

UV emitting borate phosphors for phototherapy lamps

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Photoluminescence properties of UV and blue emitting borate phosphors prepared by simple and time saving combustion synthesis technique are presented and discussed in the context of application in phototherapy lamps. Emission characteristics of these phosphors are found to be similar to those of commercial lamp phosphors used for phototherapy.

Keywords: Borate, Combustion, UV-A, UV-B, Phototherapy

1 Introduction

The ultraviolet radiation spectrum occupies the electromagnetic wavelengths continuum from 200-400 nm. Biological and physical characteristics allow its convenient division into three bands, UVC (200-280 nm), UVB (280-315 nm) and UVA (315-400 nm). UVA is sometimes further subdivided as UVA2 (315-340 nm) and UVA1 (340-400 nm). UVC is used in germicidal applications and most drinking water purifiers use UVC sources. UVB and UVA are used in many applications such as photocopying and phototherapy.

The use of UV light for phototherapy is well established¹. UV therapy is useful for treating more than 40 types of skin diseases and disorders, such as psoriasis², vitiligo³, Ofuji's disease⁴, erythropoietic protopor-phyria⁵, chronic graft-versus-host disease⁶ (cgvhd), pit-yriasis rosea⁷ and uremic pruritus⁸, atopic dermatitis⁹, lichen sclerosus et atrophicus¹⁰ (LSA), morphea, scleroderma¹¹, cutaneous T-cell lymphoma¹¹ and lupus erythematosus¹³.

It was found that the light belonging to longer wavelengths of UVB region was more effective while the shorter wavelengths were much less effective or even harmful. A narrow UVB source emitting¹⁴ at about 311 nm was made available around 1988. Psoralen UVA treatment (PUVA) is another method to treat skin disease. Parrish *et al*¹⁵. reported the use of oral psoralen agent followed by treatment with UV-A radiation to cure psoriasis. In the treatment of hyperbilirubinemia¹⁶ the light in the violet-blue region is used. Currently dermatologist use UV lamps having specific emissions in the UV region. The selection of the emission wavelength depends on the action

spectra for particular disease. Depending upon the effectiveness of wavelength region of radiation sources phototherapy can be classified into (1) narrow band UVB phototherapy, (2) psoralen UV-A phototherapy and (3) phototherapy with near UV-visible light.

In the present paper, the photoluminescence (PL) properties of various borate phosphors in view of their application in phototherapy lamps have been reported. All the phosphors described in this paper are prepared by combustion method.

2 Experimental Details

Borate phosphors were prepared by a combustion method¹⁷⁻²¹. Heat generated in the exothermic reaction between ammonium nitrate and urea is used to carry out the synthesis. Table 1 presents the details of the ingredients used in syntheses of various borate host phosphors. All the chemicals used are of A R grade. Following the combustion, the resulting fine powders were annealed for 90 min at temperatures ranging between 700 and 900°C and then rapidly cooled to room temperature. The powder XRD analyses were performed on Rigaku Miniflex II X ray diffractometer. PL measurements at room temperature were performed on Hitachi F-7000 spectrofluorimeter in the range 200-600 nm.

3 Results and Discussion

The powder X-ray diffraction patterns of the as prepared borate hosts SrZr (BO₃)₂, Al₄B₂O₉ and LaMgB₅O₁₀ are shown in Figs 1(a), 2(a) and 3(a), respectively. The patterns are consistent with the corresponding ICDD files shown in Figs 1(b), 2(b) and 3(b).

3.1 Phosphor for narrowband UVB therapy lamp

The UVB narrowband phototherapy proven to be the most effective for the treatment of psoriasis, vitiligo, ofujis disease, erythropoetic protoporphyria and many other photo responsive skin disorders²⁻¹⁴. Conventional

broad band UVB lamps emit light in the broad range over the UVB spectrum, including light (220-290 nm) causing sun burning. The narrowband UVB (290-320 nm) emitting phosphor without part of shorter wavelength range causing sun burning is thus required.

