

# Review on Luminescence Mechanism In Rare Earth Doped Sulphate Phosphors

Pandey Shashi\*

Department of Physics, G. H. Raisoni polytechnic, Nagpur-440023, India (M.S.)

**Abstract** – The rare earth activated phosphors nearly fulfill all requirements needed for their application in different fields. They show a strong absorption for the UV mercury radiation, their quantum efficiency is close to unity and they exhibit a nearly optimum emission spectrum. Luminescent materials are used for various purposes such as making lamps, CR tubes and TV screens, electroluminescent lamp and display panels, LED's, detectors for X-ray imaging, scintillation detectors, laser crystals, dosimetry of ionizing radiation's, paints, inks and whiteners, solar concentrators and in chemical and bio-chemical analysis and medical diagnosis. The first class for which the emitting electronic states exhibit a weak interaction with the host lattice and the second class for which this interaction is strong.

**Keywords-** Phosphors, Luminescence, Rare earth elements, excitation, f-f transition.

---

## INTRODUCTION

In general there are two classes of activator ions: The first class for which the emitting electronic states exhibit a weak interaction with the host lattice and the second class for which this interaction is strong. A phosphor basically consists of a host lattice in which activator ions are incorporated. These ions form energy levels responsible for the luminescence process.

The first class comprises most of the trivalent rare earth ions, because the luminescence transitions take place inside their inner 4f shells well shielded by outer electrons. The second class is represented by different kind of ions: (i) the transition metal elements for which the luminescent transitions takes place between d-d and d-s states and, in some host lattices, the conduction band can also be involved in the luminescent transitions, (ii) the  $s^2$  ions (e.g.  $Sb^{3+}$ ,  $Bi^{3+}$ ,  $Sn^{2+}$  and  $Pb^{2+}$ ) having a filled s shell in the ground state, and (iii) most elements of the IVB, VB and VIB groups (e.g.  $Ti^{4+}$ ,  $V^{5+}$  and  $Mo^{6+}$ ) giving rise to a charge transfer luminescence, which means that electrons of neighboring anions are involved in the luminescent transitions.

The weakly interacting rare earth activators (e.g.  $Tm^{3+}$ ,  $Tb^{3+}$  and  $Eu^{3+}$ ) show a so-called characteristic luminescence [49] with narrow emission lines. The spectral position of these lines is nearly independent of the host lattice. On the contrary, the strongly interacting activators exhibit broad emission bands. A further consequence for the rare earth ions is that the mutual interaction between the activators themselves is normally weak, too. Thus, a higher concentration of rare earth ions can usually be incorporated without perceptible concentration quenching as compared to the concentrations used for the second class of activators.

The physical processes involved in UV excitation can be described by considering the energy flow in the phosphor. For UV excitation the radiation is either absorbed in the host lattice and produces electron-hole pairs, which transfer their energy to the activator ions, or is absorbed by incorporated impurity ions. The impurity absorption process takes place in most of the applied lamp phosphors for the 254 nm mercury radiations. The impurity ions directly act as activators or as sensitizers. In the latter case the energy is transferred to the activator ion by a non-radiative energy transfer process. Energy migration in a sub lattice mostly formed

by  $Gd^{3+}$  ions [50] is often used to improve the non-radiative energy transfer.

### PRESENT STATUS AND OUTLOOK

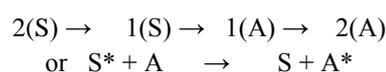
The rare earth activated phosphors nearly fulfill all requirements needed for their application in different fields. They show a strong absorption for the UV mercury radiation, their quantum efficiency is close to unity and they exhibit a nearly optimum emission spectrum. A disadvantage of the rare earth phosphors is their rather high price. Therefore, in future various phosphor developments will be focused on cost reduction. This can be done by either finding new non-rare earth based phosphor systems or by the reduction of the amount of rare earth material needed. The latter may be realized by decreasing the activator concentration in host lattices combined with more efficient energy transfer to the activator ions (e.g. via energy migration in sub lattices) or by using only one host lattice for two or three types of activators, each emitting in different spectral regions. The study of energy transfer in inorganic phosphors is an area of intensive research due to its fundamental interest in condensed matter as well as for its practical utility in devices [51].

The luminescence properties of phosphors with respect to their performance in lamps are understood rather well. However, several properties discussed cannot be predicted accurately and must be determined experimentally, e.g. the activator host lattice interaction, the saturation at high excitation density and the thermal quenching behavior. Therefore, more profound understanding of the underlying mechanisms is required for further phosphor developments. The choice of phosphor even in the case of nearly ideal phosphor systems always remains a compromise between different device performance criteria.

### Mechanism of Energy Transfer

This process is observed when there are two different ions in a matrix. We may excite one ion, the donor, and observe fluorescence from another ion, the acceptor. We shall discuss here only the energy transfer between rare earth ions in sulphate matrix.

Rare earth's are especially suitable for energy transfer studies because of their well-defined and narrow electronic levels, to which absorption occurs and from which fluorescence is observed. Symbolically, energy transfer can be written



The donor system returns from the excited state  $2(S)$  to the ground state  $1(S)$  and the energy released is used to bring the activator system from the ground state  $1(A)$  to its excited state  $2(A)$ . In case of the rare earth, the transfer is a non-radiative one, i.e. no phonon will appear in the system, during the transfer. Forster [52, 54] predicted that for the organic system, the rate of energy transfer is proportional to the overlap of the donor emission, and the acceptor absorption spectra. The discussion of Forster was extended by Dexter [55] for ions in inorganic crystals.

### Energy transfer between unlike centers

If luminescent centers come closer together, they may show interaction with each other which results in new phenomena. Consider two centers, S and A, with a certain interaction. The relaxed-excited-state of S may transfer its energy to A. This energy transfer has been treated by Forster and Dexter and is nowadays well understood.

