Enhancement of photoluminescence emission of Gd$^{3+}$ activated borate phosphors for phototherapy lamps: A review

M M Lanje$^1$, M M Yawalkar$^1$, J S Dahegaonkar$^2$* and S J Dhoble$^1$

$^1$Department of Physics, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur-440033, India
$^2$Department of Zoology, Sevadal Mahila Mahavidyalaya, Nagpur-440015, India

*Corresponding author E-mail: arnajid1610@gmail.com

Abstract. In this review paper, we discuss about photoluminescence emission of Gd$^{3+}$ in various inorganic phosphors. Narrow band UVB (NB-UVB) emission of Gd$^{3+}$ in 312-315 nm is well sought after in medical field to treat photo-responsive diseases like atopic dermatitis, vitiligo, psoriasis, etc. However, this 4f-4f, $^6P_1 \rightarrow ^8S_7/2$ intra-configurational transition of Gd$^{3+}$ is weak and hence needs to be sensitized. Suitable sensitizers like Bi$^{3+}$, Pr$^{3+}$ are found to enhance the PL emission of Gd$^{3+}$. Such phosphors with sensitized Gd$^{3+}$ emission is highly suitable for phototherapy lamps.

Keywords: Phototherapy, narrow-band UVB, gadolinium, sensitized luminescence.

1. Introduction

Sunlight therapy or heliotherapy, since ancient times, is used to treat various cutaneous diseases in humans. The sacred Indian book, ‘Atharva Veda’ has alluded to the treatment of leucoderma by sunlight, along with ingestion of seeds of Bavachee plants [1]. Dried mature seeds of this plant, ‘Psoralea corylifolia’ contain furocoumarins- photosensitizing psoralen compounds found beneficial for curing skin disorders [2]. The paramount benefit of sunlight is its ability to enhance the body’s vitamin D supply.

Modern Phototherapy started in 19th century, with the use of artificial light source for phototherapy by Niels Rydberg Finsen. He (1896) developed a chemical ray’s lamp and could successfully use it for the treatment of lupus vulgaris. At the Phototherapy Institute in Copenhagen, he cured over 800 patients from lupus vulgaris using carbon-arc. Finsen also called as ‘the father of ultraviolet therapy’ received Nobel Prize in medicine - the only Nobel Prize in dermatology. The award was conferred, “in recognition of treatment of lupus vulgaris with concentrated light rays” [1]. Filtered sunlight has also been reported by Slusher et. al. as safe and effective phototherapy treatment of hyperbilirubinaemia [3].

Phototherapy of hyperbilirubinaemia was first reported in ‘Lancet’, one of the oldest, medical journals in 1958 by Rochford Hospital, Essex, England. Sister Jean Ward, working as a nurse at Rochford General Hospital at Essex in England, paved the way to its discovery. Consultant paediatrician R.H. Dobbs and resident registrar Richard Cremer, described that Sister Jean,’on
warm summer days would wheel the more delicate infants out into the porch courtyard, sincerely convinced that the combination of fresh air and warm sunshine would do them much more good than the stuffy overheated atmosphere of an incubator’ [4]. Rochford Hospital continued with these experimental treatments and later, Cremer together with P.W. Perryman, a biochemist, revealed that exposure to sunlight or artificial blue light from 40W fluorescent tubes would reduce the bilirubin levels present during jaundice in newborn infants [5]. Jaundiced newborn infants in Brazil, Uruguay, Chile, Italy, France and England were treated by sunlight after Cremer’s demonstration. However, the word ‘Phototherapy’ was first used by Ferreira et al. in September 1960, on experimental treatment of 77 jaundiced infants [4,6].

1.1. Phototherapy

Phototherapy is the use of light to cure skin diseases, upon exposure to natural sunlight or man-made lamps [7]. Radiation from sun is a mixture of electromagnetic differentiations into several regions according to wavelength.

Ultraviolet (UV) wavelength band of the electromagnetic spectrum with wavelength in the range of 200–400 nm is further on the basis of its effect on the human derma:. UVA (320–400 nm) or long wave UV, UVB (280–320 nm) termed as the erythermal region, and UVC (200–280 nm) as the germicidal region. UVA region is classified as UVA1 with wavelength in the region 340–400 nm and UVA2 with 320–340 nm wavelengths. These UV radiations (UVR) are absorbed by the biological molecules called chromophores. They are biological molecules like DNA, RNA, protein or drugs [8].

