Т. 90, № 2 **ЖУРНАЛ ПРИКЛАДНОЙ СПЕКТРОСКОПИИ** МАРТ — АПРЕЛЬ 2023
V. 90, N 2 **JOURNAL OF APPLIED SPECTROSCOPY** MARCH — APRYL 2023

PHOTOLUMINESCENCE STUDIES OF BLUISH-WHITE EMISSION FROM Dy^{3+}-ACTIVATED Li_2CaSiO_4 PHOSPHOR

M. P. D. Parimala [1], M. C. Rao [1,2*], Vikas Dubey [3], K. V. R. Murthy [4]

[1] Department of Physics, Krishna University, Machilipatnam, India;
e-mail: raomc72@gmail.com
[2] Department of Physics, Andhra Loyola College, Vijayawada, India
[3] Department of Physics, Bhilai Institute of Technology Raipur, New Raipur,
Chhattisgarh, India
[4] Department of Applied Physics, Faculty of Engineering and Technology,
M. S. University of Baroda, Vadodara, India

Dy^{3+}-doped Li_2CaSiO_4 phosphors were prepared by high temperature solid-state reaction. Structural studies were carried out using X-ray diffraction technique. Scanning electron microscopy was used to get information about the morphology of the prepared samples. Also, photoluminescence analysis of the phosphor samples for different concentrations of the doping ion with variable excitations was presented. When doped with Dy^{3+}, Li_2CaSiO_4 emits intense emission bands at 485 and 576 nm (excited at 353 nm). Our study shows that the as-prepared phosphor may be useful in white light-emitting diodes as a bluish component. The corresponding transitions of the doping ion and concentration quenching effect were studied in detail. The CIE 1931 (x, y) chromaticity coordinates (x = 0.24 and y = 0.31) show the distribution of the spectral region calculated from photoluminescence emission spectra.

Keywords: *photoluminescence, phosphor, transitions, rare earth, white light-emitting diodes.*

ИЗУЧЕНИЕ ФОТОЛЮМИНЕСЦЕНТНОГО ГОЛУБОВАТО-БЕЛОГО ИЗЛУЧЕНИЯ ЛЮМИНОФОРА Li_2CaSiO_4, АКТИВИРОВАННОГО Dy^{3+}

M. P. D. Parimala [1], M. C. Rao [1,2*], V. Dubey [3], K. V. R. Murthy [4]

УДК 535.37

[1] Университет Кришны, Мачилипатнам, Индия; e-mail: raomc72@gmail.com
[2] Колледж Андхра Лойола, Виджаявада, Индия
[3] Бхилайский технологический институт, Райпур, Нью-Райпур, Чхаттисгарх, Индия
[4] Университет Бароды, Вадодара, Индия

(Поступила 11 мая 2022)

Люминофоры Li_2CaSiO_4, легированные Dy^{3+}, изготовлены методом высокотемпературной твердотельной реакции. Структура и морфология образцов исследованы методами рентгеновской дифракции и сканирующей электронной микроскопии. Представлен фотолюминесцентный анализ образцов с различными концентрациями легирующего иона при возбуждении на разных длинах волн. При легировании Dy^{3+} Li_2CaSiO_4 испускает интенсивные полосы на длинах волн 485 и 576 нм ($\lambda_{возб}$ =353 нм). Показано, что изготовленный люминофор может быть полезен в белых светодиодах в качестве голубоватого компонента. Изучены соответствующие переходы легирующего иона и эффект концентрационного тушения. Координаты цветности CIE 1931 (x, y) (x = 0.24 и y = 0.31) показывают положение спектральной области, рассчитанное по спектрам фотолюминесценции.

Ключевые слова: *фотолюминесценция, люминофор, переходы, редкоземельный элемент, белый светодиод.*

Introduction. Dy^{3+}-doped phosphor is very important owing to its blue-yellow (B/Y) emission, which can be useful for white light-emitting diode application [1–8]. This kind of phosphor is more in demand and attractive because of high chemical and physical stability, various crystal structures, excellent weather resistance, low price, and many other advantages. Recent study adds that owing to encouraging luminescent properties, alkaline earth silicate material doped with rare earth has been paid increasing attention, which makes it a promising candidate for various applications for white light-emitting diodes (WLEDs) and various color-emitting phosphors. Thus, the development of new phosphors for WLED applications is highly desirable.

