Review article

Exploring Gd^{3+}-activated calcium-based host materials for phototherapy lamps: A comprehensive review

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ABSTRACT

Apart from the use of sun therapy for the cure of many skin diseases and disorders of bygone days, nowadays artificial light sources of a narrowband (NB) ultraviolet-B (UV–B) have effectively revolutionized the treatment of such skin diseases. The crucial role of gadolinium (Gd^{3+}) ions in calcium-based hosts lies in their narrowband emission spectrum, specifically at 311–315 nm, attributed to the $^6P_{7/2}$ to $^8S_{7/2}$ transition. Calcium-based materials, known for their chemical stability, facilitate Gd^{3+} embedding, enabling UV activation and express emission in the narrowband range. This emission spectrum is well-suited for skin treatments, aligning with the action spectrum of various skin diseases. Gd^{3+} activated host materials in fluorescent lamps are considered prime sources of NB-UVB emissions. Calcium-based host materials are proving to be popular environments for embedding of dopants for such emissions. Calcium-based phosphor materials are leading the research in phototherapy applications due to their strong UV-B emissions, especially when activated by Gd^{3+} ions. Applications of phosphor host materials of this nature are generally chemically and thermally stable, have a low synthesis temperature and which produce enhanced NB-UVB emissions specifically suited for phototherapy lamps. This paper is a review of calcium -based phosphor host materials in Gd^{3+} activated materials or through energy transfers from sensitized dopant ions for enhanced NB-UVB emissions that is pertinent for treatments of many skin diseases such as psoriasis, vitiligo, eczema, and many other skin conditions.

1. Introduction

Skin diseases are generally known to be among the main ailments found around the world. There are up to 100 types of skin dermatoses, such as atopic dermatitis, psoriasis, morphia, scleroderma, vitiligo, solar urticaria, cutaneous T-cell lymphoma, acne vulgaris, lupus erythematosus, etc. [1,2]. The use of artificial ultraviolet (UV) light to cure and treat skin diseases is called phototherapy [3]. Phototherapy uses constricted light in a narrowband region as an alternative source of UV light instead of sunlight. Niels Finsen was one of the first people to use UV light to cure cutaneous tuberculosis. He subsequently received the Nobel Prize for his groundbreaking research in the field of phototherapy [4]. Of the many skin diseases that are prevalent around the world, psoriasis can be regarded as one of the most chronic non-contagious ailments, affecting approximately 9–11 % of the world population [1,5,6]. To effectively treat these diseases, we need to use phototherapy lamps, which makes use of UV light. UV light is classified into three broad regions [7,8]:

UV-C: which ranges from 200 nm to 280 nm,

UV-B: which ranges from 280 nm to 320 nm, and.

UV-A: which ranges from 320 nm to 400 nm.

Of the various ranges of UV light, UV-C can be regarded as dangerous for the skin, while the other two groups, UV-B and UV-A, can be considered biologically safe for treating skin ailments in humans [3,4,6]. If the UV-B light range is further narrowed to a band region of 311–315 nm, this type of light is found to be most therapeutically valuable in medical dermatology. It was found that light emissions at the 313 nm wavelength was most responsive to human skin tissues with minimal erythemal side effects [1,4,9]. Furthermore, this narrowband region was found to have an antiproliferative effect on the human skin, implying that cell division or growth is inhibited [4,6,10]. One could also say that the impact of this light on skin tissues or cells contributes to skin rejuvenation because it aligns with the action spectrum of various skin ailments [9]. In general, phosphor materials, in the form of inorganic hosts doped with small amounts of impurities such as rare-earth ions Ce^{3+}, Pr^{3+}, Gd^{3+}, and Eu^{2+}, are used in the manufacture of phototherapy lamps. In most cases, Gd^{3+} ions act as an activator due to their UV-B (non-erythemal region) emissions, while the others act as sensitizers. The role of activators is to absorb excitation energy and transfer it to the host or sensitizers. In terms of band structure, activators absorb excitation energy, allowing them to be excited to a higher quantum state where they remain unstable and are subsequently de-excited to the ground state with the emission of photons. The chemical features of Gd^{3+} activator ions include an electronic configuration of $[Xe]^4f_75d^16s^2$, where the $^4f_7$ electrons are shielded from the outer 5 p and 6 s^2 outer shells. The 7 electrons in the 4f orbital of Gd^{3+} ions have a spin angular momentum of $\mathbf{S} = 7/2$, an orbital angular momentum of $\mathbf{L} = 0$, and a total angular momentum of $\mathbf{J} = \mathbf{S} + \mathbf{L} = 7/2$, with the ground state referred to as $^8S_{7/2}$ [3,11]. The higher excited states of Gd^{3+} ions are ^6P_J, ^6D_J, ^6I_J, or ^6G_J [11]. Mostly, Gd^{3+} ions are known to produce weak sharp (4f - 4f) emissions due to their parity-forbidden nature and therefore need to be sensitized (Ce^{3+}, Pr^{3+}, Pb^{2+}, Bi^{3+}) to enhance their fluorescence emission intensity in the NB-UVB region [11]. The role of sensitizers is to absorb excitation energy and transfer it to the Gd^{3+} activators, thereby producing enhanced NB-UVB emissions. Thus, the NB-UVB emission at 313 nm (most common) corresponds to the $^8P_{7/2} \rightarrow {}^8S_{7/2}$ transition from the metastable state to the ground state [12].

The use of Gd^{3+}-activated calcium-based host materials in this review is significant because when calcium Ca^{2+} ions (0.114 nm), having a similar radius to that of Gd^{3+} ions (0.120 nm), it causes minimal crystal distortions [13–17]. Furthermore, the use of wide band-gap calcium-based host materials doped with Gd^{3+} ions for NB-UVB emissions, results in a distinctive U-type electron para-magnetic resonance (EPR) spectra, supporting the idea that these materials can generate UV-B emissions for various dermatological applications [18,19]. It must be mentioned that not all calcium-based host compounds are inherently biocompatible, but certain compounds, such as hydroxyapatite calcium phosphates, are well-documented for its superior biocompatibility properties. In this review, we selected Gd^{3+} activated calcium-based host materials, which in some cases may favour biocompatibility. This approach ensures that the selected materials exhibit both the desired UV-B emitting properties and maybe have biocompatibility properties, making them suitable for dermatological applications [18,20,21].

Hydroxyapatite calcium phosphates were found to closely replicate the mineral composition present in the body and are thereby considered to be well tolerated by the skin, with minimal erythemal effects [20,22]. Other calcium compounds, such as calcium magnesium silicate were found to be just as useful in dermatology due to it having superior physical and chemical properties, which are cost-effective in their preparation, have excellent water resistance properties and have a strong absorption in the UV region. These are just some good examples about calcium-based materials because they might have some biocompatible properties, which makes them better suited for various skin treatments. In this review, we will focus on about all calcium-based compound that are available in the literature for applications in phototherapy.

In this review, we will focus on calcium-based host materials that produce NB-UVB emissions around 313 nm for the following reasons (although non-calcium-based materials can also be effective in phototherapeutic treatments of many skin diseases, just mentioned here for comparative purposes):

(a) Gd^{3+} as an activator and the use of sensitizers
(b) Role of calcium in different host materials
(c) Choice of host materials
(d) UV excitation and emission wavelengths
(e) Different synthesis methods
(f) Thermal and chemical stability

2. Gd^{3+} doped Ca-based host materials for NB-UVB emissions

(a) Gd^{3+} as an activator and the use of sensitizers

Many rare-earth ions such as Ce^{3+}, Pr^{3+}, Eu^{2+} could be used as activators, but our choice of Gd^{3+} ion is ideal for phototherapy lamps. Gd^{3+} ions are preferred mainly due to the narrowband emission peak at 313 nm, which is not possible by other rare-earth ions. Gadolinium has a large optical energy gap between its stable ground state and its first excited state (about, 32000 cm^{-1}). Gd^{3+}, with a $^4f_7$ electronic configuration and its 4f-4f transitions that are parity forbidden, is shielded from the outer 5s and 5p shells. This allows Gd^{3+} activated hosts materials to produce weak, sharp emissions at around 313 nm ($^6P_{7/2} \rightarrow {}^8S_{7/2}$). Thus, Gd^{3+}ion will require a sensitizing dopant ion so that its energy can be transferred non-radiatively to Gd^{3+} ion, in producing enhanced single line emission at 313 nm [11]. Many sensitizers, such as Sb^{3+} [23,24], Bi^{3+} [25], Pb^{2+} [26] and Pr^{3+} [26] ions, were found to effectively enhance the UV-B emissions of Gd^{3+} activated host materials. The role of these sensitizers was to effectively transfer the excitation energy to Gd^{3+} activator ions in various host materials. Of these sensitizer ions, Pr^{3+} was optimally used as a co-dopant ion for its intensity

enhancement, an illustration of such an energy transfer process between Pr^{3+} and Gd^{3+} ion, is shown in Fig. 1 below [4]. Gd^{3+} ion, as an activator, produces a magnetic dipole transition at around 308 nm and an electric dipole transition at around 313 nm. A similar energy diagram scheme is also reflected in Ref. [27].

