalent. The sulfur-oxygen stretches of inorganic sulfates are found from 1350 to 1450 cm<sup>-1</sup>. In our results of FTIR spectrum of prepared Na<sub>2</sub>SO<sub>4</sub> (Fig. 2) the sulfur-oxygen stretch is found at 1376 cm<sup>-1</sup>. Like any other bonds, sulfate bonds can bend, giving rise to one or two bands normally in the 680 to 610 cm<sup>-1</sup> range. These bands are seen in the spectrum of Na<sub>2</sub>SO<sub>4</sub>:Tb (Fig. 2) near 612 and 722 cm<sup>-1</sup>.

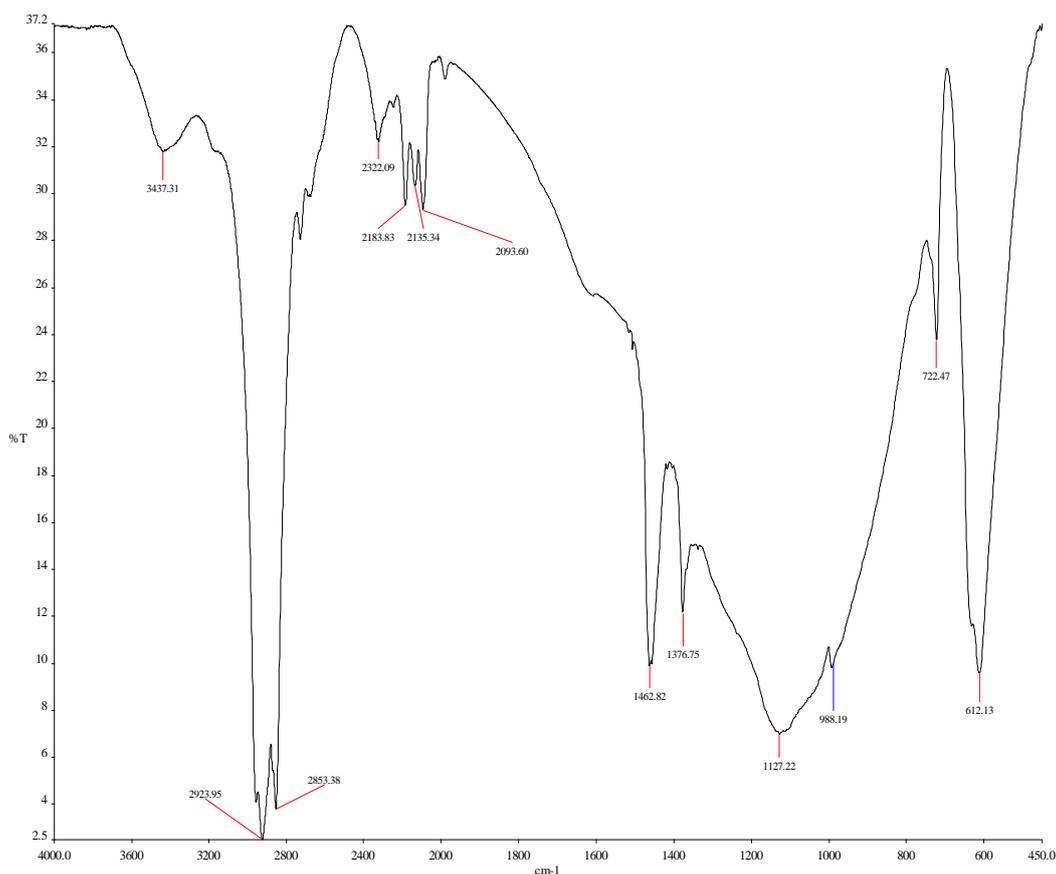
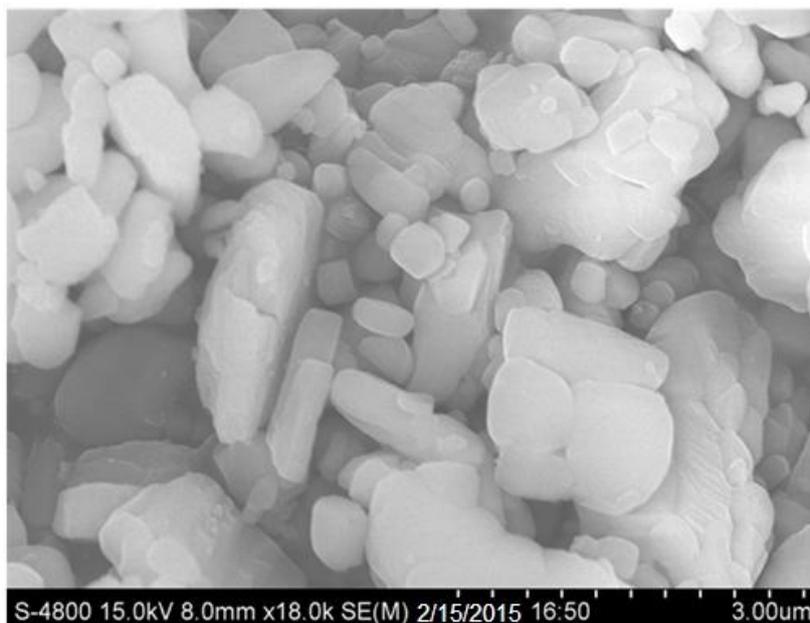