Dexter, following the classic works by Forster, considered energy transfer between a donor (or a sensitizer) S and an acceptor (or activator) A in a solid. This process occurs if the energy differences between the ground- and excited states of S and A are equal (resonance condition) and if a suitable interaction between both systems exists. The interaction may be either an exchange interaction (if we have wave function overlap) or an electric or magnetic multipolar interaction. In practice the resonance condition can be tested by considering the spectral overlap of the S emission and the A absorption spectra. The Dexter result looks as follows:

$$P_{12} = (2\pi/\hbar) | \langle 1, 2^* | H_{SA} | 1^*, 2 \rangle |^2 \int g_s(E) g_A(E) dE.$$

Here the integral presents the spectral overlap,  $H_{SA}$  the interaction Hamiltonian and  $|j\rangle$  and  $|J^*\rangle$  are the electronic ground- and excited state functions, respectively, with  $j = 1, 2$ . Here 1 refers to S and 2 to A. The distance dependence depends on the interaction mechanism.

A high transfer rate, i.e. a high value of  $P_{12}$ , requires a considerable amount of:

(i) resonance, i.e. the S emission band should overlap spectrally the A absorption band(s),

(ii) interaction, which may be of the multipole - multipole type or of the exchange type. Only for some specific cases the interaction type is known nowadays.

Not always all of the excitation energy is transferred. If only part of it is transferred, this is called cross-relaxation [55, 56]. For improving the light output of a phosphor, people have made many efforts in developing new hosts, to make the best use of doping or by effective sensitization; usually in the sensitization case one activator is used with one sensitizer.

### CHARACTERISTICS FEATURES OF LUMINESCENCE

#### Ce<sup>3+</sup>

The Ce<sup>3+</sup> ground state is split (<sup>2</sup>F<sub>5/2</sub>, <sup>2</sup>F<sub>7/2</sub>). These are the only levels possible for 4f configuration. f → f transitions in Ce<sup>3+</sup> are in IR region. At room temperature, they occur as unresolved bands with maximum at about 2200 - 2300 cm<sup>-1</sup> and half width of 250 - 300 cm<sup>-1</sup>. At low temperature, the band splits into somlines, which are due to f → f transitions and electro-vibronic transitions [108,109].

The excited state, above <sup>2</sup>F<sub>7/2</sub> level, belongs to 5d configuration in the form of broad bands. Most commonly observed emission is characteristics of 5d → 4f transition. Both absorption and emission have a usually broadband character, showing splitting characteristic of <sup>2</sup>F<sub>j</sub> states. The Stoke's shift is due to interaction with host crystal. As the position of 5d band itself depends on the host, not only the Stoke's shift, but also the spectral positions of both the absorption and the emission bands, depend on the host. In (Y, Ce) PO<sub>4</sub>, the emission is around 324 and 350 nm, while in (Y, Ce)<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>, the emission is in the form of a very broad from 500 nm to well beyond 700 nm, having maximum at around 550 nm, and in sulphides such as CaS, Y<sub>2</sub>O<sub>2</sub>S, it is in green-red region [110]. Emission in the blue region is usual. Emission at longer wavelengths is obtained, when the center of the 5d level is at relatively low energies (strong Nephelauxetic effect), and the crystal field is very strong. Another feature of the Ce<sup>3+</sup> emission is that as both absorption and emission are resulting from allowed transitions, the decay time is short (of the order of few ns). Ce<sup>3+</sup> phosphors are thus useful where rapid decay times are required (e.g. in time of flight camera and in scintillator). Luminescence of Ce<sup>3+</sup> gets concentration quenched at 1-2 at. % Ce-concentration [111], due to Ce<sup>3+</sup> → Ce<sup>3+</sup> transfer, followed by transport to killer site. Ce usually shows

high quenching temperature in silicates, borates and phosphates. Since, Ce<sup>3+</sup> has strong absorption in many hosts, and emission matching with 4f levels of other RE impurities, it can be used as a sensitizer for other rare earths [112].

#### Dy<sup>3+</sup>

Dy<sup>3+</sup> emission falls mainly in two lines in the visible region, arising from <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub> (470 - 500 nm) and <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> (570 nm) transitions. The relative intensities of the two bands depend on the local symmetry [113]. When the ratio of blue to green emission is appropriate, one can obtain white emission using Dy<sup>3+</sup>. This property has generated some interest in Dy<sup>3+</sup> luminescence. UV cannot efficiently excite Dy<sup>3+</sup> because its CT state as well as the 5d levels are situated above 50000 cm<sup>-1</sup>. Dy<sup>3+</sup> can be sensitized by Bi<sup>3+</sup> [109], Gd<sup>3+</sup>, Ce<sup>3+</sup>, Pb<sup>2+</sup>, and vanadate [114-116] ions. Gadolinium aluminium borate (GdAl<sub>3</sub>B<sub>4</sub>O<sub>12</sub>) doped with Bi<sup>3+</sup> and Dy<sup>3+</sup> is an efficient lamp phosphor. Bismuth absorbs UV energy and transfers it to Gd. The energy migrates in Gd sub-lattice and is finally transferred to Dy<sup>3+</sup>. YVO<sub>4</sub>: Dy<sup>3+</sup> is another lamp phosphor. Dy doped phosphors are also useful in dosimetry of ionizing radiation using thermoluminescence. CaSO<sub>4</sub>: Dy, CaF<sub>2</sub>: Dy and MgB<sub>4</sub>O<sub>7</sub>: Dy are some of the phosphors used in personnel monitoring in thermoluminescence dosimetry.