(b) Role of calcium in different host materials

Calcium-based host materials play an important part in the development of phototherapy lamps when used in conjunction with Gd^{3+} ions. The replacement of Ca^{2+} ions with Gd^{3+} ions and the resulting UVB-emitting properties are accountable for the material's effectiveness in phototherapy. Much research is focused on biomaterials, such as hydroxyapatites [$Ca_5(PO_4)_3OH$] in which Ca is an important ingredient [28]. Ca-based host materials have been used in conjunction with Gd^{3+} ions because of the similarity of their ionic radii; however, due to their different valences, additional mechanisms are required to address the resulting charge imbalances, such as charge compensators, which would be typically found in group 1 elements. If Gd^{3+} replaces Ca^{2+} in the phosphor host material, the role of calcium in absorption becomes redundant, when the host material already exhibits efficient absorption characteristics in the UV range. This was observed for the $Ca_2P_2O_7$ host material [29]. By co-doping these materials with Gd^{3+} ions, offers these materials an opportunity to enhance its narrowband UV-B emissions that are important in phototherapy lamps. Furthermore, the presence of Ca^{2+} ions in the host materials provides chemical and thermal stability. In many electrons spin resonance (ESR) studies, it was determined that Gd^{3+} ions could effectively replace Ca^{2+} ions but with some level of distortion of the crystal fields [30]. Calcium-aluminum-based compounds exhibit three phases, namely, $CaAl_2O_4$, $CaAl_4O_7$, and $Ca_{12}Al_{14}O_{33}$ in the phase diagram [31]. Amongst these phases, $CaAl_4O_7$ compounds doped with Gd^{3+} ions have found useful applications in phototherapy lamps.

(c) Choice of host materials

Several host materials, such as borates, phosphates, aluminates, oxides, and sulphates doped with Gd^{3+} as an activator, were found to be effective in phototherapy applications [26]. Calcium composite compounds have been mostly studied for their biomedical applications (see Table 1). They possess unique properties with advanced benefits. The emission of UV-B light emanates from phosphor materials that are encapsulated in the fabric of the lamp. When the patient is exposed to this light, in addition to its healing properties, some calcium-based host materials are biocompatible, which minimizes the risk of potential exposure and adverse reactions and mitigates against any toxic effects [32]. These compounds, when doped with rare earth ions such as Gd^{3+} ions can be used as light emitting materials that find focused use in phototherapeutic applications as well. The ionic radius of Ca^{2+} is 0.118 nm, while that of Gd^{3+} is 0.1107 nm, which is different for substitutional replacement. Thus, we will need 2 ions of Gd^{3+} and one ion of Li^+ (0.092 nm) to bring about charge compensation. In terms of an equation, we have $2V_{Ca}^{2+} + Gd^{3+} + Li^+ \rightarrow Gd^{3+} + Li^+$, showing how the vacancy can be compensated by group 1 elements (Na^+, Li^+, K^+, etc.) [4]. However, substitutional replacements of ions of similar radii will depend on the coordination number as well as information of the environment of the ions in which they are situated. EPR and ESR studies will confirm the positioning of Gd^{3+} by Ca^{2+} ions. Apart from these compounds having relevance for phototherapeutic applications, calcium-based compounds are capable of absorbing UV or visible light with steady release in the visible region with prolonged afterglow effects, long after the excitation source is switched off, is referred to as persistence luminescence. Not all Gd^{3+} activated calcium host materials display persistence luminescence. However, if the patient is exposed to extended UV-B radiation, it could have potential side effects. Therefore, is advisable to monitor the UV-B radiation in a controlled manner and with limited time usage for optimal therapeutic results. Such observation was made for the $CaSnO_3$:Gd^{3+} phosphor material [33], where cyan afterglow effects were observed for 73.9 s.

Other alkaline (Ba, Sr) elements having charges of +2, which are found in group 2 like the charge of Ca, and which are part of the phosphor host compound, and which finds applications in phototherapy, are also discussed below to draw comparisons of elements in the same group.
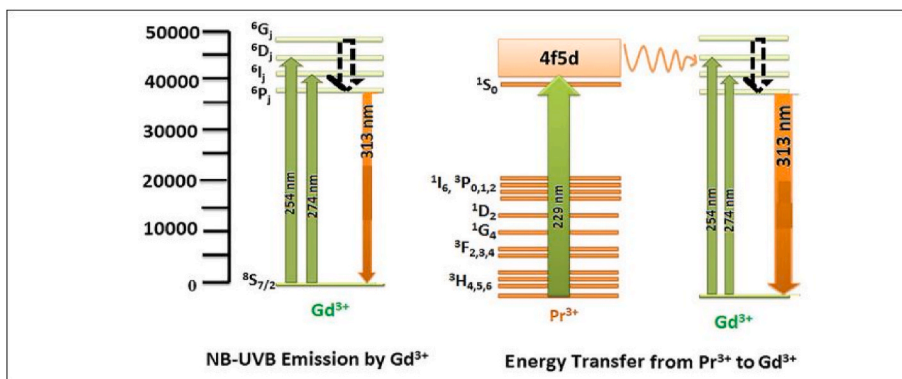

Fig. 1. Shows the energy transfer from Pr^{3+} (sensitizer) ions to Gd^{3+} (activator) ions. (Reused with permission form reference [4]).

Table 1

Summary of the vital characteristics of each of these Ca-based compounds.

No	Compound	Synthesis technique	Crystal structure	Optimal Excitation wavelength (nm)	Optimal Emission wavelength (nm)	Comment
1	$NaCaPO_4:Gd^{3+}$	Solid-state reaction	Rhombohedral	274	313	The PL excitation spectra of the $NaCaPO_4$ compound, doped with Gd^{3+} ions, show an intense excitation peak at 274 nm, while the emission spectra show an intense emission peak at 313 nm (see Fig. 2 below). Since the concentration of Gd^{3+} was varied, the emission peaks display an overlapping spectrum, with the highest peak occurring at a concentration of 0.5 mol %. Furthermore, due to the differences in the atomic radii of the various ions—Na^+ (0.103 nm), Ca^{2+} (0.099 nm), and Gd^{3+} (0.094 nm)—it implies that Gd^{3+} acts as a charge compensator in achieving enhanced luminescence. The highest emission intensity is around 750 a.u., making this material a promising candidate for phototherapy applications [35].
2	$Ca_3Al_2O_6:Gd^{3+}$	Combustion	Cubic	273	314	The PL excitation spectra of $Ca_3Al_2O_6$: Gd^{3+} material consist of 6 excitation peaks, with the most intense one being at 273 nm and the one with slightly lower shoulder-type intensity located at 276 nm. Upon 314 nm excitation, this compound produces 2 characteristic peaks: one at 308 nm of very low intensity and another one of enhanced intensity at 314 nm. This material has 6 non-equivalent Ca^{2+} sites, which could become available for Gd^{3+} substitution. The ESR values indicate that Gd^{3+} ions are located at slightly distorted Ca^{2+} sites within the cubic lattice structure. The enhanced NB-UVB emission produced by this Gd^{3+} activated phosphor material can also be considered as a candidate for phototherapeutic applications [30].
3	$Ca_9RE(PO_4)_7:RE = Gd$	Solid-State Reaction	Whitlockite	273	311	Beta-tricalcium phosphate (TCP) combined with $Ca_9RE(PO_4)_7:RE = Gd^{3+}$ is classified as an interesting host candidate, especially for its luminescence characteristics. The latter has a whitlockite crystal structure, implying it has 5 distinct (M1 to M5) Ca^{2+} sites that are possible for Gd^{3+} substitution. It is indicated in this paper that sites at M1 to M3 and M5 are potential sites for Gd^{3+} substitution. The M4 site is completely vacant, while the M5 site is fully occupied by the Ca^{2+} ion. Like the previous example, the excitation spectra consist of many excitation peaks, with an intense one observed at 273 nm and another one of slightly lower intensity, shoulder-type peak at 276 nm. The emission spectra consist of an intense emission intensity peak at 311 nm, and because of the site availability in the host matrix, the luminescence intensity is accordingly affected. This material can likewise be considered as a candidate for phototherapy lamps [36].
4	$Ca_5(PO_4)_3(OH):Gd^{3+}$	Sol-gel	278	185	312	The excitation spectra of the compound reveal several intensity peaks close to

(continued on next page)

Table 1 (*continued*)