UVA1 radiation has gained widespread recognition in the field of dermatology and rheumatology [9], to treat diseases like extragenital lichen sclerosus, Scleroderma, T-cell lymphoma, Lupus erythematosus etc [10]. Psoralen photochemotherapy combines the use of Psoralen - a photosensitizer and long wave UVA (near 361 nm) radiation for the treatment of multiple skin disorders [11].

Broadband UVB explained by Goeckerman in 1925 was used for many cases of psoriasis, until replaced by super-efficient Narrowband UVB which could greatly clear psoriatic lesions and reduce inflammation in the skin. This cost effective, non-immuno-suppressive treatment is ascertained as a phototherapeutic modality for the management of psoriasis. [12]. With proper selection of doses, UVC promotes wound healing. It’s lethal and mutagenic consequences causes harm to the microorganisms and at the same time preserves viability of mammalian cells [13].

Chief medical use of phototherapy also is in the treatment of hyperbilirubinemia or jaundice. Absorbed light breaks down the accumulated bilirubin into its water soluble and excretable products. Biliblankets and fibreoptic or Compact fluorescent light tubes and blue LEDs, do not produce heat and are termed medically safe for the treatment of Neonatal Jaundice. Phototherapy is being recently used for diabetic retinopathy and treatment of hair loss.

Phototherapy used in diagnosis and therapy prognosis assessment of cancer is known as Photodynamic therapy and imaging. It is also used to control or prevent photo dermatoses like polymorphus light eruption or solar urticaria. [14]. Excimer laser and Targeted phototherapy are efficient treatment modalities with lesser side-effects as they directly focus the light on targeted lesions in complex areas of body like ear, nose etc [7].

Phototherapy and Photochemotherapy are administered depending on the action spectrum of the disease. For ex: NB-UVB (311 nm) is used mostly to treat atopic dermatitis, vitiligo, psoriasis, chronic actinic dermatitis etc. Bath- PUVA is used for treating contact dermatitis, scleroderma, graft versus host disease, lichen sclerosus, etc. UVA1 is used to cure Necrobiosis lipoidica, Scleroderma, Chronic actinic dermatitis etc. Blue light spectrum is used for the treatment of hyperbilirubinemia [8].
2. Work done in phototherapy

Absorption of ultraviolet radiations by chromophores present in the skin causes production of DNA photoproducts. As a result, photochemical reactions occur that subsequently bring about biological changes essential for the repair of tissue structures. [15]. UV light from phototherapy lamps is focussed on the diseased body part. Phosphor materials activated with Eu²⁺, Pb²⁺, Gd³⁺ and Pr³⁺ are considered efficient for utilization in phototherapy lamps. Many commercial phototherapy phosphors use Gd³⁺ and Eu²⁺ as activators [16].

Trivalent Gd³⁺ has ⁸S⁷/₂ as its ground level and 6Pj, 6lj, 6Dj, 6Gj as the excited levels. Excitation of the Gd³⁺ ions from the ground to higher energy level results in ⁶P⁷/₂ → ⁸S⁷/₂ transition in NB-UVB region near 312-315 nm. Hence, Gd³⁺ is one of the suitable activators much sought after by researchers in their quest for advanced phosphors applicable in new technologies. This emission is highly suitable in medical field for the treatment of photo-responsive diseases. So, variety of host lattices are studied for Gd activator to get good Gd activated phosphors that show remarkable NB-UVB emission. Such phosphors are in great demand for phototherapy lamps to treat skin diseases like atopic dermatitis, vitiligo, psoriasis, seborrhic dermatitis, etc [17].

Borate atom has planar sp² along with three dimensional sp³ hybridized orbitals and hence can easily hold three to four oxygen atoms to shape various anionic groups. As, inorganic borates can be easily synthesized, are structurally feasible for doping on multiple cationic sites available in the host lattice, they are extensively used in research and for commercial purpose. Diversity of structure types, supreme optical quality, and low temperature of synthesis, transparent for a large range of wavelength, good chemical stability and wide band gap make borates a desired choice in phosphors for phototherapy, optical and laser devices, plasma display panels, LED etc. LaB₃O₃:Gd³⁺, Pr³⁺ and CeMgB₂O₄:Gd³⁺ are the well-recognized NB-UVB phosphors used for commercial purpose, mostly in phototherapy lamps [7,18]. Here, we discuss some of the Gd activated phosphors with their potential in phototherapy.