#### Eu<sup>2+</sup>

The luminescence of Eu<sup>2+</sup> ions in different hosts has recently attracted much attention due to its peculiar properties. Its excitation and emission spectra are usually broadband due to transition between the 4f<sup>7</sup> (<sup>8</sup>S<sub>7/2</sub>) ground state and the crystal field components of the 4f<sup>6</sup> 5d excited state configuration [122,123]. Eu<sup>2+</sup> emission results from two types of transitions. The most common is that due to 4f<sup>6</sup> 5d → 4f<sup>7</sup> (<sup>8</sup>S<sub>7/2</sub>). As the position of the band corresponding to 4f<sup>6</sup> 5d configuration is strongly influenced by the host, the emission can be anywhere from 365 nm (e.g. in BaSO<sub>4</sub>) to 650 nm (e.g. in CaS). Blasse [124] has listed the Eu<sup>2+</sup> doped compounds, which shows that the emission colour of Eu<sup>2+</sup> can vary in a broad range, from ultraviolet to red.

Since 4f - 5d transition is an allowed electrostatic dipole transition, the absorption and emission of Eu<sup>2+</sup> is very efficient in many hosts, which makes the Eu<sup>2+</sup> doped phosphor of practical importance. Though both the excitation and emission originate in allowed transitions, the decay time is not very short as in Ce<sup>3+</sup>, but of the order of fraction of ms; the reason being that, the transitions are not of purely f - d type, but some

admixture of other states. When  $4f^6 5d$  band is higher than  ${}^6p_j \rightarrow {}^8S_{7/2}$  transitions are observed. These transitions have longer decay time; of the order of several ms. In many compounds  $d - f$  emission is observed at room temperature, while at low enough temperatures sharp line  $e - f$  emission become dominant.

In the octahedral site, the absorption of  $\text{Eu}^{2+}$  arises from the crystal field split  $e_g$  and  $t_{2g}$  states of  $4f^6 5d$  configuration, which can be further split when the site symmetry becomes lower. For the host lattices, which have more than one crystallographic site available for divalent europium ions, the energy transfer usually takes place between the equivalent  $\text{Eu}^{2+}$  centres. This phenomenon has been observed by many researchers [125,126], and was discussed by Blasse *et al.* [127-129]. Two-photon excitation reveals the excited states of  $\text{Eu}^{2+}$ ,  $f - f$  configuration, lying higher than the  $4f^6 5d$  band, as was found in the first two-photon spectroscopic study of rare earth ion [130].

### LUMINESCENCE OF SULPHATES

Sulfates are known to be good photoluminescence and thermoluminescence materials.  $\text{CaSO}_4$ : Dy is an efficient phosphor that it is used in thermoluminescence dosimetry for ionizing radiation [131]. Alkaline earth sulfates activated with rare earth ions are known as phosphors for use in thermoluminescence dosimetry, imaging plates, and thin film electroluminescence displays [132-135]. Alkaline earth sulfates activated with  $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$  ions are promising candidates for optical information storage [136]. Gong *et al.* [137,138] show the influence of  $\gamma$ -ray irradiation on the crystal structure and photoluminescence (PL) of alkaline earth sulfates nanocrystalline activated with  $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$  ions. They stated that PL quenching in alkaline earth sulfates nanocrystalline materials is due to dipole-quadrupole interaction [139]. Other than sulfate material some investigations are in progress on halosulfate based materials. In this chapter, the synthesis of  $\text{KCaSO}_4\text{Cl}$  material by solid state diffusion method and explained energy transfer mechanism in  $\text{Eu}^{2+} \rightarrow \text{Dy}^{3+}$  and  $\text{Ce}^{3+} \rightarrow \text{Dy}^{3+}$  ions in  $\text{KCaSO}_4\text{Cl}$  halosulfate new phosphors have been reported

The growth of crystals, however, is not as straightforward as it might seem at the first sight, due to the differences in solubility of the various alkali sulphates [1] and the presence of other phases [2-5]. For these reasons the compounds have sometimes been

prepared by fusing the stoichiometric mixture of the constituent alkali sulphates in platinum crucible [2]. The single crystal obtained through solutions is prone to twinning. The normal growth is in the form of pseudo-hexagonal plates composed of 60 twins [6].

Mixed alkali sulphates with equimolar compositions have most commonly been prepared through slow evaporation of aqueous solutions containing the constituent sulphates in stoichiometric proportions. Mixed sulphates obtained by forming solid solutions of sulphates have received wide attention over the last couple of decades. The interest has been generated by properties such as the intriguing phase transition sequences which offer scope for modeling, ferroelectricity, ferroelasticity, pyroelectricity and of course, the presence of super ionic conducting phases.

According to theoretical analysis, 25 structures are possible for such compounds. Several transitions between these structures some of which are ferroelectric and ferroelastic, have also been predicted, the type of the transition sequence depending on the ratio  $c/a$ . Kurzynski and Halawa [7] in their theoretical analysis of systems  $\text{AA}'\text{BX}_4$  which can crystallize in slightly modified  $\alpha\text{-K}_2\text{SO}_4$  structure have considered mixed alkali sulphates.

Alkaline earth sulfates activated with rare earth ions are known as phosphors for use in thermoluminescence dosimetry, imaging plates, and thin film electroluminescence displays [8-11]. Alkaline earth sulfates activated with  $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$  ions are promising candidates for optical information storage [12]. Gong *et al.* [13, 14] shows the influence of  $\gamma$ -ray irradiation on the crystal structure and photoluminescence (PL) of alkaline earth sulfates nanocrystalline activated with  $\text{Eu}^{3+}$  and  $\text{Sm}^{3+}$  ions.

