www.vbripress.com/aml, DOI: 10.5185/amlett.2016.6182

Published online by the VBRI Press in 2016

NUV excited K₂SrP₂O₇:RE³⁺ (RE = Sm,Tb, Eu, Dy) phosphors for white light generation

Ketki S. Dhoble¹, J. A. Wani², S. J. Dhoble²

¹Department of Electronics & Communication, Shri Ramdeobaba College of Engineering and Management, Nagpur 440013, India

Received: 16 September 2015, Revised: 02 October 2015 and Accepted: 25 May 2016

ABSTRACT

Phosphate based compounds doped with rare earth ions are promising luminescent materials for many applications including solid state lighting. In this work photoluminescence properties of $K_2SrP_2O_7:RE^{3+}$ (RE = Sm, Tb, Eu, Dy) phosphors are presented for the first time. $K_2SrP_2O_7:RE^{3+}$ phosphors activated with the trivalent rare earth ions were synthesized by combustion method. Phosphors were characterized for phase purity, morphology and luminescent properties. Elemental analysis was done through energy dispersive spectroscopy (EDS). The emission and excitation spectra were followed to study the luminescence characteristics of $K_2SrP_2O_7:RE^{3+}$ phosphors. The as prepared powders of RE^{3+} doped $K_2SrP_2O_7$ emit red, green and yellowish white light as a result of f-f transitions. The study is novel as no such luminescence data are available for this compound. Copyright © 2016 VBRI Press.

Keywords: K₂SrP₂O₇; combustion; phosphor; luminescence; solid state lighting.

Introduction

White light-emitting diodes (LEDs) offer many advantages such as long service lifetime, thermal resistance, and high efficiency. Therefore, white LEDs are expected to be a new light source in the illumination field. Currently, the most common and simple method to produce white light is to combine a blue LED chip with a yellow light emitting phosphor YAG:Ce. However, YAG:Ce emits a greenish yellow light is deficient in a red spectral region, which leads to the fact that the white LED has a poor colour rendering property [1-4]. In order to solve this problem, the compensating red phosphors were introduced. Moreover, the other methods to achieve white LEDs are suggested, for example, they can be obtained by combining a tri-colour (red, green, and blue) phosphor or a single-phase white emitting phosphor with an ultraviolet or near-ultraviolet (UV) LED [5-9]. The latter method yields white light with better spectral characteristics and colour rendering property. Therefore, more attention has been paid to the development of new tri-colour or white emitting phosphor that can be excited in the range of UV or NUV light due to the necessity of increasing the efficiency of white LED. Some green, blue and red emitting phosphors excited by NUV chip have been prepared and extensively studied along these lines. Terbium, europium and dysprosium activators have tremendous applications in lighting technology. As an important family of luminescent materials, phosphates have drawn considerable attention because of their many important chemical and physical properties. In this context luminescence studies on phosphate phosphors were undertaken [10, 11]. Recently,

rare earth ions activated Na₂CaP₂O₇ diphosphates were reported [12]. However, to the best of our knowledge, no attention has been paid to the luminescent properties of RE³⁺ doped K₂SrP₂O₇ diphosphate phosphor. Therefore, in the present paper, the luminescent characteristics, structural properties and morphology of RE³⁺ activated K₂SrP₂O₇ phosphor are investigated. The as prepared phosphors can create the colour emission from blue, green to red. The as prepared phosphors can be effectively excited by UV and NUV light and are suitable for white LEDs.