2.1 Gd³⁺ activated narrow band UVB emitting phosphors for phototherapy lamps

2.1.1 Ba₀.₉₇Al₂O₄:Gd₀.₀₃³⁺ phosphor

Efficacy and application of a phosphor depends on its synthesis and also on the choice of host material. Oxides are easy to synthesize, possess good thermal and chemical stability and hence are the preferred choice as the host for a phosphor. Rare-earth activated barium aluminates show high quantum efficiency, long persistent behaviour and good stability and finds enormous applications in luminescent devices like fluorescent screens, display panels etc.

Singh and co-workers [17] prepared Ba₀.₉₇Al₂O₄:Gd₀.₀₃³⁺ phosphor by combustion synthesis technique to study the emission of Gd³⁺. Though the synthesis temperature required for BaAl₂O₄ is between 900–1300°C, XRD confirmed the hexagonal phase of BaAl₂O₄, obtained by combustion synthesis at 500°C furnace temperature. Using Scherrer formula the crystallite size was calculated to be 44.21 nm. An insight was gained into the electronic structure of gadolinium ions through the EPR study. g factor presents a picture of the symmetry that exists among the dopant and the corresponding host lattice and is calculated using the EPR equation \( hν = gβB \). Here, \( h \) represents the Planck’s constant, \( ν \) is the value of microwave frequency, \( β \) stands for the Bohr magneton, and the magnetic field is given by \( B \). The \( g \) factor corresponds to symmetry between the dopant and the host lattice. Gd being a paramagnetic substance gets magnetized under the influence of external magnetic field. The spin Hamiltonian given by the equation

\[
H = g_0βB S + D[S^2z - 1/3S(S + 1)] + E(S^2 X - S^2 Y)
\]

very well explains the energy levels occupied by such Gd³⁺ ions. \( g_0βB \) S is the Zeeman term, ligand-field effects are given by second-order terms with \( D \) being the axial constant for energy-level splitting and \( E \) is the corresponding rhombic constant for a zero magnetic field.
For BaAl$_2$O$_4$:Gd$^{3+}$ the resonance signals of EPR spectrum have the effective g values as 2.14, 4.56 and 6.75. Due to spin–orbit interactions of rare earth ions and the phosphor–lattice environment, the g factors get deviated from 2.0023 - the free electron value. Paramagnetic ions present at the sites with weak ligand fields, create resonance signal with g factor of 2.14. When the ions are located at the sites of strong ligand field, resonance signals with g value greater than 2.0 is obtained. 4.56 as a g factor is obtained for a resonance signal of Gd. This indicates that a strong ligand field is present, having a coordination number less than 6 with orthorhombic symmetry.

PL excitation spectrum monitored at 314 nm emission wavelengths, depicts the characteristic Gd$^{3+}$ peaks at 244, 246, 252, 275 and 279 nm owing to intra-configurational transitions of Gd$^{3+}$ ions. Transitions from $^8S_{7/2}$ which is the ground state of the Gd$^{3+}$ ions to the excited states $^6I_6$ and $^6D_j$ are detected. PL emission spectrum is recorded for the prominent 273 nm ($^8S_{7/2} \rightarrow ^6D_j$) excitation wavelength. Emission spectrum depicts an intense narrow peak at 314 nm. This peak is attributable to Gd$^{3+}$ ions’ electric dipole $^6P_{7/2} \rightarrow ^8S_{7/2}$ transition. The present NB-UVB emission finds great importance in the medical field for the treatment of cutaneous diseases by means of phototherapy lamps [17].