Table 1 — Molar ratios of constituents

| S No | Phosphor | Molar ratios of constituents |
|------|---|--|
| 1 | $\text{SrZr}_{0.95}\text{Pr}_{0.03}\text{Gd}_{0.02}(\text{BO}_3)_2$ | $\text{ZrO}(\text{NO}_3)_2:\text{Pr}(\text{NO}_3)_3:\text{Gd}(\text{NO}_3)_3:\text{Sr}(\text{NO}_3)_2:\text{H}_3\text{BO}_3:\text{CO}(\text{NH}_2)_2:\text{NH}_4\text{NO}_3$ 0.95:0.03:0.02:1:2:6:8 |
| 2 | $\text{Al}_{3.95}\text{Ce}_{0.05}\text{B}_2\text{O}_9$ | $\text{Al}(\text{NO}_3)_3:\text{CeCl}_3:\text{H}_3\text{BO}_3:\text{CO}(\text{NH}_2)_2:\text{NH}_4\text{NO}_3$ 3.95:0.05:2:11:3 |
| 3 | $\text{La}_{0.99}\text{Ce}_{0.01}\text{MgB}_5\text{O}_{10}$ | $\text{La}(\text{NO}_3)_3:\text{CeCl}_3:\text{Mg}(\text{NO}_3)_2:\text{H}_3\text{BO}_3:\text{CO}(\text{NH}_2)_2:\text{NH}_4\text{NO}_3$ 0.99:0.01:1:5:6.5:6 |