Sulfates are known to be good thermoluminescence materials.  $\text{CaSO}_4$ : Dy is such an efficient phosphor that it is used in thermoluminescence dosimetry for ionizing radiation [15]. Other than sulfate materials some investigation going on halosulfate based materials. Klement [16] 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. Also the compounds  $\text{Na}_6\text{Pb}_4(\text{SO}_4)_6\text{Cl}_2$  [17,18],  $\text{Na}_6\text{Cd}_4(\text{SO}_4)_6\text{Cl}_2$  [19] and  $\text{Na}_{6.45}\text{Ca}_{3.55}(\text{SO}_4)_6 (\text{F}_x\text{Cl}_{1-x})_{1.55}$  [20] developed and characterized by XRD technique. Information on various mixed and halosulphates are reviewed here-

#### 3.1.1- $\text{KZnSO}_4\text{Cl}$

Gedam *et. al.* [21] studied mixed sulphate  $\text{KZnSO}_4\text{Cl}$  phosphor. The strong emission was observed in Ce, Ce $\rightarrow$ Dy, and Ce $\rightarrow$ Mn ions prepared by wet chemical method. Formation of the compound was confirmed by taking XRD pattern matched to JCPDS data. The broad band is observed at around 254 nm with prominent shoulder at around 274 nm in Ce<sup>3+</sup>. Two unresolved peaks are observed at 327 nm and 340 nm, which are assigned to the 5d $\rightarrow$ 4f transition of Ce<sup>3+</sup> ions giving maximum intensity for the excitation wavelength of 254 nm. The excitation energy matched with energy separation between the ground state and lowest state of the 5d level of the ion, shows that the lowest 5d level to the maximum.  $\text{KZnSO}_4\text{Cl}$ : Ce<sup>3+</sup>, Dy<sup>3+</sup> give very strong PL emission of Dy<sup>3+</sup> ion due to presence of Ce<sup>3+</sup> ion as a sensitizer. The PL emission spectra of  $\text{KZnSO}_4\text{Cl}$ : Ce, Dy phosphors shows Ce<sup>3+</sup> at 327 nm and 340 nm due to 5d $\rightarrow$ 4f transition of Ce<sup>3+</sup> ion Dy<sup>3+</sup> emission at 475 nm and 575 nm due to  $^4\text{F}_{9/2}\rightarrow ^6\text{H}_{15/2}$  and  $^4\text{F}_{9/2}\rightarrow ^6\text{H}_{13/2}$  transitions of Dy<sup>3+</sup> ion at excitation 254 nm. The sufficient energy transfer from Ce<sup>3+</sup> to Dy<sup>3+</sup> ions was observed in  $\text{KZnSO}_4\text{Cl}$  lattice. The similar results of PL enhancement of Dy<sup>3+</sup> emission were reported in 1999 by Lakshmanan [22] in  $\text{CaSO}_4$  lattice. The Mn<sup>2+</sup> emission is observed due to energy transfer from Ce<sup>3+</sup> to Mn<sup>2+</sup> ion in this host. Generally, Mn<sup>2+</sup> activated phosphors are divided in to two classes; those with green emission and those with orange to red emission [23, 24].

Recently, M.G. Brik *et. al.* in 2011 [25] reported 4f $\rightarrow$ 5d excitation and 5d $\rightarrow$ 4f emission spectra of Ce<sup>3+</sup> in  $\text{KZnSO}_4\text{Cl}$ ,  $\text{NaMgSO}_4\text{F}$  and  $\text{Na}_3\text{SO}_4\text{F}$  halosulphate phosphors. Comparatively studied electron-vibrational interaction [EVI] of the cerium 5d state with host lattices. Parameters of EVI such as Huang-Rhys factor, effective phonon energy were evaluated and positions of zero phonon lines were estimated. Emission band shapes of above phosphors modeled to confirmed validity of the obtained results.

### 3.1.2- $\text{KMgSO}_4\text{Cl}$

The  $\text{KMgSO}_4\text{Cl}\cdot 2.75\text{H}_2\text{O}$  materials have the historical name Kainite [26]. The compounds  $\text{KMgSO}_4\text{Cl}$ : (pure),  $\text{KMgSO}_4\text{Cl}$ : (Ce, Ce; Dy, Ce; Mn and Eu) phosphors were prepared by wet chemical method showed very strong emission and energy transfer also took place [27]. PL excitation spectra of Ce<sup>3+</sup> phosphor shows broadband is observed at 254 nm with a prominent shoulder around 274 nm ( $\lambda_{\text{em}}=340$  nm). The PL emission spectra of Ce<sup>3+</sup> ions in  $\text{KMgSO}_4\text{Cl}$  phosphors with different concentration under 254 nm

shows two unresolved peaks at 327 nm and 340 nm, which are assigned to the 5d $\rightarrow$ 4f transition of Ce<sup>3+</sup> ions. Energy transfer between pairs of rare earth ions at dilution levels below the self-quenching limits take place through multipolar interactions like dipole-dipole interactions or dipole-quadrupole interaction [28-30].

Ce<sup>3+</sup> ion can be used as a sensitizer as well as an activator, depending on the splitting of the 5d excited levels by the crystal field symmetry. Much work has been done on the energy transfer from Ce<sup>3+</sup> to different activator ions in different host lattice [31-33]. A strong PL emission of Dy<sup>3+</sup> ions was observed at 482 nm and 571 nm in  $\text{KMgSO}_4\text{Cl}$ :Ce,Dy phosphor due to presence of Ce<sup>3+</sup> ion, as a sensitizer. Dy<sup>3+</sup> emission at 482 nm and 571 nm is due to  $^4\text{F}_{9/2}\rightarrow ^6\text{H}_{15/2}$  and  $^4\text{F}_{9/2}\rightarrow ^6\text{H}_{13/2}$  transitions of Dy<sup>3+</sup> ion at excitation 254 nm.