Recently, Shreya et al. (2020) have reported Ca_2LaTaO_6 phosphor doped with Dy ion and found suitable application in phosphor-converted WLEDs (pc-WLEDs) [9]. Previously, Siband et al. (2021) had discussed $RbBaScSi_3O_9$ activated by Ce, Eu, and Dy, which can be applicable for pc-LEDs [10]. Singh et al. (2017) synthesized the Dy-activated $BaTiO_3$ phosphor and its thermo-luminescence study using a suitable large-scale production method for dosimetric application [11]. Herein, we prepared the Dy^{3+}-activated Li_2CaSiO_4 phosphor with variable concentrations of the doping ion of 0.01–0.20 wt (in grams) and calculated its spectral parameters using Commission Internationale de l'Éclairage (CIE) coordinates.

Materials and methods. Dy^{3+}-doped Li_2CaSiO_4 with variable concentrations of x = 0.01, 0.05, 0.10, 0.15, and 0.20 wt (in grams) was mainly prepared by the solid-state synthesis route. High purified Li_2CO_3, $CaCO_3$, SiO_2, and Dy_2O_3 were primarily taken without further purification as starting materials. At first, all the initial materials were weighed and mixed together in proper proportions. Then, these mixed powders were put into alumina crucible for calcinations at 500°C for 2 h and after cooling, the samples were collected for further sintering at 900°C for 2 h in air.

The X-ray diffraction (XRD) patterns of the samples were captured using a Bruker AXS D8 Advance mainly functioning in the Bragg–Brentano focusing geometry. The CuK_α radiation of about λ = 1.54060 Å has been used majorly as an X-ray source. These instruments were generally operated at a high voltage of 40 kV and a small operating current of 30.00 mA. The XRD patterns were noted with a scan rate of about 5.00°/min in the 10–80° range. The scanning electron microscope (SEM), JEOL JSM-6390LV, was accustomed to examining the morphology of these samples. Spectro-fluorophotometer instruments (RF-5301PC, Shimadzu) were used to record the excitation spectra and photoluminescence emission of the samples under UV-visible excitation. The CIE chromaticity coordinates were calculated from the emission spectra of the phosphor samples using LUMPAC software.

Results and discussion. The XRD pattern of the Dy^{3+} ion-activated Li_2CaSiO_4 phosphor is presented in Fig. 1, for an optimized concentration of 0.10 wt (in grams). The sample is mono-phased and crystallizes in a cubic structure, which was matched with JCPDS No. 47-0120. All peaks are assigned according to the literature with no further evidence for any impurities. It is possible that some Dy^{3+} ions will replace Ca^{2+} ions in the present phosphor because of larger ionic radii [12]. This result also demonstrates that Dy^{3+} ions are in the position of Ca^{2+} ions, because the size of the Dy^{3+} ion (r = 0.091 nm) is nearer to that of the Ca^{2+} ion (r = 0.100 nm) [13–25].

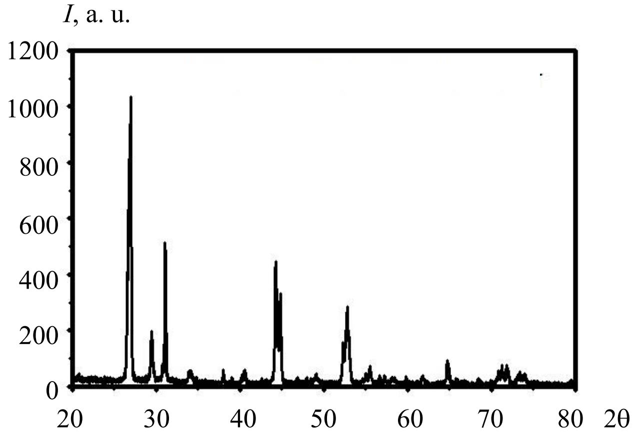

Fig. 1. XRD pattern of Dy^{3+} (0.10 wt (in grams)) activated Li_2CaSiO_4 phosphor.

Scherer’s formula was used to determine crystallite size:

$$D = 0.9\lambda/(\beta\cos\theta), \tag{1}$$

where D denotes particle size, β denotes full-width at half of maximum (FWHM) of the peak, λ is the wavelength of X-ray diffraction source, and θ is the angle of diffraction.