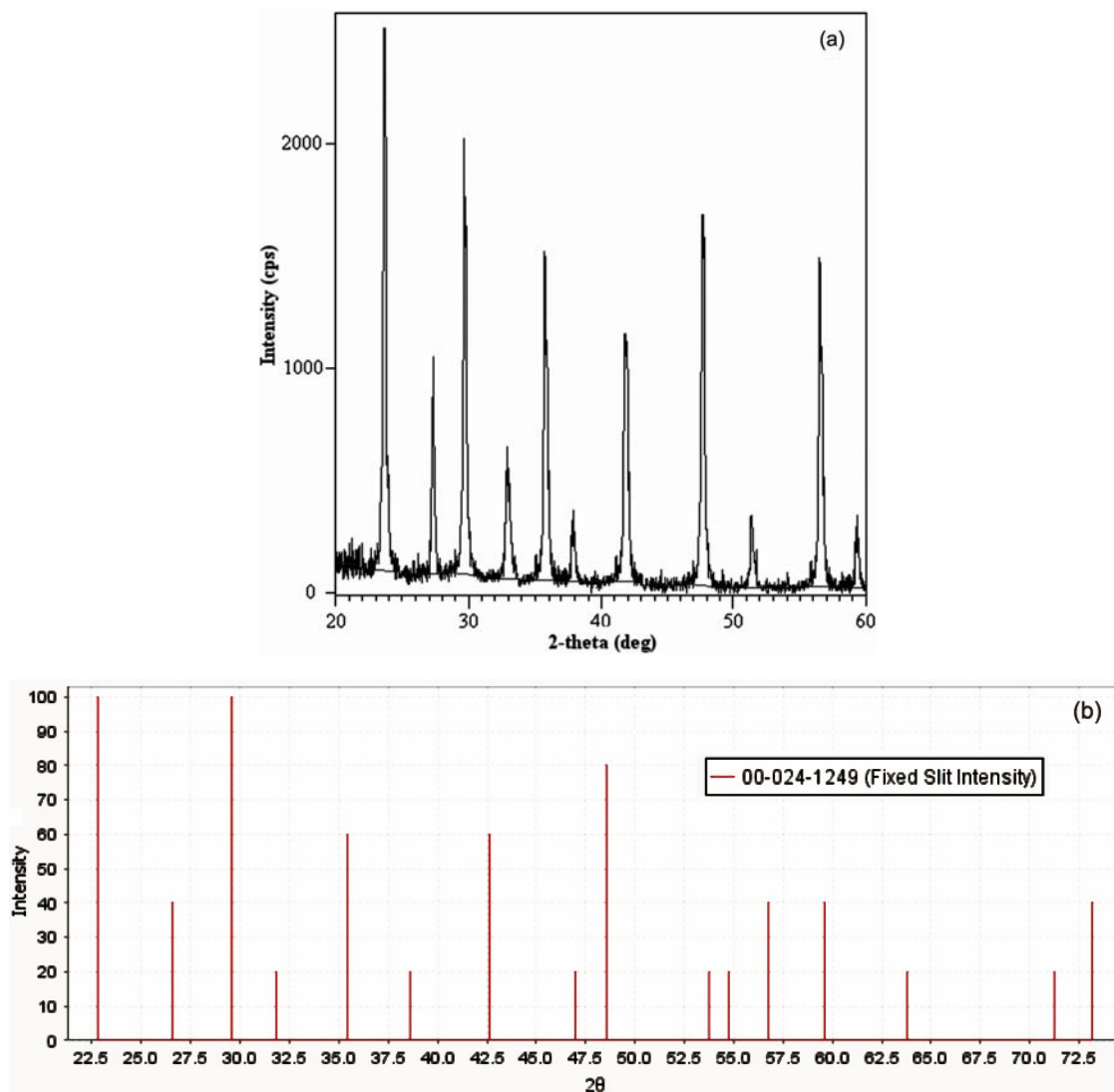


Fig. 1 — (a)-XRD pattern of $\text{SrZr}(\text{BO}_3)_2$ and (b) ICDD File: 00-024-1249

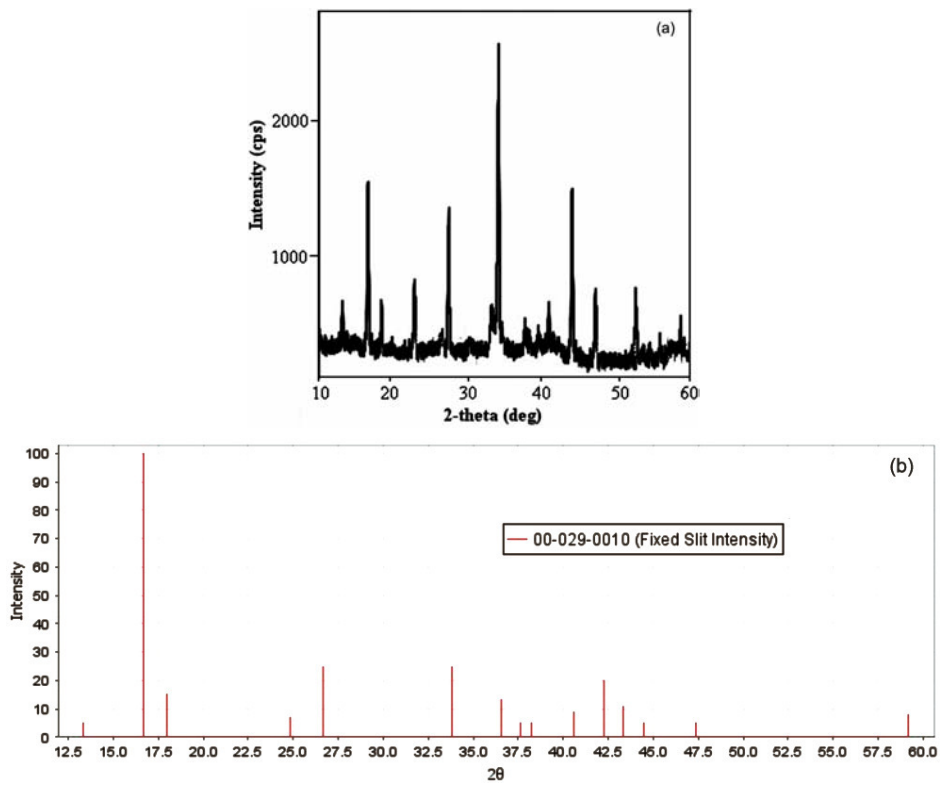


Fig. 2 — (a) XRD pattern of $\text{Al}_4\text{B}_2\text{O}_9$ and (b) ICDD File: 00-029-0010