No	Compound	Synthesis technique	Crystal structure	Optimal Excitation wavelength (nm)	Optimal Emission wavelength (nm)	Comment
						each other, with the highest peak occurring at 278 nm. On the other hand, the PL emission spectra consist of several peaks, with the highest peak not being that of Gd^{3+} at 312 nm but those due to Gd–O and PO_4^{3-} components. This material is not ideal for phototherapeutic treatment of skin diseases, but this material is good for thermal and electrical conductivity. Furthermore, this material has a low Stokes shift of 16.031 cm^{-1}. To improve its therapeutic properties, it needs to be sensitized [37].
5	$Ca_5(PO_4)_3OH$: Gd^{3+}, Pr^{3+}	Co-precipitation	Hexagonal	222	313	When this same compound $Ca_5(PO_4)_3OH$: Gd^{3+} is co-doped with Pr^{3+} ion, the excitation spectra show an enhanced peak at 222 nm which is due to Pr^{3+} ion and a low intensity peak at 276 nm due to Gd^{3+} ion (see Fig. 3 below). Here Ca^{2+} occupies 2 non-symmetric sites that could be replaced by Gd^{3+} ions. The addition of Pr^{3+} ion suppresses the Gd^{3+} emission, as well as the red one at 603 nm. Enhanced emission intensity is produced at 313 nm which is due to the energy transfer from Pr^{3+} ions to Gd^{3+} ions (about 400 a.u). This happens for a concentration ratio of 10:2 (Gd^{3+}: Pr^{3+}). Comparisons of the co-doped material with the singly doped Gd^{3+} ion reveals a 5-fold increase in intensity emissions. This material is a good candidate for phototherapeutic applications [38].
6	$Ca_9Mg(PO_4)_6F_2$: Gd^{3+}, Pr^{3+}, Li^+	Combustion	Hexagonal	274	313	When $Ca_9Mg(PO_4)_6F_2$:Gd^{3+} is co-doped with Pr^{3+}, the excitation spectra show an intense peak at 229 nm due to Pr^{3+} ions and a much lower intensity peak at 274 nm due to Gd^{3+} ions (**see Fig. 4 (a) and (b) below**). The intense emission band at 313 nm is due to the energy transfer from Pr^{3+} ion to Gd^{3+} ion. The impact of the charge compensator ion (Li^+) ion is to enhance the intensity emission at 313 nm (about 900 a.u). The emission intensity is about 3 times more than that of a singly doped Gd^{3+} compound. This material is an ideal candidate for phototherapy lamps [4].
7	$CaMgP_2O_7$:Gd^{3+}	4 methods: Solid-state, wet chemical, combustion, sol-gel	Monoclinic	274	314	The excitation spectra for all chemical methods in this paper reveal an intense peak at 274 nm, with a smaller shoulder peak at 276 nm. The emission spectra at 314 nm are most pronounced for the sol-gel method (350 a.u) and combustion method of synthesis, followed by weak intensity peaks for the other two methods. The emission intensity for the sol-gel method is about 10 times higher than that for the wet chemical and solid-state methods, while the combustion method is about 6 times higher than the other two methods. EPR values indicate that Gd^{3+} ions lie in slightly distorted positions at Ca^{2+} sites within the monoclinic structure. Thus, this paper demonstrates the advantages of using the sol-gel and

Table 1 (*continued*)

No	Compound	Synthesis technique	Crystal structure	Optimal Excitation wavelength (nm)	Optimal Emission wavelength (nm)	Comment
						combustion methods of synthesis for preparing samples [3].
8	$CaZrO_3:Gd^{3+}$	Combustion	Orthorhombic	273	312	Like with all other excitation spectra, $CaZrO_3:Gd^{3+}$ displays an intense peak at 273 nm and a slightly lower shoulder intensity peak at 276 nm. The emission spectra likewise show a very low peak at 308 nm and an intense one at 312 nm. EPR value shows that Gd^{3+} ion sits at Ca^{2+} sites within its crystal structure. Interestingly, at room temperature the crystal structure is orthorhombic but at high temperatures it is cubic in nature. This material, with enhanced emission at 312 nm, is considered a potential candidate for phototherapy lamps [19].
9	$CaCO_3:Gd^{3+}$	Carbonization	Cubic	274	311	The excitation spectra of $CaCO_3:Gd^{3+}$ reveals 2 peaks; one of a lower intensity at 252 nm and another of a higher intensity at 274 nm. Under UV excitation of 274 nm wavelength, the emission spectra reveal only one intense peak at 311 nm. With variation in Gd^{3+} concentrations, the concentration of 2 mol % produces the best luminescence at 311 nm. Thus, this material with a single enhanced emission at 311 nm can be considered for phototherapy lamps [39].
10	$CaZr_4O_9:Gd^{3+}$	Combustion	Cubic	274	313	A similar pattern unfolds for Gd^{3+} excitation spectra in this paper: an intense excitation peak at 274 nm and a lower shoulder intensity peak at 276 nm. The PL emission spectra also show similar emissions: one weak peak at 308 nm and an intense peak at 313 nm. EPR measurements reveal the presence of Gd^{3+} ions at Ca^{2+} ion sites. With enhanced emissions at 313 nm, makes it a candidate for phototherapy lamps [40].
11	$CaAl_{12}O_{19}:Gd^{3+}$	Combustion	Hexagonal	271.8	310.4	Excitation spectra of this compound reveals many excitation peaks, with an intense peak at 271.8 nm followed by a slightly lower shoulder peak at 274.4 nm. The emission spectra, as usual shows 2 peaks, one low intensity peak at 304.1 nm and an intense peak at 310.4 nm. The emission intensity of this is relatively low compared to other materials; it needs to be sensitized to have a higher intensity peak. EPR studies shows that Gd^{3+} ions are positioned at Ca^{2+} ion sites. The same material when co-doped with Gd^{3+} dopants produce enhanced emissions. This material is an average material for phototherapy lamp [41].
12	$CaLaZnO_5:Gd^{3+}$	Sol-gel	Tetragonal	227	314	Excitation spectra of this compound shows overlapping intensity peaks as a function of concentration occurring at 227 nm. On the other hand, the emission spectra also show overlapping emission peaks at 314 nm as a function of concentration, with the highest intensity occurring for a concentration of 0.045 mol % of Gd^{3+} ion. ESR studies show that the Gd^{3+} ions occupy distorted Ca^{2+} sites in the host material. This material with an

Table 1 (*continued*)

No	Compound	Synthesis technique	Crystal structure	Optimal Excitation wavelength (nm)	Optimal Emission wavelength (nm)	Comment
						enhanced emission for 0.045 mol % concentration of Gd^{3+} ion is a candidate for phototherapy lamps [42].
13	$KCaR(PO_4)_2$, R=Gd, Y	Stoichiometric mixtures	Hexagonal	274	313.8	The excitation spectra of this material consist of several peaks, with an intense peak at 274 nm and another one of lower intensity at 276 nm (shoulder). The emission spectra consist of several peaks arising from $^6P_{5/2}$ and $^6P_{7/2}$ emissions, with an intense peak at 313.8 nm. The role of K^+ ion was to increase the emission intensity of the Gd^{3+} ion. This material with its intense emission at 313.8 nm can be used in phototherapy lamps [43].
14	$Ca_{10}(PO_4)_6(OH)_2$:Gd^{3+}	High temperature synthesis	Hydroxyapatite	274	314	The excitation spectra of this material show a relatively high peak at 276 nm and a minor peak at 280 nm. The emission spectra show a strong peak at 314 nm and weak peaks at 319.6, 325 and 351 nm due to vibronic bands. This material has a relatively low emission compared to other phosphor materials and would not be the best choice for phototherapy lamps [44].
15	$Ca_2La_8(SiO_4)_6O_2$:Gd^{3+}	Sol-gel	Hexagonal apatite	230	314	The PLE excitation spectra of the oxyapatite materials doped with Gd^{3+} ions reveal several excitation peaks, with a broad peak occurring at 230 nm, which is attributable to the absorptions by the host material, while a weak peak due to Gd^{3+} absorption occurs at 274 nm. The PL emission spectra consists of a weak emission at 308 nm and an intense emission in the UV region at 314 nm. The emission intensity increases with concentration up to a 0.09 mol % of Gd^{3+} ions, and thereafter decreases due to concentration quenching. See Fig. 5 for PLE and PL spectra. EPR studies indicate that Gd^{3+} ions replace the larger La^{3+} ions, leading to distortions of the environment surrounding the Gd^{3+} ions. Additions of Gd^{3+} ions at Ca^{2+} sites lead to charge compensation and charge vacancies, and a lowering of the symmetry of the site surrounding the Gd^{3+} ions. Thus, this material with a concentration of x = 0.09 mol % is considered for application in phototherapy lamps [45].
16	$Ca_3MgSi_2O_8$:Gd^{3+}	Sol-gel	Monoclinic (merwinite structure)	273	312	The PLE excitation spectra of this phosphor material is composed of a few low intensity excitation bands and an intense excitation band at 273 nm which is due Gd^{3+} transitions. However, Stark splits in the form of shoulder peaks occur at around 276 nm, while the maximum excitation peak occurs at 273 nm which is due Gd^{3+} ions. The PL emission spectra of this material consists of a narrowband at around 313 nm, which increases with concentration up to x = 0.05 mol % and thereafter decreases due to concentration quenching. Doping of the host material with Gd^{3+} ions to replace Ca^{2+} ions at atomic lattice sites, leads to reductions in the cell volume. Thus, this material with a