Experimental

The samples were synthesized by a time and energy saving combustion method. According to the molecular formula $K_2Sr_{1-x}P_2O_7:xRE^{3+}$ (x= concentration of rare earth ion), the raw materials KNO₃, Sr(NO₃)₂, (NH₄)H₂PO₄, urea, Sm₂O₃, Tb₄O₇, Eu₂O₃ and Dy₂O₃ (all materials are of analytical grade) were measured and mixed stoichiometrically in an agate mortar for few minutes till a paste was formed. The paste so formed was and transferred to crucible and put into a muffle furnace preheated at 550 °C to set in the combustion process. Likewise, procedure was adopted for other two dopant ions as well as for all concentrations to prepare a series of RE³⁺ activated K₂SrP₂O₇ phosphors. Finally, all samples prepared in this way were pulverized for few minutes to yield a fine powder. The final phase formation of the host compound was identified by powder X-ray diffraction (XRD) (X'-Pert. PRO-ANNALYTICAL X-ray Diffractometer with Cu K α = 1.5406 Å at 40 kV and 30 mA) at a scanning step of 0.001, in the 2θ range from 10 to 70°. Excitation and emission spectra were measured using RF-5301PC Shimadzu Spectrofluorophotometer with

²Department of Physics, R.T.M. Nagpur University, Nagpur 440033, India

^{*}Corresponding author. E-mail: sjdhoble@rediffmail.com

slit width 1.5 nm. All the measurements were performed at room temperature.

Results and discussion

X-ray powder diffraction pattern

To verify the phase formation and crystalline nature of $K_2SrP_2O_7$ compound, powder X-ray diffraction test of $K_2SrP_2O_7$ was carried out. The powder X-ray diffraction test was carried out by X'- Pert PRO ANALYTICAL X-ray Diffractometer with Cu $K\alpha = 1.5406$ angstrom. The XRD pattern of $K_2SrP_2O_7$ reported in this work is shown in **Fig. 1**. We searched its standard data file in JCPDS data and a file with card number JCPDF 77-0727 was available there. While comparing with the standard data file, as prepared compound exhibited well match (**Fig. 1**). The phosphate compound $K_2SrP_2O_7$ was reported to crystallize in a monoclinic structure comprised of the space group $P2_1/c(14)$ with lattice parameters a=9.168, b=5.712, c=14.720 and β =105.79.

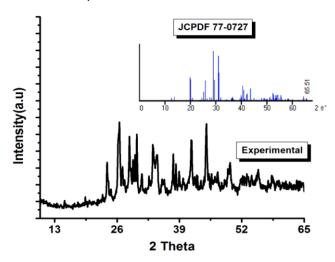


Fig. 1. X-ray powder diffraction patterns of $K_2SrP_2O_7$ and its standard JCPDS file.

Morphology and energy dispersive spectroscopy (EDS) studies of $K_2SP_2O_7$ matrix

The scanning electron microscopic (SEM) image of $K_2SrP_2O_7$ phosphor is shown in **Fig. 2**. The morphological studies were carried out by the JEOL, 6380A scanning electron microscope.

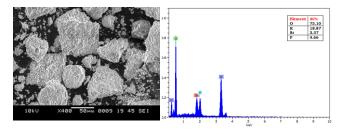


Fig. 2. SEM image and EDS spectrum of K₂SrP₂O₇.

The (SEM) characterization showed that the prepared phosphor has micron size particles. These particles are identical to each other and powders of these particles seem to be homogeneous. Therefore, it seems reasonable to say that particles of $K_2SrP_2O_7$ have developed into a good shape with nearly porous like surfaces, after preparing combustion method. The average particle size through SEM characterization was found to be around $50\mu m$. To determine the composition of the prepared products, an EDS spectrum is presented in **Fig. 3**. It is found that the host matrix is composed of K, Sr, P, and O.