2.1.2 LaPO$_4$: Gd$^{3+}$

Chauhan et. al [19] successfully prepared Gd$^{3+}$ activated inorganic lanthanum phosphate (LaPO$_4$) by recrystallization method. PL excitation spectra of LaPO$_4$:Gd$^{3+}$ phosphor was recorded at room temperature by monitoring the 312 nm emission wavelength. The spectra depicts strong absorption peak at 275 nm. Upon excitation at 275 nm wavelength, the phosphor emits magnificently at 312 on account of $^6P_J \rightarrow ^8S_{7/2}$ Gd$^{3+}$ ions transition. Maximum concentration of Gd$^{3+}$ ions that produced intense emission in LaPO$_4$:Gd$^{3+}$ phosphor was found to be 0.04 mol%. Critical distance $R_0$ for LaPO$_4$:Gd$^{3+}$ phosphor was estimated to be 15.37 Å and the Stokes shifts was 4312 cm$^{-1}$. This narrow band UVB emitting, LaPO$_4$: Gd$^{3+}$ luminescent material has good potential as a phototherapy lamp phosphor [19].

2.1.3 SrY$_2$O$_4$: Gd$^{3+}$

Recently, Singh et. al [20] synthesized Gadolinium ion-activated SrY$_2$O$_4$ phosphors using sol-gel method. The photoluminescence spectra of the phosphor for different concentrations of Gd$^{3+}$ ions were recorded in order to get insight into the luminescence behaviour of SrY$_2$O$_4$ phosphor. Excitation of SrY$_2$O$_4$:Gd$^{3+}$ at 275 nm portrayed two bands in the NB-UVB spectral regions: one at 309 nm originated due to $^6P_{5/2} \rightarrow ^8S_{7/2}$ electric dipole transition and another at 315 nm by $^6P_{5/2}$ to $^8S_{7/2}$ transition of Gd$^{3+}$ions. The strong emission of the phosphor at 315 nm could be exploited for a NB- UV light. EPR spectra disclosed that Gd$^{3+}$ ions show variation in crystal field strength. The results confirm the utility of SrY$_2$O$_4$:Gd$^{3+}$ phosphor for phototherapy lamp applications which renders UVB light [20].

2.1.4 Na$_3$Y$_{1-x}$Si$_2$O$_7$:Gd$_x$

Gd$^{3+}$ ions occupied octahedral Y$^{3+}$ sites in the Na$_3$YSi$_2$O$_7$ host lattice. This narrow-band, ultraviolet-emitting series of another material Na$_3$Y$_{1-x}$Si$_2$O$_7$:Gdx reported by Singh et.al. [21] was synthesized using sol–gel process with Gd concentration varying between 0.01 to 0.11 mol%. On excitation at 273 nm, the developed Na$_3$Y$_{1-x}$Si$_2$O$_7$:Gdx sample exhibited an ultraviolet emission when Gd ions underwent transition from $^6P_{7/2}$ to $^8S_{7/2}$ energy state resulting in a sharp and dominant peak at 313 nm [21].
2.1.5 \( \text{CaMgP}_2\text{O}_7: \text{Gd}^{3+} \)

Low sintering temperatures, excellent thermal as well as charge stabilities have gained importance for phosphate materials as luminescent materials. Kunghatkar et. al [22] have successfully synthesized \( \text{CaMgP}_2\text{O}_7 \) phosphor with gadolinium as activator by different synthesis techniques like solution combustion, sol-gel, solid-state reaction and wet chemical. XRD, SEM, EPR, and PL were made use of to study the phosphor briefly. XRD confirms that \( \text{Gd}^{3+} \) doping does not lead to any significant variation in the crystal structure. \( \text{CaMgP}_2\text{O}_7 \) forms a monoclinic crystal structure with \( \text{P}2_1/\text{n} \) as the space group. In \( \text{CaMgP}_2\text{O}_7 \), \( \text{Ca}^{2+} \) ion shows coordination with eight oxygen ions and \( \text{Mg}^{2+} \) with six oxygen ions supplied by \( \text{P}_2\text{O}_7^{4-} \). \( \text{Gd}^{3+} \) ions may possibly substitute \( \text{Mg}^{2+} \), \( \text{P}^5^- \) or \( \text{Ca}^{2+} \) ion site in \( \text{CaMgP}_2\text{O}_7 \) host lattice. Solid state method created irregular rod like particles with an average size of 5\( \mu \)m, sol-gel formed spherically shaped particles of 2\( \mu \)m size. Agglomerated particles of 2 \( \mu \)m were formed on adoption of solution combustion as well as wet chemical synthesis. \( \text{CaMgP}_2\text{O}_7: \text{Gd}^{3+} \) presented effective \( g \) value near to 5.88, 2.88, and 1.91 due to location of \( \text{Gd}^{3+} \) ions at sites with cubic symmetry. Photoluminescence emission at 314 nm wavelength when excited at 274 nm excitation proved proper incorporation of \( \text{Gd}^{3+} \) ions in the present host lattice. Different characterization methods revealed that good results are achieved with sol-gel and solid state and are better for the preparation of phosphate group than the remaining two methods. The phosphor prepared by all the four methods exhibited intense excitation peak at 274 nm on account of \( ^8\text{S}_{7/2} \rightarrow ^6\text{D}_{j} \) transition of \( \text{Gd}^{3+} \) ions and weak peaks at 247 nm and 253 nm due to \( ^8\text{S}_{7/2} \rightarrow ^6\text{J}_{2j} \) transitions, when monitored by its emission at 314 nm. \( ^6\text{P}_{7/2} \rightarrow ^4\text{S}_{7/2} \), the 4f-4f electric dipole transition is seen in the form of emission peak at 314 nm. Emission intensity was witnessed to increase along with dopant concentration till 7 mol\% without concentration quenching. Highest intensity was witnessed for the phosphor obtained by sol gel method with lowest intensity for the one obtained by sol-gel method. The emission in narrow band ultra violet region is applicable in phototherapy treatment and can be made intense by the use of sensitizing material for \( \text{Gd}^{3+} \) [22].