Table 1 (*continued*)

No	Compound	Synthesis technique	Crystal structure	Optimal Excitation wavelength (nm)	Optimal Emission wavelength (nm)	Comment
						concentration of x = 0.05 mol % is considered for applications in phototherapy lamps [46].
17	$CaAl_{12}O_{19}:Gd^{3+}$	Combustion	Hexagonal magnetoplumbite structure	272	310.04	The PLE excitation spectra consists of various excitations bands in the 240 nm–280 nm wavelength range, with a maximum excitation band occurring at 271.8 nm due to Gd^{3+} ions. Distinct shoulder-like peaks are observed around the maximum emission peak at 310.4 nm. Of particular importance here is that Gd^{3+} (0.108 nm) ions replaces Ca^{2+} (0.114 nm) ions at lattice sites, and not even the smaller Al^{3+} (0.0680 nm) ions at its lattice sites. EPR studies confirms that Gd^{3+} ions replaces the Ca^{2+} ions, and creates charge compensation effects, as well as Ca^{2+} vacancies at remote locations rather than close to the Gd^{3+} environment, minimizing crystal distortions. This phosphor material with emissions at 310.4 nm can be regarded as a candidate for application in phototherapy lamps [47].
18	$CaLaB_7O_{13}:Gd^{3+}$	Sol-gel	Monoclinic	272	313	The PLE excitation spectra consists of a high intensity peak at 272 nm due to Gd^{3+} ions. Evidence of Stark effects are also observed for these samples (shoulder peaks around the maximum peak) The PL emission spectra consists of a sharp peak at 313 nm, whose intensity is tuned with concentration variations. For this sample, it is likely that Gd^{3+} (0.110 nm) ions have replaced the La^{3+} (0.120 nm) ions with minimal distortions to the crystal lattice, but mostly preserving charge compensation effects. The maximum intensity occurs for a concentration of x = 0.09 mol %, and for a concentration greater to this value, concentration quenching effects occur. EPR studies gives values of between 2.07 and 4,07 indicating that Gd^{3+} ions occur at the cubic, octahedral, or tetrahedral sites, with minimal distortions created. Thus, this material for a concentration of x = 0.09 mol % is considered as a candidate for application in phototherapy lamps [48].
19	$CaLa_4Si_3O1_3:Gd^{3+}$	Sol-gel	Oxyapaptite	228	314	The photoluminescence excitation (PLE) spectra consist of a high intensity peak at 228 nm, which is due to host absorption, as well as a low intensity absorption peak at 273 nm which is due to Gd^{3+} ions. The PL emission spectra consists of a high intensity peak at 314 nm and a very small one at 308 nm. The PL maximum emission spectra occurs for a concentration of x = 0.11 mol, after which concentration quenching effects occurs. As with other materials, Gd^{3+} (0.093 nm) ions replace the La^{3+} (0.103 nm) ions of quite similar ionic radius. EPR studies indicate that g has a value of between 2 and 6, which corresponds to U spectrum of Gd^{3+} ions, implying they occupy sites of weak fields

Table 1 (*continued*)

No	Compound	Synthesis technique	Crystal structure	Optimal Excitation wavelength (nm)	Optimal Emission wavelength (nm)	Comment
						of cubic, octahedral, and tetrahedral symmetry with minimal field distortions. Thus, this material with a concentration of x = 0.11 mol % is good for application in phototherapy lamps [49].
20	$CaMgSi_2O_6:Gd^{3+}$	Sol-gel	Monoclinic	273	313	The PLE excitation spectra consists of an intense excitation peak at 273 nm which is attributed to Gd^{3+} transition, as well as Stark effects around 276 nm. The PL emission spectra consists of intense narrowband emission at 313 nm, the maximum intensity emission occurs for 45.1 mg of Gd and for values greater than this, concentration quenching occurs. Gd^{3+} ions have effectively replaced Ca^{2+} ions of similar radius, instead of the larger Mg^{2+} ions. The impact of Ca^{2+} replacement (besides charge compensation) is the creation of Ca^{2+} vacancies or defect sites within the host material. The X band of EPR studies have indicated fine lines of Gd^{3+} ions with lower symmetries. Thus, this material with x = 45.1 mg Gd is considered as a candidate for applications in phototherapy lamps [50].
21	$CaAl_4O_7:Gd^{3+}$	Sol-gel	Monoclinic	272	314	The PLE excitation spectra consists of an intense peak at 272 nm (including Stark effects), which is attributed to Gd^{3+} ions. The PL emission spectra consists of intense peaks at 314 nm, with the maximum peak coinciding with a concentration of x = 0.03 mol %, and thus for further increases in concentrations, quenching occurs. According to EPR studies, Gd^{3+} ions have effectively replaced Ca^{2+} ions instead of Al^{3+} ions, but with the disadvantage of creation of Ca^{2+} vacancies, which distorts the field surrounding of the Gd^{3+} ions. Thus, this material with a concentration of x = 0.03 mol % have the potential to be used as a UVB-emitting phosphor materials in phototherapy lamps [31].
22	$Ca_2MgSi_2O_7: Gd^{3+}$	Solid-state	akermanite	274	314	The PLE excitation spectra consists of a broad excitation band at around 274 nm, which is attributed to Gd^{3+} absorptions. The PL emission band consists of intense narrow bands at 314 nm, with a maximum occurring for a concentration of x = 2 mol % of Gd^{3+} ions. Concentration quenching occurs for concentrations greater than 2 mol %. For this sample, Gd^{3+} ions have effectively replaced Ca^{2+} ions instead of Mg^{2+} ions. This material at a concentration of x = 2 mol % is ideal for applications in phototherapy lamps, as its emission intensity is very close to the commercial $LaPO_4:Ce^{3+}$ lamps used for treatment of psoriasis [1].
23	$CaY_2Al_4SiO_{12}:Gd^{3+}$	Sol-gel	Cubic	273	314	The PLE spectra consists of excitation bands, with the highest occurring at 273 nm, which is attributed to Gd^{3+} absorptions (inclusive of Stark effects). The PL emission spectra exhibits

Table 1 (*continued*)

No	Compound	Synthesis technique	Crystal structure	Optimal Excitation wavelength (nm)	Optimal Emission wavelength (nm)	Comment
						narrowband emission, with the highest occurring for x = 0.09 mol %, which quenches for concentrations exceeding this value. In this study, Gd^{3+} (0.1050 nm) ions have effectively replaced Y^{3+} (0.1019 nm) ions rather than Ca^{2+} (0.1120 nm) ions, thus preserving charge neutrality. EPR studies reveal that the g values are in the range of 1.6–6.5 which are associated with weak, intermediate to strong cubic symmetric fields. This material with a concentration of x = 0.09 mol % is considered as a candidate for applications in phototherapy lamps [51].
24	$CaZrO_3$:RE^{3+}, RE = Gd^{3+}	Gel-combustion method	Orthorhombic	274	310	This material has been re-explored by another research group, by including several RE ions, including Gd^{3+} ions. The PLE spectra consists of a single high intensity peak at 274 nm and a high intensity narrow emission peak at 310 nm. The emission spectra for these singly doped materials are very high, with low non-radiative transitions and is cost-effective with the lack of co-doping. A high quantum yield of 71 % makes this material an excellent emitter of photons. This material has a U-type EPR spectrum which is indicative that Gd^{3+} stabilizes the Ca^{2+} ion site. This material produces highly energetic UV-B emissions that are useful for photo-thermal therapy [18].
25	$NaCaYF_6$:Ln^{3+} (Ln = Ce, Gd)	Hydrothermal	Gagarinite	272	310.6	The PLE spectra of this material consists of an intense excitation peak at 272 nm, while the emission spectra consist of narrow emission bands at 310.6 nm, plotted as a function of concentration. Maximum emission occurs for a concentration of 1 mol % Gd^{3+} ions. For this structure, the Y ions are replaced by Gd^{3+} ions. Disorder in this structure occurs when Y and Ca^{2+} ions occupy the same sites. When co-doped with Ce^{3+} ions, there is energy transfer from Ce^{3+} (5 mol %) ions to Gd^{3+} (0.5 mol %) ions, resulting in enhanced emissions (6000 a. u). This can be very useful for phototherapy lamps due to its enhanced emissions at 311 nm [52].
26	Alumino borosilicate glasses: Gd^{3+}	Melt- quench technique	–	274	310	The PLE excitation spectra of this glass material consists of an intense excitation band at 274 nm and a high intensity emission spectrum at 310 nm, plotted as function of concentration. A concentration of 2 mol % produces the highest emission. ESR studies validate the presence of Gd^{3+} ions at Ca^{2+} sites. With this high emission at 310 nm, these glasses can be used as a source of UV-B emitting light sources for phototherapy applications [53].
27	Ca_2ZnSiO_7:Gd^{3+}	Sol-gel	Hardystonite	273	312	The PLE spectra reveals excitations bands, with a peak at 273 nm and a narrow peak PL emission band at 312 nm. EPR studies show the presence of Gd^{3+} ions at Ca^{2+} ions sites. This material with emissions at