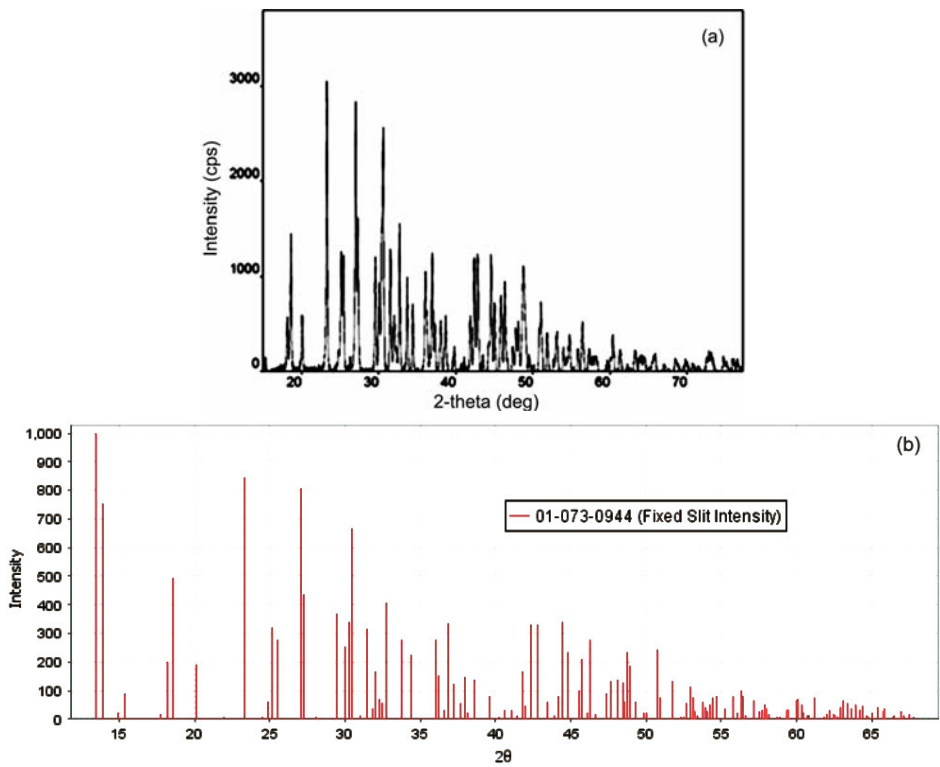


Fig. 3 — (a) XRD pattern of $\text{LaMgB}_5\text{O}_{10}$ and (b) ICDD File: 01-073-0944

The rare earth impurity Gd^{3+} impurity may be useful as an activator in the phosphor used in artificial UV lamp for phototherapy since the common emission of Gd^{3+} ion peaks at 311 nm arises due to transition between ${}^6P_{7/2}$ to ${}^8S_{7/2}$ levels. The emission band of Gd^{3+} is very narrow and lays in the wavelength range 290-320 nm, which is essential for phototherapy lamp. The Gd^{3+} ion itself does not exhibit very intense emission²⁰. The ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition of Gd^{3+} is very weak as it is a parity forbidden f-f transition and hence, requires sensitization for efficient emission. Such type of sensitization results into intense Gd^{3+} emission, can be done by co-doping the host with Pr^{3+} impurity along with Gd^{3+} . Thus, excitation due to $4f^2 ({}^3H_4) \rightarrow 4f^1 5d^1$ transitions of Pr^{3+} , transfers the energy to 6I_1 excited state of Gd^{3+} . After relaxing to 6P_j states, the final emission is in the form of a narrow band around 312 nm. The mechanism of the energy transfer is explained in Fig. 4.

Figure 5 shows the photoluminescence of $SrZr(BO_3)_2:PrGd$ prepared by combustion method. The excitation spectrum (curve-a) recorded at 313 nm emission consists of broad band about 230 nm, can be assigned to $4f^2-4f^15d^1$ intra-configurational transition of Pr^{3+} and small narrow band about 274 nm corresponds to Gd^{3+} absorption. The emission spectrum (curve-b) recorded at 230 nm excitation consists of narrow band (FWHM = 6 nm) peaking at 313 nm can be assigned to ${}^6P_{7/2}-{}^8S_{7/2}$ transition of Gd^{3+} . The photoluminescence spectra of $SrZr(BO_3)_2:PrGd$ thus show efficient $Pr^{3+} \rightarrow Gd^{3+}$ energy transfer. The emission spectrum of the phosphor is almost similar to that of commercial (Philips TL/01) lamp phosphor²².