The phosphor with \( \text{Gd}^{3+} \) as the activator show weak intensity of the NB-UVB emission near 313 nm as the 4f7 transitions of \( \text{Gd}^{3+} \) has a very low absorption strength. This emission can be enhanced by adding a co-activator to the compound. This co-activator functions like a sensitizer; absorbs the energy that is incident on it and transfers to \( \text{Gd} \) ions, which subsequently emit with enhanced intensity. A suitable sensitisier, sensitizes gadolinium emission and gives a luminescent material with high efficiency [23]. Such luminescent materials with enhanced emission are discussed below.

2.2 Enhanced narrow band UVB emission of \( \text{Gd}^{3+} \) using sensitizers in borate phosphors for phototherapy lamp

2.2.1 \( \text{BaB}_8\text{O}_{13}: \text{Pr}^{3+}, \text{Gd}^{3+} \) phosphor

Sumedha et. al. [24] have reported efficient \( \text{Gd}^{3+} \) emission in \( \text{BaB}_8\text{O}_{13}:\text{Gd}^{3+} \) phosphor synthesized by solid state synthesis. Excitation spectrum consists of peaks at several wavelengths like 246 nm, 252 nm, a brilliant peak at 274 nm and 278 nm. These peaks originate on account of \( ^8\text{S}_7/2 \rightarrow ^6\text{D}_{9/2} \) transition, \( ^8\text{S}_7/2 \rightarrow ^6\text{D}_{9/2} \), \( ^8\text{S}_7/2 \rightarrow ^6\text{I}_{11/2} \) and \( ^8\text{S}_7/2 \rightarrow ^6\text{I}_{11/2} \) transition of \( \text{Gd}^{3+} \) ions respectively. Photoluminescence (PL) emission spectra obtained at the intense dominant peak of 274 nm shows brilliant and sharp 314 nm emission peak corresponding to electric dipole transition from \( ^6\text{P}_{9/2} \) to \( ^8\text{S}_7/2 \) and another 308 nm peak due to \( ^6\text{P}_{9/2} \rightarrow ^8\text{S}_7/2 \) transition. Emission intensity was reported to increase as the activator concentration was varied from 0.1 to 2 mol \%. This NB-UVB emission of \( \text{BaB}_8\text{O}_{13}: \text{Gd}^{3+} \) phosphor at 314 nm can be harnessed for curing psoriasis.