(*continued on next page*)

Table 1 (*continued*)

| No	Compound	Synthesis technique	Crystal structure	Optimal Excitation wavelength (nm)	Optimal Emission wavelength (nm)	Comment
28	β-Ca$_2$SiO$_4$:Gd^{3+}	High temperature solid-phase method	monoclinic	274	312	312 nm can be considered for phototherapy applications [54]. The PLE spectrum of the Ca$_2$SiO$_4$: xGd material consists of peak at 274 nm and peak PL emission at 312 nm. The strongest luminescent efficiency occurs for a concentration of x = 0.03 of Gd^{3+} ions. The role of Gd^{3+} ions is to bring about stability of the material when substituted at Ca^{2+} ion sites. Thus, this material for its optimal concentration of x = 0.03 is good for phototherapy applications [55].
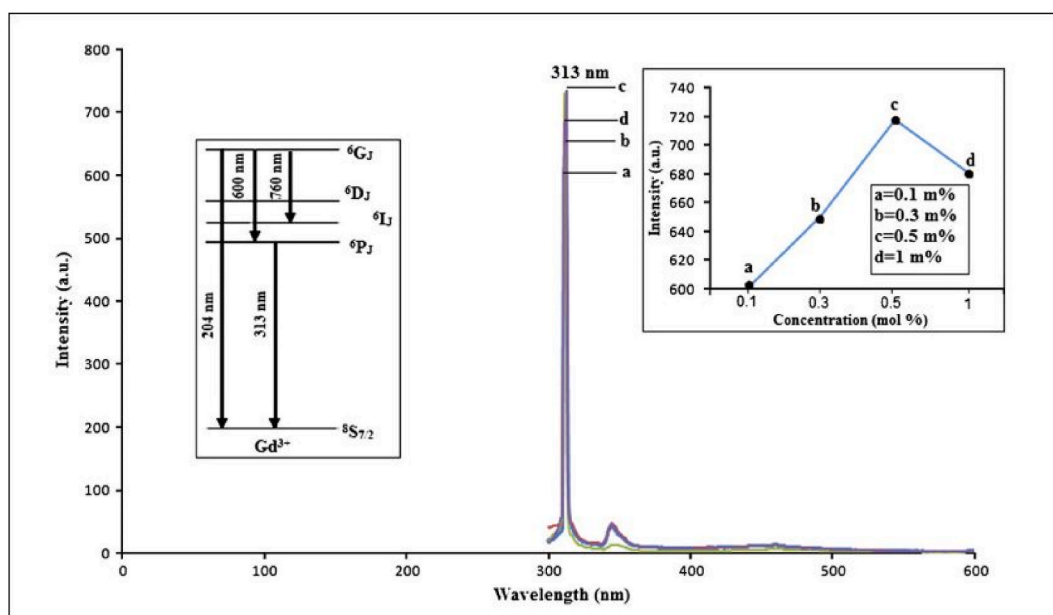
Fig. 2. PL emission spectra of NaCaPO$_4$:Gd^{3+} phosphor material, excited using a UV wavelength of 274 nm wavelength of light (Reused with permission from Ref. [35]).

(1) BaAl$_2$O$_4$:Gd^{3+} phosphor materials

Singh et al. [10] studied the UV-B emissions of Gd^{3+} activated barium-based BaAl$_2$O$_4$ host materials. This material, prepared by combustion technique, reveals a high intensity UV-B emission at 314 nm, monitored under a photoluminescence (PL) excitation wavelength of 273 nm. This Gd^{3+} sensitized host material was found to be highly suitable for phototherapy lamps.

(2) NaSrPO$_4$:Gd^{3+} phosphor materials

Singh et al. [23] studied the UV-B emissions of strontium-based NaSrPO$_4$ host materials, activated by Gd^{3+} ions. They found this material, which was prepared by the co-precipitation route, produced high intensity UV-B emissions at 313 nm, when monitored by a PL excitation wavelength of 273 nm. This phosphate material is a potential candidate for phototherapy applications.

(3) BaB$_8$O$_{13}$:Gd^{3+}, Pr^{3+} phosphor materials

Tamboli et al. [26] studied the UV-B emissions of a borate-based BaB$_8$O$_{13}$ host material, doped with Gd^{3+} ions and co-doped with Pr^{3+} ions. This sensitized host material, which was synthesized via the solid-state reaction method, produced enhanced UV-B emissions at 313 nm, when monitored by a PL excitation wavelength of 274 nm. The observed emission at 313 nm for the co-doped material was
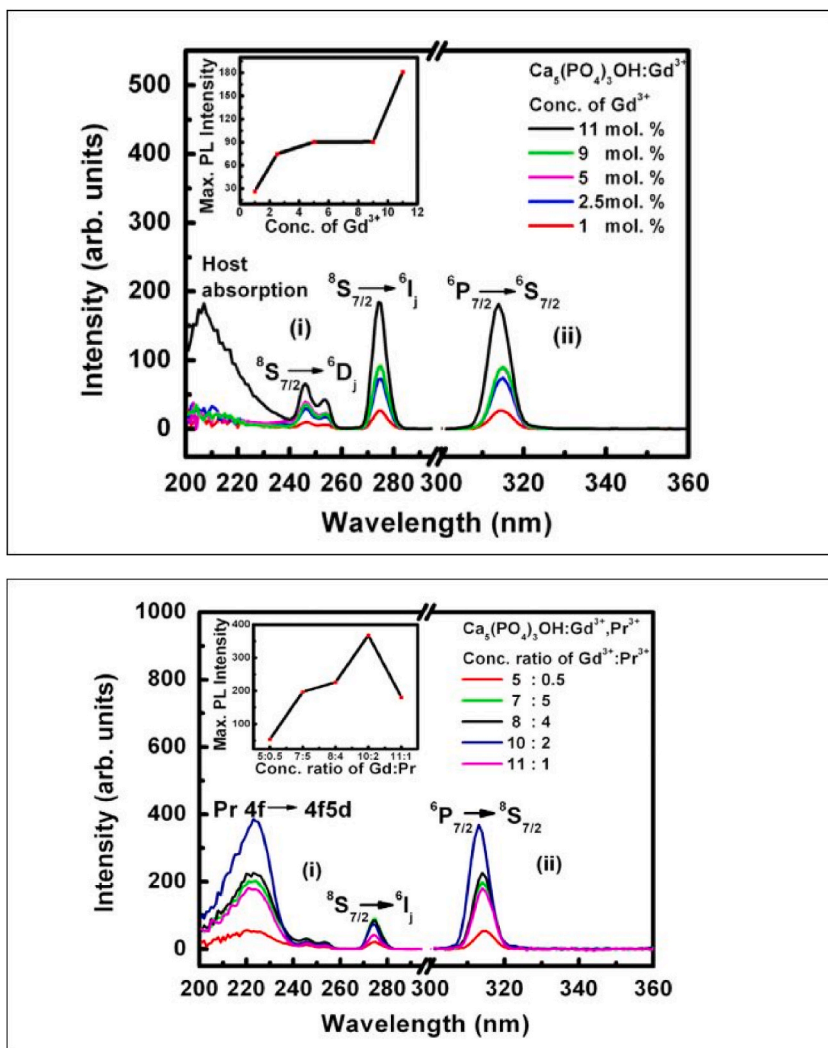
Fig. 3. (a): The first figure represents the PLE and PL spectra of the singly doped $Ca_5(PO_4)_3OH$: Pr^{3+} phosphor material. (Reused with permission from Ref. [38]).
(b): Shows the PLE and PL spectra of the $Ca_5(PO_4)_3OH$: Gd^{3+}, Pr^{3+} co-doped phosphor material (Reused with permission from Ref. [38]).

found to be twice the intensity observed for a singly doped Gd^{3+} host material. This behavior is attributed to the effective energy transfer from Pr^{3+} ions to Gd^{3+} ions. This co-doped borate host material is very useful for phototherapy applications.

(4) $LiSr_4(BO_3)_3$: Gd^{3+}, Pr^{3+} phosphor materials

Chauhan et al. [27] studied the UV-B emissions of a composite borate $LiSr_4(BO_3)_3$ host material, doped with Gd^{3+} ions and co-doped with Pr^{3+} ions. This sensitized inorganic $LiSr_4(BO_3)_3$ material, when prepared by the solid-state reaction method, produced enhanced UV-B emissions at 313 nm, when monitored by a PL excitation wavelength of 276 nm. This enhanced emission is likewise due to the effective energy transfer from Pr^{3+} to Gd^{3+} ions. This material is also regarded as a useful candidate for phototherapy applications.

Whilst there are many more non-calcium-based host materials, activated by Gd^{3+} ions, calcium-based host materials have been at the forefront in research for its applications in phototherapy, which will be discussed in Table 1.