Fig. 3 FTIR spectra of Na<sub>2</sub>SO<sub>4</sub>: Dy sample

### 3.4 Scanning Electron Microscopy (SEM)

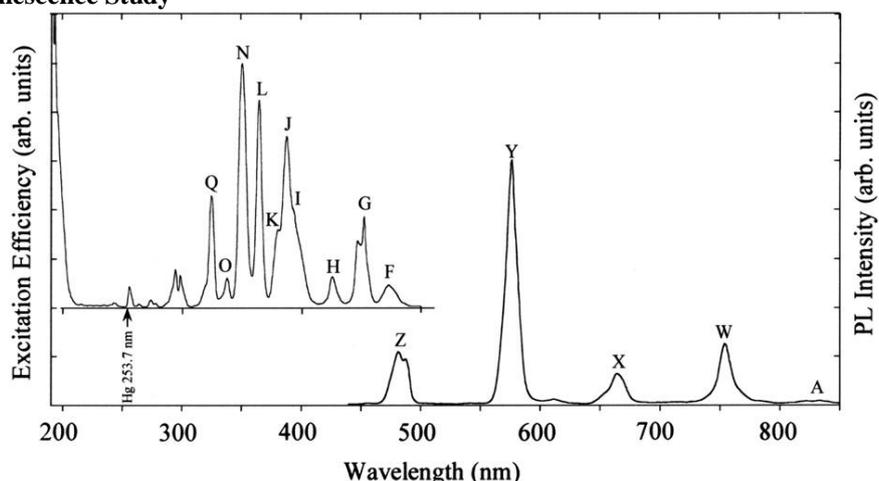
The microstructure of the prepared Dy doped Na<sub>2</sub>SO<sub>4</sub> powder sample is studied by SEM and is shown in fig.4 The SEM Photograph shows regular morphology with different particle size. The particle size can be categorized in to three types : one that shows particle with particle size 1µm. The second kind of particle has assize of about 3µm and third one has a particle size5µm 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 5µm range. Smaller crystals are less efficient because of the lower bulk emission intensity. Also, tighter packing of the smaller particles will increase the probability that the emitted light will get lost within the screen. Larger crystal cause difficulties in coating the phosphor particles in to smooth, thin screens. This powder sample can easily be termed an ultra fine phosphor because the particle size is less than 5µm. Many coworkers have studied of rare



**Fig.4** SEM photograph of Dy<sup>3+</sup> doped Na<sub>2</sub>SO<sub>4</sub>

Earth doped alkaline earth sulfate and they found less PL efficiency in case of nanocrystalline sample than the microcrystalline sample. For example, Gong et al.[13] have observed such phenomena in case of rare earth doped BaSO<sub>4</sub> nanocrystallites. They have attributed this to the spin- orbit coupling interaction interaction. In view of these observations we choose microcrystalline Dy<sup>3+</sup> doped Na<sub>2</sub>SO<sub>4</sub> for the present study.

### 3.5 Photoluminescence Study



**Fig.5** Optical spectrum (left) and PL spectrum (right) of Na<sub>2</sub>SO<sub>4</sub>:Dy<sup>3+</sup>. Excitation spectrum (left) was obtained by monitoring the yellow luminescence at 575 nm, and PL spectrum (right) was obtained under 350 nm excitation. Vertical arrow shows the wavelength of Hg line at 253.7nm

Fig.5 shows the PL and excitation spectra of Na<sub>2</sub>SO<sub>4</sub>:Dy<sup>3+</sup> at room temperature. The PL spectrum (Fig.5 (right)), obtained under the excitation in the prominent N excitation band at 350 nm (Fig.5 (left)), consist of five bands at (Z) 481,(Y) 577,(X) 666,(W) 756 and(A) 830 nm. These five bands can be identified with the <sup>4</sup>F<sub>9/2</sub>→<sup>6</sup>H<sub>J</sub> (J= 7/2, 9/2, 11/2,13/2 and 15/2,respectively) transition within the <sup>4</sup>f<sub>9</sub> configuration of Dy<sup>3+</sup>(Fig.5). Rowlands et al.[14] observed that the 3D-TL spectra of slowly cooled Na<sub>2</sub>SO<sub>4</sub>:Dy<sup>3+</sup>. Glow peaks were located at 90 and 170°C, and peaks obtained by slicing the 3D-TL spectrum at a glow peak were located at (Z) 480,(Y) 580,(X) 665 and (W) 760nm. These peaks corresponds well to the first four peaks in fig.5 ( right).According to Rowlands et.al [14],the slowly cooled Na<sub>2</sub>SO<sub>4</sub> is in crystallographic phase III at room temperature, where as in our result is in phase V. Differences in the spectral peak wavelengths caused by crystallographic phases are negligible. It should be noted that the emission intensity ratios among the Z,Y, X and W bands may depend on crystallographic phases I-V of Na<sub>2</sub>SO<sub>4</sub>. For example, the emission intensity ratio of Y- band corresponding to the electric dipole transition to the Z band corresponding to the magnetic dipole transition depends on the asymmetry around Dy<sup>3+</sup> ions[15-16].