To further increase the PL intensity of 314 nm emission peaks in \( \text{BaB}_8\text{O}_{13}:\text{Gd}^{3+} \) phosphor, \( \text{Pr}^{3+} \) is used as a sensitizer. Sensitizer traps the excitation energy and gives it to the activator that produces characteristic emission with enhanced intensity. \( \text{BaB}_8\text{O}_{13}: \text{Pr}^{3+}, \text{Gd}^{3+} \) was prepared with constant \( \text{Gd}^{3+} \) concentration at 2 mol \% and varying the \( \text{Pr}^{3+} \) concentration from 0.05 to 0.05 mol.
%.$\text{Pr}^{3+}$ contribution to the PL excitation spectrum is seen in the form of a broad absorption band located at 220 nm in addition to the sharp characteristics excitation peaks of $\text{Gd}^{3+}$ ions at 246 nm, 252 nm and 274 nm produced by its 4f–4f transitions (Figure 2.8). This broad absorption band accredited to 4f$\rightarrow$4f5d transition of $\text{Pr}^{3+}$ ions generate a single narrow peak located at 313 nm with twice the intensity observed from $\text{Gd}^{3+}$ excitation at 274 nm. This phenomenon takes place when $\text{Pr}^{3+}$ sensitizes $\text{Gd}^{3+}$ emission by transfer of the absorbed energy. This energy transfer is maximum for 0.2 mol % concentration of the sensitizer in the present phosphor, further increase in $\text{Pr}^{3+}$ concentration leads to concentration quenching which decreases the emission. $\text{BaB}_8\text{O}_{16}$: $\text{Pr}^{3+}$, $\text{Gd}^{3+}$ possess capability that can be exploited for phototherapy lamps [24].

2.2.2 (LaY)$\text{BaB}_6\text{O}_{16}$:$\text{Bi}^{3+}$,$\text{Gd}^{3+}$

Gawande et al. [25] studied (LaY)$\text{BaB}_6\text{O}_{16}$:$\text{Bi}^{3+}$,$\text{Gd}^{3+}$ prepared by solution combustion synthesis technique with La= 0.78, Y=0.1, Bi=0.02 and Gd =0.1 mol%. XRD confirms hexagonal crystal structure of the compound well matching with ICDD file no: 00-041-0620 having the lattice parameters as a = b = 7.878 Å, c = 15.632 Å. SEM images reveal the irregular agglomerated grains with average particle size in the range of 1–5 μm. The PL excitation spectrum monitored at 312 nm reveals a broad peak, with tremendous intensity with maximum at 260 nm, on account of $^1\text{S}_0$ to $^3\text{P}_1$ transition of $\text{Bi}^{3+}$ ions. Emission spectrum was studied at 254 nm, as it coincides with the Hg excitation at 253.7 nm. It consists of $^6\text{P}_{7/2}$ – $^8\text{S}_{7/2}$ generated emission peak of Gd ions at 312 nm. The competent energy transfer from $\text{Bi}^{3+}$ ions to that of $\text{Gd}^{3+}$ results in considerable increase of the $\text{Gd}^{3+}$ emission intensity in (LaY)$\text{BaB}_6\text{O}_{16}$:$\text{Bi}^{3+}$,$\text{Gd}^{3+}$ compound [25].

2.2.3 $\text{Y}_{0.96}\text{Gd}_{0.04}\text{BO}_3$ phosphor, $\text{Y}_{0.95}\text{Gd}_{0.05}\text{Bi}_{0.005}\text{BO}_3$ phosphor and $\text{Y}_{0.99}\text{Gd}_{0.00}\text{Pr}_{0.00}\text{BO}_3$ phosphor