Photoluminescence properties of $K_2SrP_2O_7$: RE^{3+} (RE=Sm, Tb, Eu, Dy) phosphors

Sm3+ has 4f5 configuration and therefore many transitions can occur between 4f levels [13]. As shown in Fig. 3 (a), the excitation spectrum of K₂SrP₂O₇:Sm³⁺ consists of many sharp lines starting from 320 nm to 500 nm. The whole excitation spectrum peaks can be attributed to Sm³⁺ ions because no wavelength peak in the range 220 nm to 500 nm is observed for K₂SrP₂O₇ host. No charge transfer (CT) band corresponding to Sm³⁺–O²⁻ interaction was observed in $K_2SrP_2O_7:Sm^{3+}$ phosphor (**Fig. 3 (a)**). It could be possible that CT band is located in VUV region is beyond our Spectrofluorophotometer scan range. The excitation spectrum was monitored at emission wavelength 598 nm. We observed that among various excitation wavelengths, Sm³⁺ doped K₂SrP₂O₇ phosphors could preferentially be excited by 405 nm as it results in intense reddish orange light around 598 nm. As the excitation wavelength 405 nm is quite far away from mercury excitation (254 nm), it is assumed that K₂SrP₂O₇:Sm³⁺ phosphor will turn out to be eco-friendly. Intense absorption at 405 nm also indicates that K₂SrP₂O₇:Sm³⁺ phosphors can be effectively excited by NUV-LEDs. The excitation wavelength 405 nm corresponds to ${}^{6}H_{5/2} \rightarrow {}^{4}K_{11/2}$ transition of Sm³⁺ ions [13-18]. The orange red light of Sm³⁺ possesses three emission peaks (Fig. 3 (b)) in the visible region near 562, 598, and 644 nm, which are associated to the intra f-f subshell transitions from the excited level ${}^4G_{5/2}$ to ground levels $^6\mathrm{H}_{5/2}$, $^6\mathrm{H}_{7/2}$, and $^6\mathrm{H}_{9/2}$, respectively. The first one at 562 nm $(^4G_{5/2} \rightarrow ^6H_{5/2})$ is a magnetic-dipole transition, the second at 598 nm (${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$) is a partly magnetic and partly forced electric-dipole transition, and the third at 644 nm $(^4G_{5/2} \rightarrow ^6H_{9/2})$ is purely electric dipole transition which is sensitive to the crystal field [13-18]. Also, PL intensity increased with increase in concentration of Sm3+ ions as shown in Fig. 3(i). The most intense emission was observed at 1m % concentration of Sm³⁺ ions (Fig. 3 (i)). Moreover, Sm³⁺ activated luminescence in K₂SrP₂O₇ phosphors did not suffer concentration quenching. A series of Tb³⁺ doped K₂SrP₂O₇ phosphors were obtained by combustion method. The excitation spectrum of K₂SrP₂O₇:Tb³⁺ phosphor which was obtained by monitoring the green emission at 543 nm is shown in Fig. 3(c). The excitation spectrum shows many bands starting from 303nm and ending at 379 nm, which are attributed to the f-f transitions of Tb³⁺. Obviously, the most intense excitation results in intense emission. **Fig. 3(d)** shows emission spectra of $K_2SrP_2O_7:Tb^{3+}$ phosphor. The $K_2SrP_2O_7:Tb^{3+}$ phosphor shows emission bands ranging from 400 to 650 nm, originating from the ⁵D₃ and ⁵D₄ excited states to the ⁷F_J ground states of Tb³⁺ transitions. The emission lines at 418, 437 begin from ⁵D₃

excited state whereas 488, 543, 581 and 623 nm originate from the 5D_4 excited state.