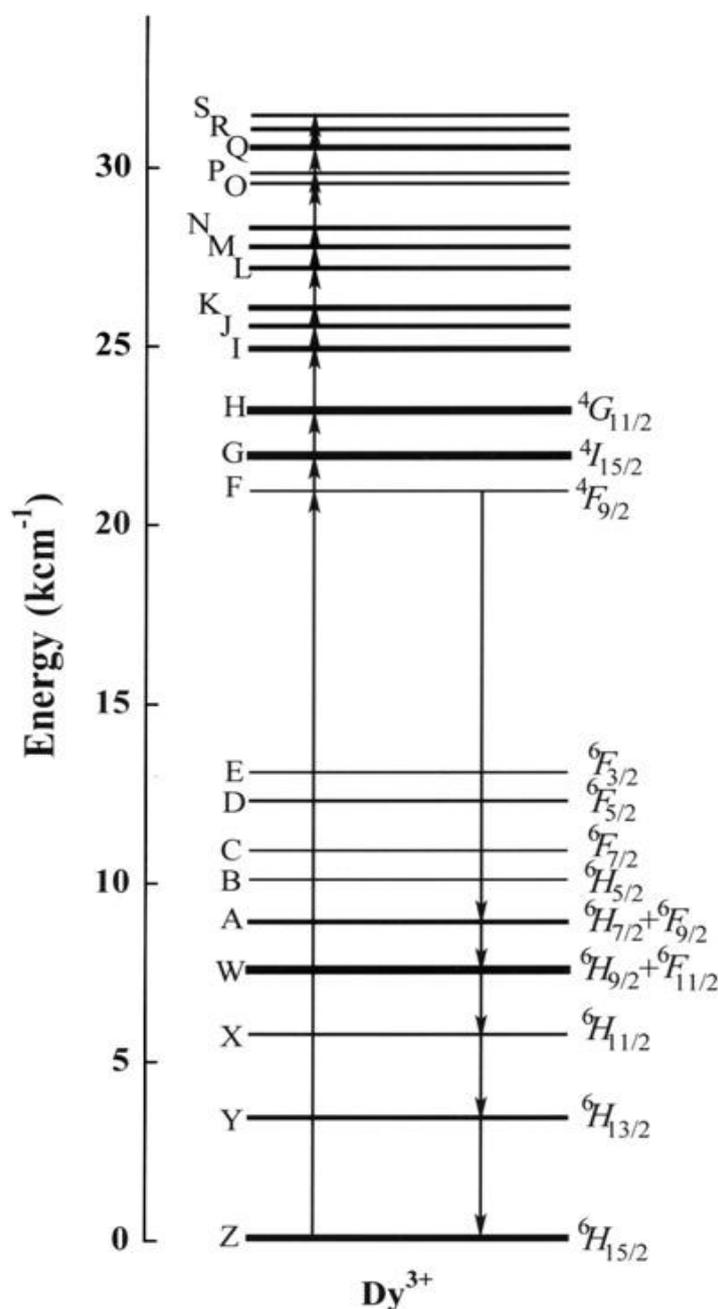


Fig. 6 Schematic energy level of Dy<sup>3+</sup> in the thenardite lattice.Z-S corresponds to the Dy<sup>3+</sup> levels named by Dieke[17] .Arrow shows the excitation and emission transitions.

The excitation spectrum (Fig.5(left)) was obtained by monitoring the prominent yellow luminescence in the Y band at 575 nm, which corresponds to the  $^4F_{9/2} \rightarrow ^6H_{13/2}$  transition within Dy<sup>3+</sup> ( Fig.6).The excitation bands labeled as F-Q corresponds to the electronic transitions from  $^6H_{15/2}$  to the upper states within Dy<sup>3+</sup>. The slope of the curve at wavelength of 190-210 nm suggests that there is another band with high luminescence efficiency at wavelength shorter than 190 nm. The PL spectrum obtained under 195 nm excitation was the same as that shown in Fig.5 (right). The prominent excitation band with a peak at wavelength shorter than 190 nm may be attributed to a ligand-to-Dy<sup>3+</sup> charge transfer transition. The existence of this prominent excitation band in the vacuum range suggest that this phosphor may be favorable as CL,X-ray luminescence and TL phosphors, although it is not fluorescent under excitation with the Hg 235.7nm line.

#### IV. Conclusions

The PL and excitation spectra of Na<sub>2</sub>SO<sub>4</sub> activated with Dy<sup>3+</sup> 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 Na<sub>2</sub>SO<sub>4</sub>:Dy<sup>3+</sup> phosphor. These result suggest that Na<sub>2</sub>SO<sub>4</sub>:Dy<sup>3+</sup> phosphor may be favorable as the phosphor for UV-LED fluorescent tubes, X-ray luminescence and TL phosphor.

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