The excitation spectra of  $\text{KMgSO}_4\text{Cl}$ :Ce,Dy shows the broad band in UV region of spectrum containing excitation of Ce<sup>3+</sup> (254 nm) and emission of Ce<sup>3+</sup> at 327 nm and 340 nm occur due to energy transfer from Ce<sup>3+</sup> to Dy<sup>3+</sup> ions. The emission spectra of the  $\text{KMgSO}_4\text{Cl}$  host overlap with excitation spectrum of Dy and this provides the fundamental condition for energy transfer from Ce<sup>3+</sup> to Dy<sup>3+</sup> ions in  $\text{KMgSO}_4\text{Cl}$ . This host is also suitable for the Ce<sup>3+</sup> $\rightarrow$ Mn<sup>2+</sup> energy transfer. The Mn<sup>2+</sup> ions show a green emission when located on a tetrahedral site while they show a red emission when located on an octahedral site. Therefore the doped Mn<sup>2+</sup> ion may substitute tetrahedral Mn<sup>2+</sup> sites in the halosulphate structure composition.  $\text{KMgSO}_4\text{Cl}$ : Ce<sup>3+</sup>, Mn<sup>2+</sup> new halosulphate phosphor was synthesized by wet chemical method. The PL characteristics of phosphors did not show individual Mn<sup>2+</sup> emission. Strong Mn<sup>2+</sup> emission observed at 560 nm due to transition of  $^4\text{T}_1\rightarrow ^6\text{A}_1$  of Mn<sup>2+</sup> ion in  $\text{KMgSO}_4\text{Cl}$ : Ce, Mn phosphor.

Photoluminescence (PL) excitation spectra of  $\text{KMgSO}_4\text{Cl}$ :Eu shows broadband at around 254 nm. The PL emission spectra of Eu<sup>2+</sup> ion observed at around 445 nm. The strong PL emission of Eu<sup>2+</sup> ion is observed in  $\text{KMgSO}_4\text{Cl}$  phosphor, the dopant ions Eu<sup>2+</sup> instead of giving a single emission peak, give bands around 445 nm arising from transitions of the 4f<sup>6</sup>5d configuration to the  $^8\text{S}_{7/2}$  level of the 4f<sup>7</sup> configuration [34,35]. The spectrum also has small shoulders around 420 nm and 435 nm. As per an encyclopedia Britannia company (Merriam-webster), Kainite  $\text{KMgSO}_4\text{Cl}\cdot 3\text{H}_2\text{O}$  is a natural salt consisting of hydrous sulphate and chloride of magnesium and potassium that is used as a fertilizer

and as a source of magnesium and potassium compounds.

### 3.1.3-NaMgSO<sub>4</sub>F

The NaMgSO<sub>4</sub>F:2H<sub>2</sub>O materials has mineralogical and historical name Uklonskovite and that of Name SO<sub>4</sub>F is Anhydrouklonskovite. As per the data available of crystal structure of Anhydrouklonskovite [36]. The Symmetry class: monoclinic-beta; Space group: P 2(1)/m; unit cell parameters: a = 7.2020, b = 7.2140, c = 5.7340, beta = 113.2300; number of formula unit (Z) = 2; unit cell volume (V<sub>c</sub>) = 273.76 Å<sup>3</sup>; number of atomic position per full Unit Cell (P/U) = 28; molar volume (V<sub>m</sub>) = 82.45 cm<sup>3</sup>/mol; Number of reflexes used in structure determination (NR) = 655; X-ray density (ρ) = 2.45 g/cm<sup>3</sup>; R-factor(R) = 0.0230; wavelength for calculated powder diffraction patterns (Cu) = 1.54056, mass attenuation coefficient (μ/p) = 29.397 cm<sup>2</sup>/g; theta-interval for CPDP: T/I = 1-45.

NaMgSO<sub>4</sub>F (pure); NaMgSO<sub>4</sub>F (Ce, Ce; Dy and Ce; Mn) phosphors prepared by a wet chemical method [37]. The PL excitation spectra of NaMgSO<sub>4</sub>F:Ce<sup>3+</sup> phosphor (λ<sub>em</sub> = 341nm) shows broadband at around 254nm with a prominent shoulder around 267,253 and 237 nm. The PL emission spectra of Ce<sup>3+</sup> ions in NaMgSO<sub>4</sub>F phosphors with different concentration under excitation of 254 nm wavelength of light. Two unresolved peaks are observed at 327nm and 341nm, which are assigned to the 5d→ 4f transition of Ce<sup>3+</sup> ions. The intensity 327nm is less as compared to 341nm peak. With increasing concentration of Ce<sup>3+</sup> ions the peak intensity of 341nm, increases the maximum intensity observed for 10 mole% concentration of Ce<sup>3+</sup> ions. This indicates that the NaMgSO<sub>4</sub>F lattice is more suitable for higher concentrations of Ce<sup>3+</sup> ions. The PL emission spectra of NaMgSO<sub>4</sub>F: Ce<sup>3+</sup> phosphor show very strong Ce<sup>3+</sup> emission at 327 and 341nm due to 5d→ 4f transition of Ce<sup>3+</sup> ions. The NaMgSO<sub>4</sub>F: Ce phosphor may be useful candidate for scintillation applications. Polycrystalline halosulphate phosphors NaMgSO<sub>4</sub>F:(Ce→Mn;Ce→Dy; Cu) by a wet chemical method and studied for thermoluminescence (TL) characteristics.

I.M. Nagpure et.al. [38] synthesized NaMgSO<sub>4</sub>F: Eu by wet chemical method. The strong PL excitation and emission spectra were observed. The sharp excitation peak was observed at around 393 nm with prominent shoulder at around 384 nm, emission wavelength was monitored at 614 nm. PL emission of NaMgSO<sub>4</sub>F: Eu halosulphate phosphor shows Eu<sup>3+</sup> ions

is likely to be incorporated substitutionally at Na<sup>+</sup> site as ionic sizes are similar, while differences in ionic charge will result in introduction of defects and resultant increase in asymmetry. In PL emission spectrum of NaMgSO<sub>4</sub>F: Eu halosulphate phosphor strong Eu<sup>3+</sup> emission is observed, due to the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> and <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition of Eu<sup>3+</sup> ions at 594 nm and 613 nm wavelengths, under the excitation of 393 nm wavelength, and it is the characteristic of Eu<sup>3+</sup> emission in the red region. Eu<sup>3+</sup> emissions are observed in the sample and it may be useful for mercury free lamps and solid state lightening devices.