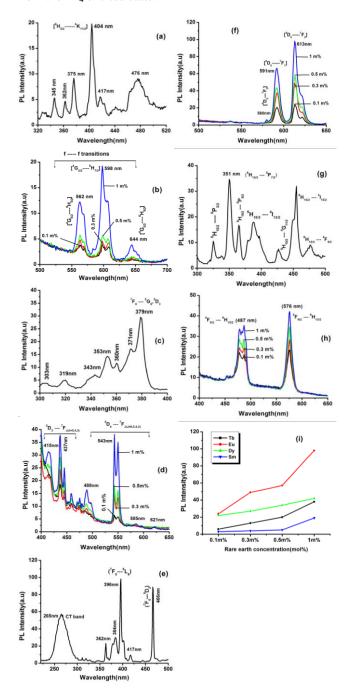


Fig. 3. PL excitation and emission spectra of $K_2SrP_2O_7$: $Sm^{3+}(a)$, (b); $K_2SrP_2O_7$: $Tb^{3+}(c)$,(d); $K_2SrP_2O_7$: $Eu^{3+}(e)$,(f); $K_2SrP_2O_7$: $Dy^{3+}(g)$,(h); and (i) concentration vs PL intensity plot of $K_2SrP_2O_7$: RE^{3+} phosphors (RE=Sm, Tb, Eu, Dy).

The emissions lines at 418 and 437 nm are assigned to the electronic transitions (${}^5D_3 \rightarrow {}^7F_5$) and (${}^5D_3 \rightarrow {}^7F_4$) respectively. Similarly, the emissions lines at 488, 543, 581 and 623 are ascribed to the electronic transitions (${}^5D_4 \rightarrow {}^7F_5$), (${}^5D_4 \rightarrow {}^7F_4$) and (${}^5D_4 \rightarrow {}^7F_3$) respectively. At high doping concentrations, the cross relaxation process favors the emission from 5D_4 state [19-22]. So, in present case, the cross relaxation process dominates. The $K_2SrP_2O_7$:Tb $^{3+}$ phosphor emits green light,

and the 543-551 nm emission is stronger than the other two emissions. The reason is that this transition has the largest probability for both electric-dipole and magnetic-dipole [19-22] induced transitions. As shown in Fig. 3 (i), dependence of PL emission intensity on concentration of activator ions was also investigated and it was found that most intense emission occurred at concentration 1m% Tb³⁺. No concentration quenching of luminescence was observed because PL emission intensity did not reduce on enhancing the concentration of Tb^{3+} ions. As depicted in **Fig. 3** (e), Eu^{3+} ion doped $K_2SrP_2O_7$: Eu^{3+} exhibits a wide excitation spectrum spanning from CT band to sharp lines in NUV region. The excitation spectra of K₂SrP₂O₇:Eu³⁺ phosphor has a broad excitation band in the range 220-300 nm and 300nm onwards sharp excitation peaks in the near NUV (320–396 nm) and visible (420– 470 nm) regions. The broad excitation band peaking at around 265 nm can be attributed to charge transfer (CT) between O²⁻ and Eu³⁺ while the sharp excitation peaks are due to f-f transitions of Eu³⁺ ions [23-26]. The strong absorption was seen only at 265 nm, 396 nm and 466 nm as these three wavelengths results in intense reddish orange emission around 591 nm and 613nm respectively. The excitation spectrum was monitored at 613 nm emission wavelength. In the emission spectra (Fig. 3 (f)) various peaks at 580nm, 591nm and 613nm respectively, were observed under excitation wavelengths 265nm, 396nm and 467nm. In the present case emission spectrum observed at 396nm is shown only. The emission spectrum was dominated by the red and orange peaks at 613nm and 591nm due to the electric dipole and magnetic dipole ${}^5D_0 \rightarrow {}^5F_2$ and ${}^5D_0 \rightarrow {}^5F_1$ transitions respectively [23-26]. We also observed that PL intensity varied with change in doping concentration of Eu³⁺ ions in K₂SrP₂O₇ phosphor. This variation trend is shown in Fig. 3(i). The highest PL intensity was obtained at 1m% Eu^{3+} in $K_2SrP_2O_7$: Eu^{3+} phosphor (**Fig. 3(i)**). **Fig. 3(g)** shows the excitation spectrum of K₂SrP₂O₇:Dy³⁺ phosphor. This excitation spectrum was monitored at 576nm emission wavelength. The excitation spectrum of Dy³⁺ ions indicates several lines in the wavelength region of 300 - 500 nm, which are due to excitation of 4f electrons through f-f transitions of Dy3+ ions. Excitation peaks at 324 nm, 351 nm, 364 nm, 396 nm, 426 nm and 454 nm correspond to the transitions from the ground state ${}^{6}\mathrm{H}_{15/2}$ to the excited states; ${}^4P_{7/2}$, ${}^4P_{3/2}$ and ${}^4F_{7/2}$ respectively. **Fig. 3(h)** shows the emission spectra of $K_2SrP_2O_7$:Dy³⁺ phosphor. In the emission spectrum, the yellowish white light is made up of blue (483 nm) and yellow (574 nm) regions. They correspond to the emission from the ${}^{4}F_{9/2}$ excited state to the ⁶H_{15/2} and ⁶H_{13/2} ground states, respectively. It is quite familiar that the hypersensitive ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition with $\Delta J = 2$, is extremely affected by the outside surrounding environment i.e., the crystal field and the magnetic dipole ${}^{4}\mathrm{F}_{9/2} \rightarrow {}^{6}\mathrm{H}_{15/2}$ transition is unsusceptible to the crystal field strength around the Dy³⁺ ions. When Dy³⁺ is placed at a low symmetry local site (without inversion symmetry), the yellow emission is often dominant in the emission spectrum and when Dy3+ is at a high symmetry local site (with inversion symmetry center), the blue emission is stronger than the yellow emission and is dominant in the emission spectrum [27-31]. The former case occurs for Dy³⁺ doped K₂SrP₂O₇ phosphors. Fluorescence emission intensity varied with increase in concentration of Dy^{3+} activator ions and the most intense emission was obtained at $1\,\mathrm{m}\%$ Dy^{3+} (**Fig. 3(i)**). To locate the position of CIE points of $K_2\mathrm{SrP}_2\mathrm{O}_7$: RE^{3+} phosphors in CIE diagram (**Fig. 4**); CIE coordinates were calculated on the basis of emission spectra. The CIE coordinates so obtained are (x=0.498,y=0.489), (x=0.334,y=0.551), (x=0.523,y=0.384) and (x=0.274,y=0.316) for $K_2\mathrm{SrP}_2\mathrm{O}_7$: Sm^{3+} , $K_2\mathrm{SrP}_2\mathrm{O}_7$: Tb^{3+} , $K_2\mathrm{SrP}_2\mathrm{O}_7$: Eu^{3+} and $K_2\mathrm{SrP}_2\mathrm{O}_7$: Dy^{3+} respectively. These values fall in the vicinity of white light region on CIE diagram.