(d) UV excitation and emission wavelengths

The emission spectra of Gd^{3+} ions reveal transitions from the metastable states to the ground state ($^8S_{7/2}$), which fall in the NB-UVB wavelength range of 311–315 nm. This NB-UVB emission range is suitable in the medical field for treatment of many skin diseases. The peak emission wavelength is used to excite the Gd^{3+} activated host and likewise, the peak excitation peak is used to determine the
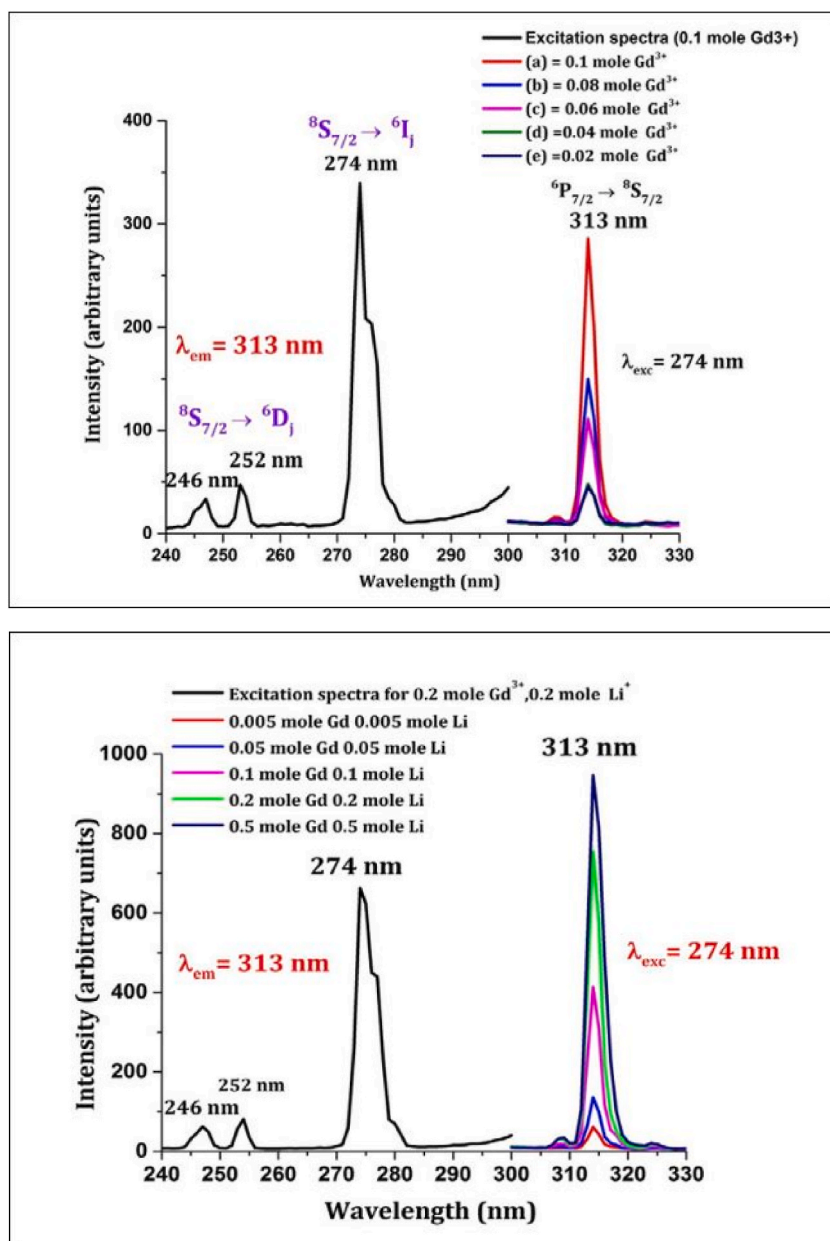
Fig. 4. (a) PLE and PL spectra of the $Ca_9Mg(PO_4)_6F_2$:Pr^{3+},Gd^{3+} phosphor material (Reused with permission form reference [4]).
(b): Shows the impact on the Li $^+$ ions on the PL emission properties of the $Ca_9Mg(PO_4)_6F_2$:Pr^{3+},Gd^{3+} phosphor material, whereby enhanced emissions are produced (Reused with permission form reference [4]).

emission spectra of the host matrix. Excitation and emission wavelengths vary with respect to different host materials. The energy gap between the ground state and the first excited state is around, 32000 cm^{-1} and will therefore require that Gd^{3+} activated material to be excited by radiation in the UV spectral range.

(e) Different synthesis methods

There are a variety of methods used for the synthesization of these phosphor materials, and they are at the discretion of the researchers. There is no standard method of synthesizing any of these samples. Some researchers have done a comparison of methods to see which method produced the best NB-UVB emission of Gd^{3+} in various host materials. Synthesis methods in these review papers range from combustion, sol-gel, co-precipitation, solid-state reaction, wet chemical, etc. Some of the most popular synthesis methods used are discussed below:
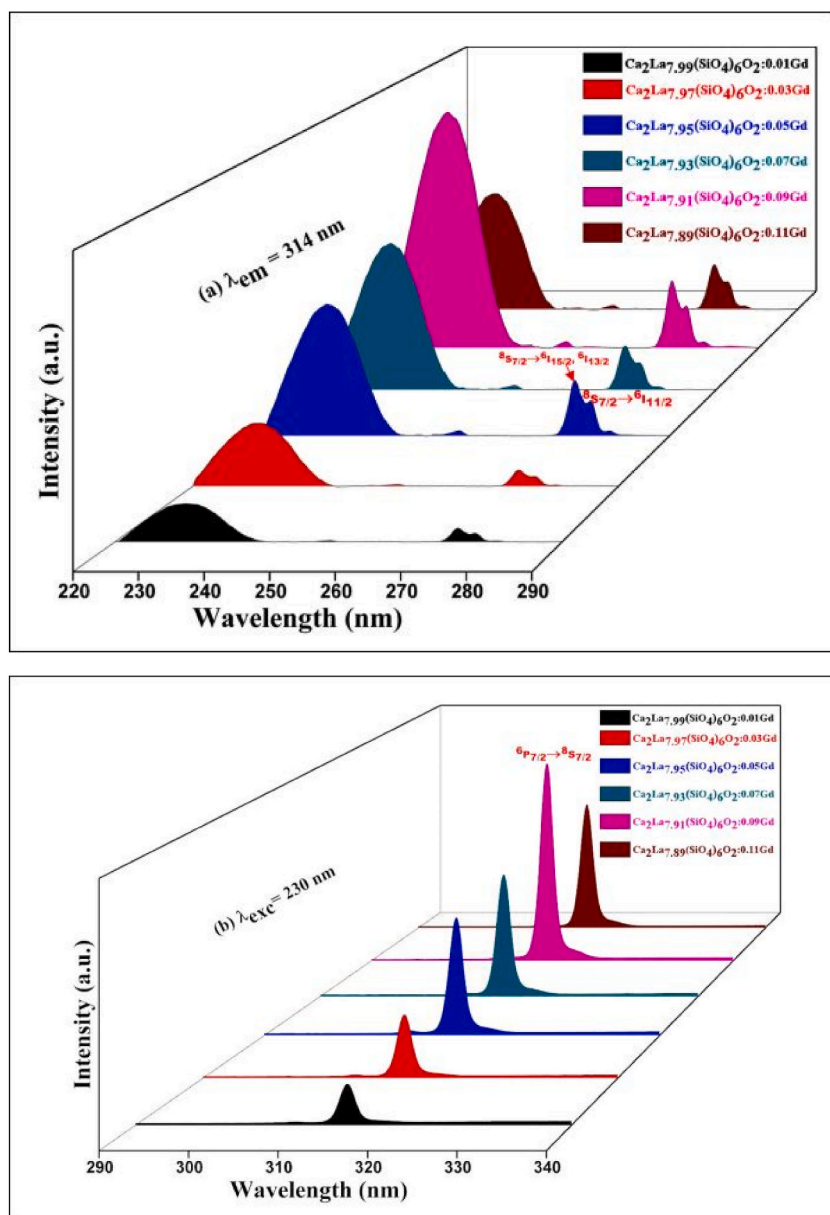
Fig. 5. (a)PLE spectra of the $Ca_2La_8(SiO_4)_6O_2:Gd^{3+}$ phosphor material. (Reused with permission from Ref. [45]).
(b): PL spectra of the $Ca_2La_8(SiO_4)_6O_2:Gd^{3+}$ phosphor material. (Reused with permission from Ref. [45]).

[i] Combustion method

The combustion synthesis method is sometimes considered a wet-chemical approach that does not require additional calcination to produce the final product. In this process, fuels (acting as reducing agents) and metal nitrates (acting as oxidizing agents) serve as precursors for the reaction. The procedure involves placing an aqueous solution [It is not always possible to use an aqueous solution of nitrates; they may also be used in solid form] of metal nitrates and a fuel into a furnace preheated to approximately 500 °C. Subsequently, this mixture undergoes an oxidative exothermic reaction, accompanied by a flame that persists for no more than 10 min. The resulting powder is then ground and prepared for characterization [34].