### REFERENCES

- [1] H.Kabelka and G. Kuchler *Ferroele.* 88 93 (1988)
- [2] Yu Jiang- Tsu, Tsai Shu-Fei and R.H.Chen *Phys. Rev. B* 38 11147
- [3] H.Hempel, H. Maack and G.Sorge *Phys.Stat.Solids* 110 459 (1988)
- [4] T. Walejko, P. Piscunowicz, T. Breczewski and T. Krajewski *Ferroele.* 81 1139 (1988)
- [5] T. Walejko, G. Pakulski and Z. Tuszynski *Ferroele.* 81 1143 (1988)
- [6] J.Y. Yen and Yu Jiang- Tsu, *Chinese J. Phys.* 25 572 (1987)
- [7] Kurzynski and Halawa, *American Patents* 3 506 49-492 (1968)
- [8] K.S.V.Nambi, *Science Today (India)* Dec.12 (1981).
- [9] N.Yamashita, I.Yamamoto, K.Ninagawa, T.Wada, Y.Yamashita and Nakao, *Jpn.J.Appl. Phys, Part- 1,* 24 1174 (1985)
- [10] T. Morishita, A. Ichii, M. Matsui, S. Tomomura and T. Konishi, *Jpn. J. Appl. Phys. Part-1,* 37 3992 (1998)
- [11] A. Konrad, T. Fries, A. Gahn, F. Kummer, U. Herr, R. Tideck, and K. Samwer, *Appl. Phys. Lett.* 86 3129 (1999).
- [12] T. Justel, H. Nikol and C. Ronda, *Angew. Chem. Int. Ed. Engl.,* 37 3084 (1998).
- [13] X. Gong, P. F. Wu, W. K. Chan and W. J. Chen, *J.Phys. Chem. Solids,* 61 115 (2000).
- [14] X. Gong, L. Liu, W. K. Chan and W. J. Chen, *Opto. Mater.* 15 143 (2000)
- [15] Heike Meyssamy, Karsten Riwozki, Andreas Kornowski, Sabine Naused, and Markus Haase *Adv. Mater.* 11 10 (1999)
- [16] R. Klement, *Naturewissenschaften* 27 568 (1939).
- [17] W. Schneider, *N. Jahrb. F. Miner, Monatshefte,* 284 (1967).
- [18] W. Schneider, *N. Jahrb. F. Miner, Monatshefte,* 58 (1969).
- [19] R. Perret and A. M. Bouillet, *Bull. Soc. Fr. Miner. Crystallog.* 98 254 (1975).
- [20] A. Piotrowski, V. Kahlenberg and R.X. Fischer, *J., Solid State Chem.* 163 398 (2002).