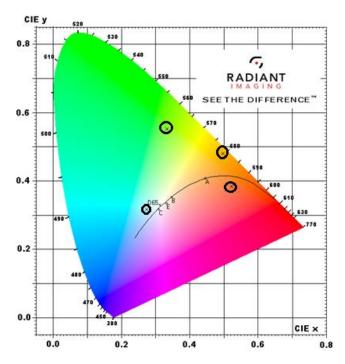


Fig. 4. CIE diagram of K₂SrP₂O₇: RE³⁺ phosphors. Encircled cross in reddish orange region shows CIE points for K₂SrP₂O₇: Sm³⁺. Encircled cross in green region represents CIE points for K₂SrP₂O₇: Tb³⁺. Encircled cross in red region represents CIE points for K₂SrP₂O₇:Eu³⁺. Encircled cross in whitish blue region represents CIE points for K₂SrP₂O₇:Dy³⁺.

Conclusion

K₂SrP₂O₇: RE³⁺ (RE=Sm, Tb, Eu, Dy) phosphors were synthesised by combustion method at 550 °C. Typical excitation and emission spectra were observed for all RE³⁺ ions doped in K₂SrP₂O₇ system. Both magnetic dipole as well as electric dipole transitions are involved in the luminescence behaviour of RE3+ activated K2SrP2O7 phosphors. Very strong absorption in NUV region for K₂SrP₂O₇: RE³⁺ phosphors indicate that it could be effectively excited by LEDs emitting in the NUV region. The CIE coordinates of K₂SrP₂O₇: RE³⁺ phosphors lie in the neighborhood of white light region on the CIE diagram, which in turn shows that they are suitable candidates for white light generation. The whole photoluminescence results show that K₂SrP₂O₇:RE³⁺ system could become an important component of pc-WLEDs for solid state lighting applications. Moreover, since excitation wavelengths of K₂SrP₂O₇:RE³⁺ systems are at much distance from mercury wavelength, therefore it is expected that the present prepared system could turn out environment friendly. References

- 1. Huang, S.; Li, G.; Opt. Mater., 2014, 36, 1555.
- DOI: 10.1016/j.optmat.2014.04.024
 Rongfang, W.; Liya, Z.; Yilin, W.; J. Rare Earths, 2011, 29, 1045.
 DOI: 10.1016/S1002-0721(10)60595-9
- Wani, J. A.; Dhoble, N.S.; Kokode, N.S.; Prasad Raju, B. D.; Dhoble, S. J.; J. Lumin., 2014, 147, 223.
 - **DOI:** <u>10.1016/j.jlumin.2013.10.007</u>
- Chen, Si; Wang, Y.; Zhang, J.; Zhao, L.; Wang, Q.; Han, L.; J. Lumin., 2014, 150, 46.
 - **DOI**: <u>10.1016/j.jlumin.2014.01.021</u>
- Nishida, T.; Ban, T.; Kobayashi, N.; Appl. Phys. Lett., 2003, 82, 3817.
- **DOI:** <u>10.1063/1.1580649</u>
- 6. Tosaka, Y.; Adachi, S.; J. Lumin., 2014, 156, 157.
 - **DOI:** <u>10.1016/j.jlumin.2014.08.010</u>
- 7. Xu, M.; Wang, L.; Jia, D.; Le, F.; J. Lumin., 2015, 158, 125.
 - **DOI:** <u>10.1016/j.jlumin.2014.09.040</u>
- Song, E.; Zhao, W.; Zhou, G.; Dou, X.; Ming, H.; Yi, C.; Curr. Appl. Phy., 2011, 11, 1374.
 - **DOI:** <u>10.1016/j.cap.2011.04.006</u>
- Ju, G.; Hun, Y.; Chen, Li; Wang, X.; Mu, Z.; Wu, H.; Kang, F.; *Optics & Laser Technology*, 2012, 44, 39.
 DOI: <u>10.1016/j.optlastec.2011.05.013</u>
- Shinde, K. N; Dhoble, S. J.; Kumar, A.; *Physica B* 2011, 406, 94.
 DOI: <u>10.1016/j.physb.2010.10.028</u>
- Nagpure, I. M.; Shinde, K. N.; Kumar, V.; Ntwaeaborwa, O.M.; Dhoble, S. J.; Swart, H.C.; *J. Alloy. Compd.* **2010**, *492*, 384.
 DOI: <u>10.1016/j.jallcom.2009.11.110</u>
- Wani, J.A.; Dhoble, N.S.; Kokode, N.S.; Prasad Raju, B. D.; Dhoble, S.J.; Adv. Mat. Lett., 2014, 5, 459.
 DOI: 10.5185/amlett.2014.amwc.1211
- Li, Y. C.; Changa, Y. H.; Lin, Y. F.; Chang, Y. S.; Lin, Y. J.; J. Alloys Compd., 2007, 439, 367.
 DOI: 10.1016/j.jallcom.2006.08.269
- Yang, Z.; Dong, H.; Liu, P.; Hou, C.; Liang, X.; Fachun Lu, Wang, C., *J. Rare Earths*, **2014**, *32*, 404.
 DOI: <u>10.1016/S1002-0721(14)60085-5</u>
- Ci, Z.; Zhu, Ge; Shi, Y.; Wang, Y.; J. Rare Earths, 2013, 31, 1049.
 DOI: 10.1016/S1002-0721(12)60401-3
- 16. Zhang, F.; Wang, Y.; Wen, Y.; Wang, D.; Tao, Ye; Opt. Mater., 2011, 33, 475.
 - **DOI:** <u>10.1016/j.optmat.2010.10.035</u>
- Luitel, Hom Nath; Watari, Takanori; Chand, Rumi; Torikai, Toshio;
 Yada, M.; *Opt. Mater.*, **2012**, *34*, 1375.
 DOI: <u>10.1016/j.optmat.2012.02.025</u>
- Yu, R.; Minoh, H.; Moon, Byung Kee; Choi, Byung Chun; Jeong, Jung Hyun; Lee, Ho Sueb; Jang, Kiwan; Yi, Soung Soo; J. Lumin., 2014, 145, 717.
- **DOI:** 10.1016/j.jlumin.2013.08.049