The scanning electron micrographs of Dy^{3+}-activated samples are presented in Fig. 2 with different resolutions (×5000 to ×30,000, range: 1 μm to 100 nm)). Micrographs clearly indicate that the particles crystallized in inhomogeneous morphology, which shows grain growth tendency and agglomeration when prepared at high temperatures and with the particle sizes from few micrometers to nanometers. This gradient in particle size is expected as these samples are known to agglomerate, need specific, long ball milling to form homogenous morphology.

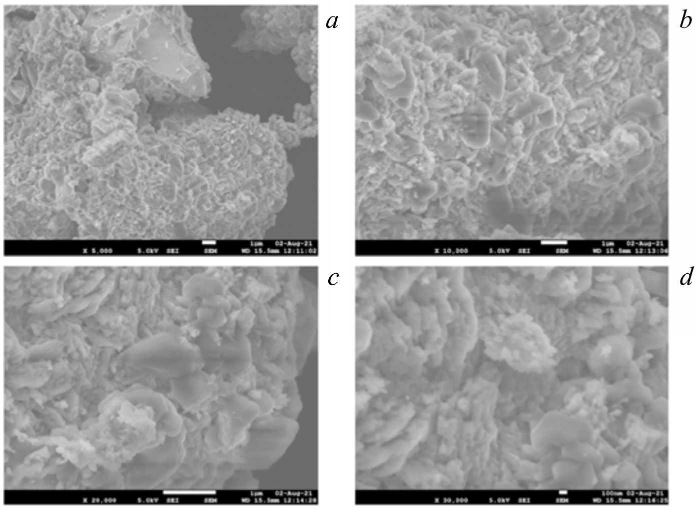

Fig. 2. SEM images of Dy^{3+} (0.10 wt (in grams)) activated Li_2CaSiO_4 phosphor under different resolutions (×5000 (a), 10,000 (b), 20,000 (c), and ×30,000 (d), range: 1 μm to 100 nm).

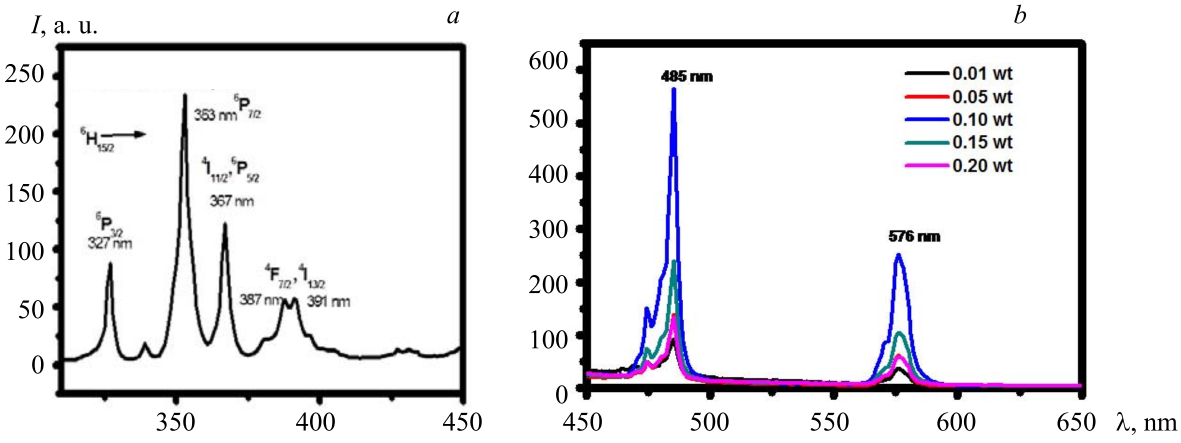

Fig. 3. a) PL excitation spectrum of Dy^{3+} (0.10 wt (in grams)) activated Li_2CaSiO_4 phosphor; b) PL emission spectra of Dy^{3+}-activated Li_2CaSiO_4 phosphor with variable concentrations. 351-4