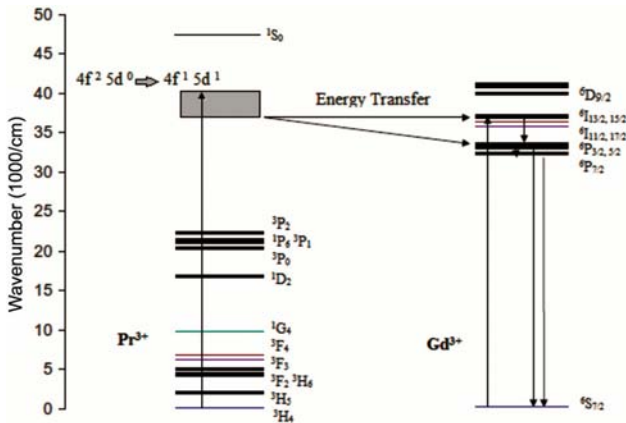


Fig. 4 — Pr^{3+} to Gd^{3+} energy transfer mechanism

3.2 Phosphor for PUVA therapy lamp

In PUVA-therapy in which lamps emit radiation over the whole UVA part of the spectrum (315-400 nm) are used in combination with photosensitizers (for example psoralenes) for the treatment of psoriasis. Treatment with PUVA remains the standard for patients with high PASI scores who do not respond or whose psoriasis²² cannot be controlled adequately by UVB.

Figure 6 shows the photoluminescence of $Al_4B_2O_9:Ce$ prepared by combustion method. The excitation spectrum (curve-a) recorded at 356 nm emission consists of broad band about 270 nm, can be assigned to the transitions from 4f ground state to the crystal field splitted 5d levels of Ce^{3+} . The emission spectrum (curve-b) recorded at 270 nm excitation consists of narrow band peaking at 356 nm, can be assigned to the Ce^{3+} emission from the lowest crystal field component of 5d¹ configuration to the 4f ground

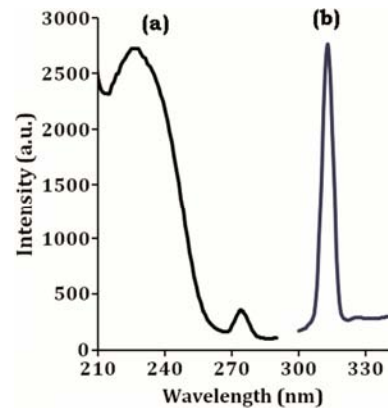


Fig. 5 — (a) Excitation spectra recorded at 313 nm emission and (b) emission spectra recorded at 230 nm excitation of $SrZr_{0.95}Pr_{0.03}Gd_{0.02}(BO_3)_2$

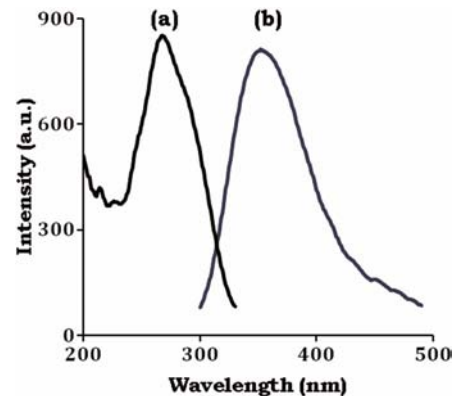


Fig. 6 — (a) Excitation spectra recorded at 365 nm emission and (b) Emission spectra recorded at 270 nm excitation of $Al_{3.95}Ce_{0.05}B_2O_9$

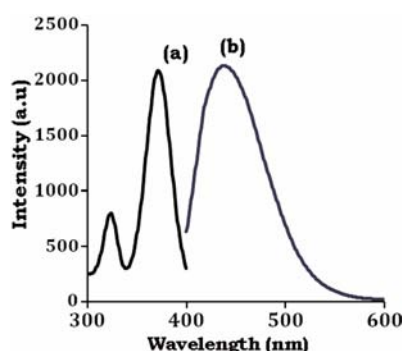


Fig. 7 — (a) Excitation spectra recorded at 440 nm emission and (b) Emission spectra recorded at 373 nm excitation of $\text{La}_{0.99}\text{Ce}_{0.01}\text{MgB}_5\text{O}_{10}$

state levels. The emission spectrum of the phosphor²² is almost similar to that of Philips TL/10 lamp.

3.3 Phosphor for treatment of hyperbilirubinemia (neonatal jaundice)

In new born infant an immature liver is not able to convert unconjugated bilirubin (decomposition product of haemoglobin) into its water soluble conjugated form. New born babies are not easily able to get rid of the bilirubin and it can build in the blood. Hyperbilirubinemia is a condition in which the bilirubin level in the blood becomes high and can diffuse into tissues in the brain, it may cause brain damage. Blue light can convert this unconjugated form of bilirubin into a more water soluble form called lumirubin by a photo-oxidative process and an isomerization process that are then excreted in the urine. The absorption spectrum of bilirubin peaks at 420 nm, thus to treat the hyperbilirubinemia a light source with emission around 430 nm is required. Hence the band just above 400 nm without UV component is desired.