Gawande et al. [26] also carried out PL study of gadolinium in $\text{YBO}_3$ compound and energy transfer with Bi and Pr as sensitizers. The XRD patterns of these three synthesized materials, was found to be according to the ICDD file no. 01-088-0356 with hexagonal crystal structure. Surface morphological study revealed irregular grains with size about 4–10 μm. In $\text{YBO}_3$: $\text{Gd}^{3+}$ phosphor, $\text{YBO}_3$: $\text{Gd}^{3+}$,$\text{Bi}^{3+}$ phosphor and $\text{YBO}_3$: $\text{Gd}^{3+}$,$\text{Pr}^{3+}$ phosphor a narrow band UVB emission is reported at 312 nm that is due to $^6\text{P}_{1}$$\rightarrow$ $^8\text{S}_{7/2}$ transition by $\text{Gd}^{3+}$ ions. Excitation peak was witnessed at 276 nm for $\text{YBO}_3$: $\text{Gd}^{3+}$, 260 nm at $\text{YBO}_3$: $\text{Gd}^{3+}$-$\text{Bi}^{3+}$ attributable to $^1\text{S}_0$ to $^3\text{P}_1$ transition by $\text{Bi}^{3+}$ ions and at 250 nm that corresponds to the intra-configurational 4f2 - 4f1 5d1 transition of $\text{Pr}^{3+}$. Excitation of $\text{YBO}_3$: $\text{Gd}^{3+}$, $\text{Bi}^{3+}$ phosphor and $\text{YBO}_3$: $\text{Gd}^{3+}$,$\text{Pr}^{3+}$ phosphor is near to mercury excitation of 253.7 nm. In $\text{YBO}_3$: $\text{Gd}^{3+}$, 0.04 mol % of $\text{Gd}^{3+}$ concentration produces highest intensity and the same is reported for 0.005 mol % of sensitized $\text{Bi}^{3+}$ doped in $\text{YBO}_3$: $\text{Gd}^{3+}$-$\text{Bi}^{3+}$ and 0.03 mol % $\text{Pr}^{3+}$ sensitizer ions in $\text{YBO}_3$: $\text{Gd}^{3+}$,$\text{Pr}^{3+}$ relative to Y. The Stokes’ shift was reported as 481 cm$^{-1}$ for $\text{Gd}$ doping$^{3+}$ 6410 cm$^{-1}$ for $\text{Gd-Bi}$ doping & 7949 cm$^{-1}$ for $\text{Gd-Pr}$ doping in the three phosphors. The intensity of narrow band UVB $\text{Gd}^{3+}$ emission at 312 nm in $\text{Y}_{0.95}\text{Gd}_{0.00}\text{Bi}_{0.005}\text{BO}_3$ was examined to be almost 4 times that of $\text{Y}_{0.95}\text{Gd}_{0.00}\text{Bi}_{0.005}\text{BO}_3$ and nearly 30 times greater than $\text{Y}_{0.99}\text{Gd}_{0.00}\text{BO}_3$. This proves that an efficient energy transfer from $\text{Bi}^{3+}$ and $\text{Pr}^{3+}$ to $\text{Gd}^{3+}$ takes place, however $\text{Pr}^{3+}$ proved to be better sensitizer for $\text{Gd}^{3+}$ ions than $\text{Bi}^{3+}$ [26].

2.2.4 $\text{LiSr}_{1-x-y}(\text{BO}_3)_x$:$\text{Gd}^{3+}$, $y\text{Pr}^{3+}$

Chauhan et al. [27] also studied the enhancement of $\text{Gd}^{3+}$ emission with the aid of $\text{Pr}^{3+}$ as the sensitizer. $\text{Pr}^{3+}$ shows a broad emission band in 260- 370 nm, which very well overlaps the excitation of $\text{Gd}^{3+}$ at 276 nm. This ensures a proper transfer of energy from $\text{Pr}^{3+}$ to $\text{Gd}^{3+}$. As a result, at an excitation wavelength of 245 nm, PL emission intensity of 313 nm $\text{Gd}^{3+}$ peak at increases as compared to single doping of $\text{Gd}^{3+}$ in $\text{LiSr}_4(\text{BO}_3)_3$ phosphor. Optimum concentration of the sensitizer was noted to be 0.01 mol % for 0.04 mol % of $\text{Gd}$. Thus $\text{Pr}^{3+}$ proves to be a good sensitizer for $\text{Gd}^{3+}$ and makes the phosphor suitable for phototherapy lamps [27].
3. Conclusion

Narrow band UVB emission is widely adopted worldwide for phototherapy as it matches the action spectrum of several skin disorders and is safe even for several exposures. Gadolinium doped phosphors are gaining widespread attention because of their narrow band emission on UV excitation. However, the challenge posed by its weak 4f-4f emission is countered by using a suitable sensitizer. Bi$^{3+}$, Pr$^{3+}$ prove to be good sensitizers for Gd$^{3+}$ as their emission spectrum overlaps the excitation spectrum of gadolinium. This ensures a successful energy transfer from the sensitizer to the activator gadolinium. Sensitized luminescence of gadolinium doped phosphors thus exhibit magnificent emission with increased emission intensity and is better suited to be used in phototherapy lamps.

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