The photoluminescence (PL) excitation and emission spectra were presented in Fig. 3 for the fixed concentration of the doping ion, i.e., Dy^{3+} (0.10 wt (in grams)), with several sharp excitation peaks centered at 327 ($^6H_{15/2}\rightarrow{}^6P_{3/2}$), 353 ($^6H_{15/2}\rightarrow{}^6P_{7/2}$), 367 ($^6H_{15/2}\rightarrow{}^4I_{11/2}$, $^6P_{5/2}$), 387 ($^6H_{15/2}\rightarrow{}^4F_{7/2}$), and 391 ($^6H_{15/2}\rightarrow{}^4I_{13/2}$) nm [26], which correspond to the emission band at blue (485 nm) and yellow (576 nm), for various transitions of the Dy^{3+} ion. From the figure, the excitation spectrum has two peaks, the main one at 485 nm has been assigned and originated from $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and 576 nm owing to the transition of $^4F_{9/2}\rightarrow{}^6H_{13/2}$ [27–29]. So, both the peaks composed produced a bluish-white emission, which was calculated using the CIE 1931 coordinates. From the emission spectra, it has been seen that the PL intensity increases with the growth of the concentration of the doping ion up to 0.10 wt (in grams); after that, the PL intensity decreases owing to the concentration quenching phenomenon.

The CIE 1931 (*x*, *y*) chromaticity coordinates show the distribution of spectral regions calculated from PL emission spectra and they were found to be (0.24, 0.31) in the bluish-white region for the phosphor in Fig. 4. In the present study, the dominant peak centered at 485 and 576 nm was presented in the CIE coordinate. From the CIE coordinate, the depicted peak at the blue region can be useful for WLEDs, e.g., bluish-white emitting phosphors converted the UV chip-based WLEDs.

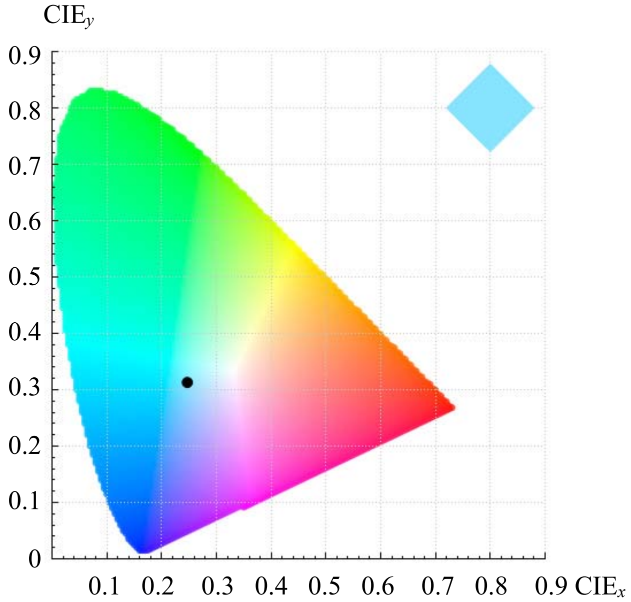

Fig. 4. CIE coordinates of Dy^{3+} (0.10 wt (in grams)) activated Li_2CaSiO_4 phosphor depicted on 1931 chart.

Conclusions. We have prepared Dy^{3+}-doped phosphors with various concentrations of the doping ion. These samples are mainly characterized using different techniques, for instance, XRD, SEM, and PL. XRD and SEM techniques showed the crystalline structure and irregular morphology of the prepared phosphors. PL measurements show excitation and emission characteristics of the prepared phosphor with different concentrations of the doping ion and various excitation effects. The PL intensity increases with the growth of the concentration of the doping ion up to 0.10 wt (in grams); after that, the PL intensity decreases owing to the concentration-quenching phenomenon. It is proposed that the prepared phosphor may be useful for WLEDs.