[ii] Solid-state reaction method

The solid-state reaction method begins with mixing the reactants in stoichiometric ratios using a medium, typically acetone, in an agate mortar container. The mixture is initially heated, typically in the range of 200 °C–450 °C, to eliminate any unwanted gases.

Table 2

Gives a summary of the excitation, emission wavelengths of Gd^{3+} activated calcium host materials, and classification of the UV-B emissions as low, medium, or high in the NB region of the UV-EM spectrum.

No	Phosphor material	Max excitation wavelength (nm)	Max. emission wavelength (nm)	Classification of UV-B emissions as low, medium, or high	Phototherapy effectiveness	Energy transfer mechanism
1	$NaCaPO_4:Gd^{3+}$	274	313	medium	Moderate Phototherapeutic agent	Gd^{3+} is an activator
2	$Ca_3Al_2O_6:Gd^{3+}$	273	314	low	Suboptimal Phototherapeutic agent	Gd^{3+} is an activator
3	$Ca_9RE(PO_4)_7:RE = Gd$	273	311	low	Suboptimal Phototherapeutic agent	Gd^{3+} is an activator
4	$Ca_5(PO_4)_3(OH): Gd^{3+}$	185	312	medium	Moderate Phototherapeutic agent	Gd^{3+} is an activator
5	$Ca_5(PO_4)_3OH: Gd^{3+}, Pr^{3+}$	222	313	high	Intense Phototherapeutic agent	Gd^{3+} is an activator while Pr^{3+} is a sensitizer
6	$Ca_9Mg(PO_4)_6F_2:Gd^{3+}, Pr^{3+}, Li^+$	274	313	high	Intense Phototherapeutic agent	Gd^{3+} is an activator while Pr^{3+} is a sensitizer, while Li+ is a charge compensator
7	$CaMgP_2O_7:Gd^{3+}$	274	314	medium	Moderate Phototherapeutic agent	Gd^{3+} is an activator
8	$CaZrO_3:Gd^{3+}$	273	312	low	Suboptimal Phototherapeutic agent	Gd^{3+} is an activator
9	$CaCO_3:Gd^{3+}$	274	311	low	Suboptimal Phototherapeutic agent	Gd^{3+} is an activator
10	$CaZr_4O_9:Gd^{3+}$	274	313	low	Suboptimal Phototherapeutic agent	Gd^{3+} is an activator
11	$CaAl_{12}O_{19}:Gd^{3+}$	271.8	310.4	low	Suboptimal Phototherapeutic agent	Gd^{3+} is an activator
12	$CaLaZnO_5:Gd^{3+}$	227	314	low	Suboptimal Phototherapeutic agent	Gd^{3+} is an activator
13	$KCaR(PO_4)_2, R{=}Gd, Y$	274	313.8	low	Suboptimal Phototherapeutic agent	Gd^{3+}/Yb^{3+} are activators
14	$Ca_{10}(PO_4)_6(OH)_2: Gd^{3+}$	274	314	low	Suboptimal Phototherapeutic agent	Gd^{3+} is an activator
15	$Ca_2La_8(SiO_4)_6O_2:Gd^{3+}$	230	314	low	Suboptimal Phototherapeutic agent	Gd^{3+} is an activator
16	$Ca_3MgSi_2O_8:Gd^{3+}$	273	312	low	Suboptimal Phototherapeutic agent	Gd^{3+} is an activator
17	$CaAl_{12}O_{19}:Gd^{3+}$	272	310.04	low	Suboptimal Phototherapeutic agent	Gd^{3+} is an activator
18	$CaLaB_7O_{13}:Gd^{3+}$	272	313	low	Suboptimal Phototherapeutic agent	Gd^{3+} is an activator
19	$CaLa_4Si_3O_{13}:Gd^{3+}$	228	314	medium	Moderate Phototherapeutic agent	Gd^{3+} is an activator
20	$CaMgSi_2O_6:Gd^{3+}$	273	313	low	Suboptimal Phototherapeutic agent	Gd^{3+} is an activator
21	$CaAl_4O_7:Gd^{3+}$	272	314	low	Suboptimal Phototherapeutic agent	Gd^{3+} is an activator

Table 2 (*continued*)

No	Phosphor material	Max excitation wavelength (nm)	Max. emission wavelength (nm)	Classification of UV-B emissions as low, medium, or high	Photothery effectiveness	Energy transfer mechanism
22	$Ca_2MgSi_2O_7$: Gd^{3+}	274	314	high	Intense Phototherapeutic agent	Gd^{3+} is an activator
23	$CaY_2Al_4SiO_{12}$:Gd^{3+}	273	314	low	Suboptimal Phototherapeutic agent	Gd^{3+} is an activator
24	$CaZrO_3$:RE^{3+}, RE = Gd^{3+}	274	310	high	Intense Phototherapeutic agent	Gd^{3+} is an activator
25	$NaCaYF_6$:Ln^{3+} (Ln = Ce, Gd)	272	310.6	high	Intense Phototherapeutic agent	Gd^{3+}/Ce^{3+} are activators
26	Alumino borosilicate glasses: Gd^{3+}	274	310	medium/high	Moderate to high Phototherapeutic agent	Gd^{3+} is an activator
27	Ca_2ZnSiO_7:Gd^{3+}	273	312	medium	Moderate Phototherapeutic agent	Gd^{3+} is an activator
28	β-Ca_2SiO_4:Gd^{3+}	274	312	medium	Moderate Phototherapeutic agent	Gd^{3+} is an activator

Note in the context of the above, the use of low, medium, and high UV-B emissions refers to the relative intensities of the UV-B emissions. More contextually, they maybe explained as follows:

Subsequently, the mixture is crushed and then heated again, this time to a temperature of around 1000 °C. This process of heating and crushing is repeated until a homogeneous mixture is achieved. Following this procedure, the sample is prepared for characterization [34].

[iii] Sol-gel method

The sol-gel method is predominantly employed to produce nano/micro-sized particles with a uniform distribution and stands out as one of the most utilized methods in this review work. This synthesis method involves mixing precursors (nitrates) in distilled water along with chelating agents (such as citric acid) and surfactants (such as polyethylene glycol (PEG)). The solution is then stirred and heated to a temperature of about 80 °C for a specific duration until a polymeric network forms, leading to the creation of a sol, which subsequently transforms into a gel solution. It is crucial to note that gelation occurs as a sudden loss of fluids. The resulting gel is then subjected to heating until organic compounds are removed. If necessary, these samples are annealed at approximately 500 °C to eliminate PEG compounds [34].

[iv] Co-precipitation method

The co-precipitation method is well-suited for producing phosphor materials based on fluoride, oxide, or oxyfluoride compounds. In most cases, chlorides, nitrates, or acetates are required as precursors for this synthesis method. This process involves dissolving these precursors (using distilled water, ethanol, and cyclohexane, for instance) together. Typically, a precipitating agent is slowly introduced with constant stirring. This leads to the formation of hydroxides, fluorides, or carbonate compounds in the form of a precipitate. The resulting precipitate is then subjected to multiple washes with distilled water to remove any undue impurities. This washing process is commonly performed through filtering or centrifugation. The final product must undergo drying in an oven to decompose the hydroxides or carbonates, and subsequently, it should be subjected to high temperature annealing to crystallize the compound [34].

(f) Thermal and chemical stability

Calcium-based compounds doped with Gd^{3+} ions exhibit enhanced chemical stability, as the rare earth ions strategically position themselves at lattice sites within the host material, preventing undesirable structural changes. Thus, the doping process, as confirmed through ESR and EPR studies, mitigates any crystal distortions. In addition, the incorporation of Gd^{3+} ions into the host material increases the thermal conductivity of the calcium-based host material, enabling it to withstand high-temperature fluctuations. Findings from this research suggest that these compounds are generally resistant to both chemical and thermal stresses. While phototherapy treatments may generate some form of heat, effective heat dissipation in this regard is essential for maintaining thermal stability and ensuring safe and efficient treatments of various skin diseases. Thus, designing high-quality phosphor materials with good thermal stability is crucial for achieving optimal performance in phototherapy applications.

3. Discussions of various Gd^{3+} doped Ca-based host materials for its NB-UVB emissions

Whilst Ca-based materials generally are known to have bioactive properties, they are also known to produce light emissions, when doped with Gd^{3+} and sensitized for enhanced emissions through energy transfer mechanisms. Several papers studied in literature have identified compounds that display phototherapeutic applications. Some of these compounds produce enhanced NB-UVB emissions whilst others produce moderate emissions.