Figure 7 shows Ce^{3+} emission and excitation spectra in $\text{LaMgB}_5\text{O}_{10}$ host. Emission spectrum (curve-b) shows broad emission around 440 nm (recorded at 373 nm excitation) almost similar to Sylvania 2466 blue, BAM phosphor²³. Emission spectrum can be attributed to transitions from lowest crystal field component of $5d^1$ configuration to the 4f ground state level of Ce^{3+} . Excitation spectra (curve-a) show strong absorption band around 373 nm recorded at 440 nm emission. The excitation spectra of $\text{LaMgB}_5\text{O}_{10}:\text{Ce}$ (1%) indicate an Hg free lamp based on near-ultraviolet (n-UV) LEDs peaking at 370–410 nm is possible with this phosphor. This will ensure absence of harmful UV component which can be present in Hg discharge based lamps.

4 Conclusions

UV and blue emitting borate phosphors for their application in phototherapy lamps are discussed. These phosphors are prepared by simple and time saving combustion synthesis technique. The photoluminescence characteristics of these borate phosphors may be compared to those of commercial phosphors.

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References

- 1 Diffey B & Hawk J, *Med Biol*, 37 (1992) 1.
- 2 Lowe N, Prystowsky J, Bourget T & Edelstein J, *J Am Acad Dermatol*, 24 (1991) 591.
- 3 Scherschun L, Kim J & Lim H, *J Am Acad Dermatol*, 44 (2001) 999.
- 4 Ota T, Hata Y, Tanikawa A, Amagai M, Tanaka M & Nishikawa T, *Clin Exp Dermatol*, 26 (2001) 179.
- 5 Warren L, George S & Australas, *J Dermatol* 39 (1998) 179.
- 6 Enk C, Elad S, Vexler A, Kapelushnik J, Gorodetsky R & Kirschbaum M, *Bone Marrow Transpl*, 22 (1998) 1179.
- 7 Leenutaphong V & Jiamton S, *J Am Acad Dermatol*, 33 (1995) 996.
- 8 Blachley J, Blankenship D, Menter A, Parker T & Knochel J, *Am J Kidney Dis*, 5 (1985) 237.
- 9 Dittmar H, Pflieger D, Schopf E & Simon, *J Hautarzt*, 52 (2001) 423.
- 10 Kreuter A, Jansen T, Stucker M, Herde M, Hoffmann K, Altmeyer P & Von Kobyletzki G, *Clin Exp D*, 26 (2001) 30.
- 11 Morita A, Kobayashi K, Isomura I, Tsuji T & Krutmann J, *J Am Acad Dermatol*, 43 (2000) 670.
- 12 Plettenberg H, Stege H, Megahed M, Ruzicka T, Hosokawa Y, Tsuji T, Morita A & Krutmann J, *J Am Acad Dermatol*, 41 (1999) 47.
- 13 Millard M & Hawk J, *Lupus* 10 (2001) 185.
- 14 Van Weelden H, Baart de la Faille H, Young E & Van der Leun J, *Br J Dermatol*, 119 (1988) 11.
- 15 Parrish J, Fitzpatrick T, Tanenbaum L & Pathak M, *New England J Med*, 291 (1974) 1207.
- 16 Dani C & Martelli E, *J Pediatrics*, 138 (2001) 438.
- 17 Nagpure P & Omanwar S, *J Lumin*, 132 (2012) 2088.
- 18 Nagpure P, Bajaj N, Sonekar R & Omanwar S, *Indian J Pure & Appl Phys*, 49 (2011) 799.
- 19 Nagpure P & Omanwar S, *International Journal of Self-Propagating High-Temperature Synthesis*, 22 (2013) 32.
- 20 Sonekar R, Omanwar S, Moharil S, Dhopte S, Muthal P & Kondawar V, *Optical Mater*, 30 (2007) 622.
- 21 Kingsley J, Suresh K & Patil K, *J Mater Sci*, 25 (1990) 1305.
- 22 Koninklijke, *Philips Phototherapy Lamps Catalogue*, 2009.
- 23 Gahane D, Bahirwar B & Moharil S, *International Journal of Mathematical, Computational, Physical & Quantum Engineering*, 7 (2013) 629.