REFERENCES

1. N. Dubey, V. Dubey, *Rev. Fluores.*, **23**, 155–184 (2017).
2. D. Singh, J. Kaur, N.S. Suryanarayana, R. Shrivastava, V. Dubey, *J. Mater. Sci. Mater. Electron.*, **28**, 2462–2470 (2017).
3. V. Dubey, R. Tiwari, R. K. Tamrakar, J. Kaur, S. Dutta, S. Das, H. G. Visser, S. Som, *J. Lumin.*, **41**, 169–180 (2016).
4. J. Kaur, D. Chandrakar, V. Dubey, R. Shrivastava, Y. Parganiha, N. S. Suryanarayana, *J. Dis. Tech.*, **12**, 171–182 (2016).
5. J. Kaur, R. Singh, P. Bose, Y. Parganiha, R. Shrivastava, V. Dubey, *J. Dis. Tech.*, **12**, 567–581 (2016).
6. V. Dubey, J. Kaur, Y. Parganiha, N. S. Suryanarayana, K. V. R. Murthy, *Appl. Rad. Isotop.*, **16**, 110–116 (2016).
7. V. Dubey, J. Kaur, S. Agrawal, *Mat. Sci. Semicond. Proc.*, **31**, 27–37 (2015).
8. R. Shrivastava, J. Kaur, V. Dubey, *J. Fluores.*, **26**, 105–111 (2016).
9. P. Shreya, P. Tadge, N. S. Rawat, D. K. Koul, C. M. Mehare, S. J. Dhoble, S. Ray, *J. Lumin.*, **226**, 335–339 (2020).

10. L. Sibang, H. Yuan, Y. Feng, X. Sun, *J. Lumin.*, **238**, 321–327 (2021).
11. R. Singh, J. Kaur, P. Bose, R. Shrivastava, V. Dubey, Y. Parganiha, *J. Mater. Sci. Mater. Electron.*, **28**, No. 18, 13690–13697 (2017).
12. W. J. Park, Y. H. Song, D. H. Yoon, *J. Mater. Sci. B*, **173**, 76–79 (2010).
13. M. P. Saradhi, U. V. Varadaraiu, *Chem. Mater.*, **18**, 5259–5267 (2006).
14. Y. Rao, X. Hu, T. Liu, X. Zhou, Y. Li, *J. Rare Earths*, **29**, 27–33 (2011).
15. Q. Liu, Y. Liu, Y. Ding, Z. Peng, Q. Yu, X. Tian, G. Dong, *J. Solgel Sci. Technol.*, **7**, 276–282 (2014).
16. Z. J. Wang, P. L. Li, T. Li, X. Zhang, Q. X. Li, Z. P. Yang, Q. L. Guo, *Mater. Res. Bull.*, **48**, 2393–2395 (2013).
17. M. B. Xie, Y. B. Li, R. L. Li, *J. Lumin.*, **136**, 303–306 (2013).
18. Y. Bing, H. Huang, *J. Alloys Comp.*, **429**, 338–342 (2007).
19. Y. Q. Li, N. Hirosaki et al., *J. Lumin.*, **130**, 1147–1153 (2010).
20. T. S. Chan, C.C. Lin, R.S. Liu, *J. Electrochem. Soc.*, **156**, No. 7, 189–191 (2009).
21. P. Molina, M. Prokic, *J. Rad. Measur.*, **45**, 78–82 (2010).
22. K. Toda, Y. Kawakami, M. K. Sato, *IEICE Trans. Electron. E*, **89C**, No. 10, 1406–1412 (2006).
23. M. C. Rao, *J. Optoelect. Adv. Mater.*, **13**, No. 1–2, 78–81 (2011).
24. K. Ravindranadh, B. Babu, C. V. Reddy, J. Shim, M. C. Rao, R. V. S. S. N. Ravikumar, *Appl. Mag. Res.*, **46**, No. 1, 1–15 (2015).
25. S. Muntaz Begum, G. Nirmala, K. Ravindranadh, T. Aswani, M. C. Rao, R. V. S. S. N. Ravikumar, *J. Mol. Struct.*, **1006**, No. 1, 344–347 (2011).
26. A. K. Vishwakarma, K. Jha, M. Jayasimhadri, B. Sivaiah, B. Gahtori, D. Haranath, *Dalton Trans.*, **44**, No. 39, 17166–17174 (2015).
27. M. Venkataravanappa, R. B. Basavaraj, G. P. Darshan, B. Daruka Prasad, S. C. Sharma, P. Hema Prabha, S. Ramani, H. Nagabhushana, *J. Rare Earths*, **36**, No. 7, 690–702 (2018).
28. B. Liu, S. Chaoshu, Z. Qi, *Appl. Phys. Lett.*, **86**, No. 19, 191111 (2005).
29. M. L. Chepyga, A. Osvet, I. Levchuk, A. Ali, Y. Zorenko, V. Gorbenko, T. Zorenko, A. Fedorov, C. J. Brabec, M. Batentschuk, *J. Lumin.*, **202**, 13–19 (2018).