(a) Low UV-B Emissions: Here, Gd^{3+}-activated calcium host materials produce UV-B emissions at relatively low intensities, making these compounds less desirable for phototherapy applications.
(b) Medium UV-B Emissions: Here, Gd^{3+}-activated calcium host materials produce moderate UV-B emissions that may be applicable in some cases but not optimized for all skin treatments.
(c) High UV-B Emissions: Here, Gd^{3+}-activated host materials produce high-intensity UV-B emissions and are most sought after for various skin treatments.

4. Discussions of the various contributions

Table 1 provides a brief description of the essential features of all calcium-based compounds doped with Gd^{3+} ions for their phototherapeutic applications. Table 2 describes the emission intensity and its role as an efficient UV-B emitter, relevant for curing various skin ailments. For actual or potential clinical applications, emissions should fall within the narrow UV-B range of 311–315 nm, which is ideal for treating conditions such as psoriasis, vitiligo, and atopic dermatitis.

Observations in Table 2 reveal that when calcium is combined with phosphate compounds in stoichiometric ratios, it produces medium to high UV-B emission intensities. Ca$_5$(PO$_4$)$_3$OH: Gd^{3+}, Pr^{3+} has shown high UV-B emissions due to the incorporation of Pr^{3+}, which absorbs excitation energy and transfers it to the Gd^{3+} activator ion. In most cases, when Gd^{3+} ions are singly doped, the PL emission intensity is low. Thus, sensitizers have a huge role to play in absorbing the excitation energy and transferring it to the activator ions. In addition to this, when charge compensators such as Li$^+$ ions are added to the same compound, further enhancement in UV-B emission intensity is observed. This demonstrates that some low-emitting UV-B materials can become more efficient with the incorporation of both sensitizers and charge compensators, as with the above case.

Another factor contributing to better emissions is the choice of synthesis techniques. Many researchers have found the sol-gel method to be most effective. Crystal structure formations also play a role in producing better emissions, though to a lesser extent. Understanding the fit of Gd^{3+} ions at Ca^{2+} crystal lattice positions involve the use of ERS and EPR studies to ensure minimal distortions. Much of the research work has employed these techniques in quantifying the positioning of Ca^{2+} by Gd^{3+} ions.

In summary, by considering the above findings, optimization of Gd^{3+} activated calcium-based host compounds hold significant promise for advancing phototherapeutic applications. By fine-tuning the stoichiometric ratios of these compounds, and by incorporating sensitizers such as Pr^{3+} (literature suggests other ions such as Bi^{3+}, Pb^{2+}, Ce^{3+}) or charge compensator ions such as Li$^+$ (group 1 elements), researchers were able to enhance the UV-B emission efficiency of these compounds, thereby making these materials highly effective for clinical dermatological treatments. Of the many synthesis methods used, the sol-gel synthesis method emerges as a particularly useful technique, enabling better control over the crystal structure and composition, which is a crucial parameter for maximizing the PL emission intensity. Furthermore, detailed studies using ERS and EPR techniques provide valuable insights into the incorporation of Gd^{3+} ions within the Ca^{2+} lattice site for these calcium-based compounds, ensuring minimal crystal distortions and optimal performance outputs. Focused research and development in this domain could lead to more effective and reliable treatments for skin diseases by employing the unique properties of these advanced nano phosphor materials.

5. Future developments

Whilst the above discussions point towards co-doping with sensitizers and the addition of charge compensators to enhance the UV-B emissions, this strategy maybe be a bit risky. According to Sharma et al. [20], the commercially used material LaPO$_4$:Ce^{3+} is too costly, requiring more doses and imposing higher financial burdens to the patients in curing ailments such as psoriasis. In their research it was found that even singly doped materials, such as Ca$_2$MgSi$_2$O$_7$:Gd^{3+} was most effective in curing such ailments and less cost effective in its treatment. Gd^{3+} ions bring about higher charge compensation when it replaces Ca^{2+} ions. In the same vein of discussion, a material in the same family, CaMgSi$_2$O$_6$:Gd^{3+} produced much lower UV-B emissions (lower charge compensation), thus the role of calcium (2+ charge) and oxygen (2- charge) is important in the fabrication of the materials. One must balance high emission intensity against cost factors to show the effectiveness of the materials.

The Fig. 6, below shows that Ca$_2$MgSi$_2$O$_7$:Gd^{3+} phosphor material is the state-of-the-art material when it comes to curing of skin ailments such as psoriasis. It is compared with the commercially available LaPO$_4$:Ce^{3+} phosphor material, which shows a lower UV-B emission at 315 nm than that of Ca$_2$MgSi$_2$O$_7$:Gd^{3+} with a higher UV-B emission at around 314 nm. This must surely be revolutionary phosphor material for the future treatment of skin diseases [20]. Whilst calcium-broad based phosphate materials show high promise for phototherapeutic treatments, non-phosphates in calcium compounds also hold the key in the field of dermatology. However, it must be mentioned that the underlying component in each of these phosphor materials is calcium. The role of magnesium in some compounds is also crucial in producing such impressive UV-B emissions. This is observed in calcium-magnesium borate/non borate type of compounds such as YMgB$_5$O$_{10}$:Gd^{3+}, Ce^{3+}, Sr(Al, Mg)$_{12}$O$_{19}$:Ce^{3+}, YMgB$_5$O$_{10}$:Gd^{3+},Ce^{3+},Pr^{3+}, CeMgB$_5$O$_{10}$:Gd^{3+}, which are commercially available for skin treatments [3,20,25,56]. Most importantly, the effect of co-doping and the nature of the material will
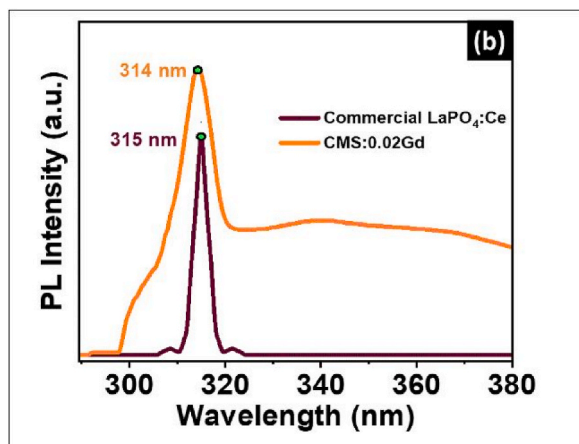
Fig. 6. Comparisons of the PL emissions of the commercial LaPO$_4$:Ce^{3+} phosphor material with that of the Ca$_2$MgSi$_2$O$_7$:Gd^{3+} phosphor material. (Re-used with permission from Ref. [20]).

impose a higher financial burden on the patient, and cognizance of it must be taken into consideration when fabricating these materials. Materials such as Ca$_2$MgSi$_2$O$_7$:Gd^{3+} which is a singly doped calcium-based compound is more effective than the commercially available phosphor materials, synthesized by the solid-state reaction method and should be the future for phototherapy treatments.

6. Concluding remarks

Several papers pertaining to Ca-based host materials were reviewed, with focused attention on NB-UVB emissions of Gd^{3+} ions at around 313 nm for applications in phototherapy lamps. This review has revealed that many factors could play a role in such emissions.

It appears that when Ca is integrated with phosphates as a composite host material, enhanced NB-UVB emissions were observed in singly or co-doped Gd^{3+} ions at around 313 nm. The best NB-UVB emission was observed when a monovalent ion is incorporated into the host matrix. The role of this ion is to compensate for the deficiency of the charge differences between Gd^{3+} ion and Ca^{2+} ion, thereby influencing the intensity of the NB-UVB emissions produced. Incorporation of suitable sensitizers into other Ca-based host materials has the potential to modify their moderate emission intensities, facilitating efficient energy transfer from the sensitizer to Gd^{3+} ions. Ca-based host materials having either cubic or hexagonal phases have displayed enhanced luminescence characteristics compared to other crystal structures. EPR and ESR studies were mostly done for Ca-based host materials, revealing the positioning of Gd^{3+} ions at Ca^{2+} lattice sites. In most cases, it was found to be positioned exactly or at slightly distorted Ca^{2+} lattice sites. The sol-gel method of synthesis is the most preferred method of preparing these materials for phototherapeutic applications.

In conclusion, it must be mentioned that not only do co-doped phosphor materials produce enhanced UV-B emissions, but singly doped materials such as Ca$_2$MgSi$_2$O$_7$:Gd^{3+} could also replace the commercially available LaPO$_4$:Ce^{3+} phosphor material in the market, opening the door for other state-of-the-art materials and constraining costs to the patient.

Ethical considerations

This review paper does not involve primary research with human or animal subjects. However, it comprehensively examines Gd^{3+} activated calcium-based compounds for relevant aspects of this study. I, the author, have written this review in the best of my ability whilst adhering to the principles of integrity and transparency, acknowledging all sources used where relevant.

Data availability

Since this is a review of a collection of papers, data pertinent to such papers are cited in the references.

Note

In the revisions, some aspects of AI ChatGPT were used for language modifications.

CRediT authorship contribution statement

Leelakrishna Reddy: Writing – review & editing, Writing – original draft, Data curation, Conceptualization.

Declaration of competing interest

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