 19. Erdogmus, E.; Korkmaz, E.; *Optik.*, **2014**, *125*, 4098.
 - **DOI:** <u>10.1016/j.ijleo.2014.03.001</u>
- Liao, J.; Zhou, Dan; You, H.; Wen, He-rui; Zhou, Q.; Yang, Bin; Optik., 2013, 124, 1362.
- **DOI:** <u>10.1016/j.ijleo.2012.03.046</u>
- Liao, J.; Zhou, Dan; Qiu, Xin; Liu, S.; Wen, He-Rui; Optik, 2013, 124, 5057.
 - **DOI:** <u>10.1016/j.ijleo.2013.03.067</u>
- Pan-Lai, Li; Yong-Sheng, W.; Su-Ling, Z.; Fu-Jun, Z.; Zheng, X.; Chin. Phys. B, 2012, 21, 127804.
 - **DOI:** 10.1088/1674-1056/21/12/127804
- 23. Zhou, X.; Wang, X.; Optik., 2013, 124, 1038.
 - **DOI:** 10.1016/j.ijleo.2013.01.013
- Kuang, Shao-Ping; Liang, Kun; Liu, Jie; Mei, Yong-Mei; Jiang, Man;
 Wu, Zhan-Chao; Li, Dong-Xiang; Optik 2014, 125, 2970
 DOI: 10.1016/j.ijleo.2013.12.037
- Cavalli, E.; Angiuli, F.; Belletti, A.; Boutinaud, P.; Opt. Mater., 2014, 36, 1642.
 - **DOI:** 10.1016/j.optmat.2013.12.020
- Wang, X.; Du, F.; Wei, D.; Huang, Y.; Seo, Hyo Jin; Sensors and Actuators B, 2011, 158, 171.
 - **DOI:** <u>10.1016/j.snb.2011.05.061</u>
- Shinde, K.N.; Dhoble, S.J.; Optik., 2012, 123, 1975.
 DOI: 10.1016/j.ijleo.2011.09.033
- 28. Pekgozlu, İ.; Cakar, S.; *J. Lumin.*, **2012**, *132*, 2312. **DOI:** <u>10.1016/j.jlumin.2012.04.025</u>

 Tong, M.; Liang, Y.; Li, G.; Xia, Z.; Zhang, M.; Yang, F.; Wang, Q., *Opt. Mater.* 2014, 36, 1566.
 POLY 10 1016 F. Act 2014 04 026

DOI: 10.1016/j.optmat.2014.04.026

 Wani, J.A.; Atone, M.S.; Dhoble, N.S.; Dhoble, S.J.; J. Lumin. 2013, 134, 640.

DOI: <u>10.1016/j.jlumin.2012.07.015</u>

31. Wani, J.A.; Dhoble, N.S.; Lochab, S. P.; Dhoble, S. J.; Nucl. Instrum.

Meth. B, 2015, 349, 56.

DOI: <u>10.1016/j.nimb.2015.01.054</u>