- [21] S. C. Gedam, S. J. Dhoble and S. V. Moharil, *J. Lumin* 121 450-455 (2006)
- [22] A. R. Lakshmanan, *Prog. Mater. Sci.* 44 1 (1999).
- [23] D.T.Palumbo and Jr. J.J.Brown, *J. Electrochem. Soc.* 117 1184 (1970).
- [24] D.T.Palumbo and Jr. J.J.Brown, *J. Electrochem. Soc.* 118 1159 (1971)
- [25] M. K. Brik and N. M. Avram, *Material Chem. and Phy.* 128 326-330 (2011)
- [26] *Bibliography: Dana's system of mineralogy*, 7<sup>th</sup> ED, vol. 2 596 (1951).
- [27] S. C. Gedam, S. J. Dhoble and S. V. Moharil, *J. Lumin.* 124 120 - 126 (2007)
- [28] B. C. Joshi, U. C. Pandey, *J. Phys. Chem. Solids*, 50 599 (1989)
- [29] K. C. Sobha, K. J. Rao, *J. Phys. Chem. Solids*, 57 (9) 1263 (1996)
- [30] A.K.Agrawal, N.C.Lohant, T.C.Pant and K.C. Pant, *J.Solid State Chem.* 54 219 (1984)
- [31] G. Blasse, *Prog. Solid State Chem.* 18 79 (1988)
- [32] J. M. Versteegen, J. L. Sommerdijk and J. G. Erriet, *J. Lumin* 6 425 (1973).
- [33] H. S. Kilinan, J. K. Kothe, G. Blasse, *J. Electrochem. Soc.* 134 2359 (1987)
- [34] G. Blasse *Lumin. in Inorganic solids ed B Di Bartolo (New York: Plenum) pp 457 (1978).*
- [35] S. V. Upadeo and S. V. Moharil, *J. Phys. Condens. Matter*, 7 957 (1995)
- [36] C. Sabelli *Bull. Mineral*, 108 150 (1985).
- [37] S. C. Gedam, S. J. Dhoble and S. V. Moharil, *J. Lumin.* 126 121-129 (2007)
- [38] I. M. Nagpure, S. J. Dhoble, S. V. Godbole, M. K. Bhide and R. B. Pode, *Indian J. Eng. & Material Sci.* Vol 16 pp. 181-184 (2009)
- [39] L. Fanfani, G. Giuseppetti, C. Tadini, P. F. Zanazzi, *Mineral. Mag.*, 43 753-759 (1980)
- [40] S. J. Dhoble, S. C. Gedam, I. M. Nagpure, S. V. Moharil, *J. Mater. Sci.* 43 3189-3196, (2008)
- [41] R. Klement, *Naturwissenschaften* 27 568 (1939).
- [42] W. Schneider, *N. Jahrb. f. Miner. Monatshefte*, 284 (1967).
- [43] W. Schneider, *N. Jahrb. f. Miner. Monatshefte*, 58 (1969).
- [44] R. Perret and A. M. Bouillet, *Bull. Soc. Fr. Miner. Crystallogr.* 98 254 (1975).
- [45] G. Cavaretta, A. Mottana, and F. Tecce, *Miner. Mag.* 44 269 (1981).
- [46] V. Tazzoli, *Miner. Mag.* 47 59 (1987).
- [47] F.T. Vazquez, *Cem. Concr. Res.* 15 581 (1985).
- [48] J. Fayos, D. J. Watkin, and M. Perez-Mendez, *Am. Miner.* 72 209 (1987).
- [49] G. Blasse and A. Bril, *Philips Tech. Rev.* 31 303 (1970).
- [50] G. Blasse, *Chemistry of Materials* 1294 (1989).
- [51] M.D.Shin and W.A. Sibley, *Phys. Rev. B* 29 3834(1985)
- [52] M.D.Shin and W.A. Sibley, *Phys. Rev. B* 29 3834(1985).
- [53] Th. Forster, *Discussions Faraday Soc.* 277 (1959).
- [54] Forster, *Ann. Physik*, 255 (1948).
- [55] D. L. Dexter, *J. Chem. Phys.* 21 836 (1953)
- [56] B. DiBartolo (ed.), *Radiationless Processes*, Plenum Press, New York, (1980).
- [57] G. Ajith Kumar, P.R. Biju, G. Jose, N.V. Unnikrishnan, *Mater. Chem. Phys.* 60 247 (1999).
- [58] P. Yang, M.K. Lu, D. Xu, D.R. Yuan, G.J. Zhou, *J. Lumin.* 93 101 (2001).
- [59] A. Pires, M.R. Davolos, *Chem. Mater.* 13 21 (2001).
- [60] I.-Ch. Chen, T.M. Chen, *J. Mater. Res.* 16 644 (2001).
- [61] Y.H. Lin, Z.T. Zhang, Z.L. Tang, J.Y. Zhang, Z.S. Zheng, X. Lu, *Mater.Chem. Phys.* 70 156 (2001)
- [62] W. Jia, H. Yuan, L. Lu, H. Liu, W.M. Yen, *J. Lumin.* 76/77 428 (1998).
- [63] D. Jia, J. Zhu, B. Wu, *J. Lumin.* 93 107 (2001).
- [64] B.C. Joshi, M.C. Joshi, B.D. Joshi, *J. Phys. Chem. Solids* 52 939 (1991).
- [65] R. Reisfeld, E. Greenberg, C. Jacoboni, R.D.E. Pape, *J.Solid State Chem.* 53 236 (1984).
- [66] M. Morita, D. Rau, H. Fujii, Y. Yoshita, H. Akiyama, *J.Lumin.* 87/89 478 (2000).
- [67] P. Yang, M. Lu, D. Xu, D. Yuan, G. Zhou, *Chem. Phys.Lett.* 336 76 (2001).
- [68] P. Yang, M.K. Lu, D. Xu, D.R. Yuan, G.J. Zhou, *Appl.Phys. A* 73 445 (2001).
- [69] T. Welker, *J. Lum.* 48 & 49 49 (1991).
- [70] B.M.J. Smets, *Mat. Chem. Phys.* 16 283 (1987).
- [71] B.M.J. Smets, *Adv.Nonradiative Proc. In Solids. Ed. DiBartolo, Plenum Press, N.Y., p.375. (1991)*
- [72] R. Raue, A.T. Vink and T. Welker, *Phil. Tech. Rev.* 44 335 (1989).
- [73] M.K. Crawford and L.H. Brixner, *J. Lum.* 37 48 & 49 (1991).
- [74] H Von Saggern, *Cryst. Latt. Def. Amorph. Mat.* 18 399 (1989).
- [75] W. Rossner and B.C. Grabmaier, *J. Lum.* 48 29 (1991).
- [76] Miejerink and G. Blasse, *J. Phys. D.* 24 626 (1991).
- [77] M. Ishi and M Kobayashi, *Prog. Cryst. Growth Char. Mat.*, 23 245 (1991).
- [78] Penzkoffer, *Prog. Q. Ele.* 12 291 (1988).
- [79] W.H. Byler and J.J. Maffis, *Pigment Hand book Ed. T.C. Paton, Wiley, N.Y. p. 88, (1988).*
- [80] B.R. Judd, *Operator Techniques in Atomic Spectra, McGraw-Hill, N.Y. (1963)*
- [81] R. Reisfeld and C.K. Jorgenson, *Structure and Bonding* 49, 119, *Hand book of Phys. and Chem Of RE*, Ed. K.A. Schneidner and Eyring L., North-Holland N.Y., 1-90. (1982).
- [82] J. Becqueral, *J. Radium* 4 328 (1907).
- [83] S. Huffner, *Opt. and Spectrosc. Of Transparent RE Compounds*, Acad. Press. N.Y. (1978).
- [84] C.A. Morrison and R.P. Leavitt, *Hand book of Phys. And Chem. of RE Vol.5*, Ed. K.A. Schneidner and Eyring L. North-Holland, N.Y. p. 461 (1982).
- [85] B.R. Judd, *Operator Techniques in Atomic Spectra, McGraw-Hill, N.Y. (1963)*

- [86] B.R. Judd, *Hand book of Phys. and Chem. Of RE*, Vol. 2, Ed. A. Schneider and Eyring L. North-Holland N.Y. p. 81 (1988).
- [87] B.G. Wyborne, *Spectroscopic properties of RE*, Willey, N.Y. (1965)
- [88] R.D. Peacock, *Structure and Bonding* 2283 (1975).
- [89] E.Y. Wong, O.M. Stafsadd, and D.R. Johnston, *Phys. Rev.* 131 990 (1963).
- [90] W.T. Carnall, G.L. Goodman, K. Rajnak. and R.S.Rana, *J. Chem. Phys.* 90 3443 (1992).
- [91] C.E.Schafer and C.K. Jorgenson , *J. Inorga. Nucl. Chem.* 8 143(1958).
- [92] Zhang S.Yuan and Xian Zhang, *Excited States of Transition Elements Ed-B. Jezowska, Trzebiatowska, World Scientific, Singapore.* (1989).
- [93] K. Reinfeld and C.K. Jorgenson, *Laser and excited states of RE*, Springer-Verlag, Berlin. (1977).
- [94] M. Gerloch and R.C. Slade, *Ligand field parameters*, Cambridge Uni.Press. (1977).
- [95] D.I.Newmen, *Aust. J. Phys.* 37 315 (1977).
- [96] C.K. Jorgenson and B.R. Judd, *Mol.Phys.* 8 281 (1964).
- [97] S.F. Mason, R.D. Peacock and B. Stewart, *Mol. Phys.* 30 1829 (1975).
- [98] S.F. Mason, R.D. Peacock and B. Stewart, *J. Chem. Phys.* 70 4830 (1979).
- [99] M.C. Downer, *Topics in Appl. Phys.*, Springer Verlag 65 29 (1989).
- [100] W.T. Carnall, P. R. Fields and K. Rajnak, *J. Chem. Phys.* 49 4412 (1964).
- [101] E. Loh, *Phys. Rev.* 175 533 (1968).
- [102] C. K. Jorgenson, *Mol.Phys.* 5 271 (1962).
- [103] G. Blasse and A. Brill, *Phys. Lett.* 23 640 (1966).
- [104] E. Nakazawa, *J. Lum.* 18/19 272 (1979).
- [105] A. Garcia, R.I banez and C. Faussier, *RE Spectroscopy*, World Scientific, Singapore, p. 412 1111 (1985).
- [106] G. Blasse, *Stucture and Bonding*, 26 43 (1976).
- [107] G. Blasse, *Prog. Solid State Chem.* 18 7, 9 (1988).
- [108] Botden, *Phil. Res. Rept.* 7 (1952).
- [109] G.P. Morgan and W.M. Yen, *Topics in Appl. Phys.* Springer, p. 65, 77 122 (1989).
- [110] G.Blasse , *Energy Transfer Process in Cond. Mat.*, Ed-B. DiBartolo, Plenum Press, N.Y. p. 251 (1983).
- [111] Z.J. Kiss, *Phys. Rev.*, 127 718 (1962).
- [112] R. A. Buchanan, H. F. Raid, and H. H. Luster, *J. Chem. Phys.*, 44 4063 (1966).
- [113] S. Yokomo, T. Abe and T. Hoshine, *J. Lumin.*, 24 309 (1981).
- [114] G. Blasse, and A. Brill, *J. Chem. Phys.*, 47 5139 (1967).
- [115] G. Blasse, and A. Brill, *J. Chem. Phys.*, 51 3252 (1969).
- [116] Su, Q., Z. Pei, L. Chi, H. Zhang, Z. Zhang and F. Zou, *J. Alloy. Comp.*, 25 192 (1993).
- [117] J. L. Sommerdijk, A. Brill, F.M.J.H. Hoex-Strik, *Philip. Res. Rept.* 32 119 (1977)
- [118] Chi, L., and Q. Su. *Chin, J. Appl. Chem.*, 10 27 (1979)
- [119]Quing Su., Z. Pei, J. Lin, F. Xue, *J. Alloy. Comp.*, 225 103 (1995).
- [120] G. Blasse, and B.C. Grabmaier, *Luminescent Materials.* Springre-Verlag, Berlin, 1994.
- [121] S.H.M. Poort, A. Meijerink, .and G. Blasse, *Solid State Commu.*103 537 (2000).
- [122] G. Blasse. W. L. Wanmaker, *Philips Res. Rep.*, 23 189 (1968).
- [123] Poort S.H.M., G. Blasse, *J. Lumin*, 72 247 (1997).
- [124] G. Blasse, *Lumin. Inorg. Solids*, 475 215 (1978).
- [125] G. Blasse, *Phys. Status Solidi*, B, 559 K131 (1973).
- [126] M. Leskela, T. Koskentalo, and G. Blasse, *J. Sol. Stat. Chem.*, 59 272 (1985).
- [127] G. Blasse, *J. Sol. Stat. Chem.*, 62 207 (1986).
- [128] A. Meijerink and G. Blasse, *J. Lumin*, 43 283 (1989).
- [129] A. Meijerink, J. Nuyten, and G. Blasse, *J. Lumin*, 44 19 (1989).
- [130]W. Kaiser, C. G. B. Garret, *Phys. Rev. Lett*, 7 229 (1961).
- [131] K.S.V. Nambi, *Science Today (India)* Dec.12 (1981).
- [132] N. Yamashita, I. Yamamoto, K. Ninagawa,T. Wada, Y. Yamashita and Nakao, *Jpn. J. Appl, Phys, Part-1*, 24 1174 (1985)
- [133] T. Morishita, A. Ichii, M. Matsui, S. Tomomura and T. Konishi, *Jpn. J. Appl Phys. part-1* 37 3992 (1998)
- [134]A. Konrad, T. Fries, A. Gahn, F. Kummer, U. Herr, R. Tideck, and K. Samwer, *Appl. Phys. Lett.* 86 3129 (1999).
- [135]T. Justel, H. Nikol and C. Ronda, *Angew. Chem. Int. Ed. Engl.* 37 3084 (1998).
- [136] A. Winnacker, R. M. Shellby and R. M. Macfarlane, *Opt. Lett.* 10 350 (1985).
- [137] X. Gong, P. F. Wu, W. K. Chan and W. J. Chen, *J. Phys. Chem..Solids*, 61 115 (2000).
- [138]X. Gong, L. Liu, W. K. Chan and W. J. Chen, *Opto. Mater.* 15, 143 (2000)
- [139]X. Gong, L. Liu, and W. Chen. *J. Appl, Phys;* 88 (7), 4389 (2000).