Photoluminescence properties of wet-chemically synthesized Tb$^{3+}$ and Sm$^{3+}$ doped K$_3$Ca$_2$(SO$_4$)$_3$Cl phosphor

Nahida Baig$^1$, J G Mahakhode$^{2*}$, Puja Kumari$^3$, Yatish R Parauha$^4$, N S Dhoble$^5$ and Samikha B. Dhoble$^4$

$^1$Department of Physics, Janaata Mahavidyalaya, Chandrapur-442401, India
$^2$Department of Electronics, D.B. Science College, Godia-441614, India
$^3$Department of Physics, Darbanga College of Engineering Darbhanga, Mabbi-846005, India
$^4$Department of Physics, R.T.M. Nagpur University, Nagpur-440033, India
$^5$Seva dal Mahila Mahavidyalaya, Sakkardara Square, Nagpur-440009, India

* Corresponding author email: jayantmahakhode@gmail.com

Abstract. In this study, we are successfully synthesized terbium and samarium (Tb$^{3+}$/Sm$^{3+}$) doped K$_3$Ca$_2$(SO$_4$)$_3$Cl phosphors by wet chemical method, and synthesized phosphors were characterized by XRD, SEM, and Photoluminescence (PL) techniques, and studied in detail. Photoluminescence analysis, we can see that under the Near-UV (NUV) excitation of 380nm, the Tb$^{3+}$ activated samples showed a prominent green emission peak at 546nm attributed to the $^5D_{4}→^7F_{5}$ transition of Tb$^{3+}$ ions. While the PL emission spectra of 404 nm light excited K$_3$Ca$_2$(SO$_4$)$_3$Cl:Sm$^{3+}$ phosphors showed three emission lines at 565nm, 598nm and 645nm attributed to $^4G_{5/2}→^6H_{5/2}$, $^4G_{5/2}→^6H_{7/2}$, and $^4G_{5/2}→^6H_{9/2}$ transitions of Sm$^{3+}$ ions, respectively. The CIE coordinates were calculated to be (0.263, 0.515) for K$_3$Ca$_2$(SO$_4$)$_3$Cl:Tb$^{3+}$ and (0.532, 0.462) for K$_3$Ca$_2$(SO$_4$)$_3$Cl:1.5mol%Sm$^{3+}$, which lie in the green and orange regions, respectively. The entire photoluminescence results indicated that phosphor K$_3$Ca$_2$(SO$_4$)$_3$Cl doped with Tb$^{3+}$ and Sm$^{3+}$ may turn out to be an important component of pc-white LEDs and display devices.

Key words. Wet chemical method; SEM; XRD; pc-white LEDs; lamp phosphor.

1. Introduction

In the last few years, lanthanide ion doped phosphor materials have attracted a lot of attention of the society, because in these years, rare earth activated phosphors has proved its utility in various applications such as optical communications, X-ray imaging, cathode ray tubes, biological labelling, lasers, white light-emitting devices (WLEDS), optoelectronic devices, vacuum fluorescent display, etc[1–3]. Presently, phosphors converted light emitting diode (PC-LED) has brought an industrial revolution in the field of lighting and has gained a lot of public acclaim due to its high-quality properties. It is the latest technology in the field of lighting, which has a tremendous market share. Currently, PC-LEDs have proved his capabilities for replacing traditional incandescent light bulb because PC-LEDs has extraordinary features such as compact size, high luminous efficiency, energy saving, long operation life, environmentally friendly nature [4–8]. Recently, the phosphor converted LED-based white light sources have gained enormous research interest due to their high applicability in indoor and outdoor lighting technology. The most widely used white LEDs are composed of InGaN-based blue-LED chip coupled with YAG:Ce$^{3+}$ yellow phosphor[9]. However, this technique has also revealed some drawbacks such as the lack of a red component, low color rendering index (CRI), high correlated color temperature (CCT). As a supplementary method, red, blue, and green-emitting phosphors are excited by ultraviolet (UV) or near-UV (NUV) LEDs. The light obtained by this method provides high quality light with better color stability and high color
rendering index.[10]. It is worth mentioning that near-UV based InGaN LEDs, which have the excitation in the range of 350nm to 420nm, have received more attention because NUV-LED can offer an efficient emission for solid-state lighting[11]. The limitations of commercially available phosphors for blue LEDs including low CRI and less thermal stability at high operating temperatures can be overcome by combining red, green, and blue (RGB) phosphors coupled with an NUV chip to generate cool and better quality of white light. Therefore, there is an urgent demand to develop novel phosphor exhibiting higher quantum efficiency and thermal stability for white LEDs. The thermally stable rare-earth ions such as Eu³⁺, Tb³⁺, and Sm³⁺ activated phosphors have been reported for NUV based white-LEDs[12, 13]. Available literature survey suggests that the selection of suitable host material is also an important factor for the preparation of luminescent materials for different applications. Recently, Yerpude et al. [14] reported the luminescence of Dy³⁺ and Sm³⁺ in SrSiO₄Cl₆ phosphor for SSL purposes. Earlier, we have reported the photoluminescence characteristics of K₃Ca₂(SO₄)₃Cl: Eu³⁺ phosphor[15]. These phosphors show efficient emission bands invisible region due to f-f and d-f transitions in rare-earth ions, and found to be ideal hosts for the trivalent rare earth (RE) ions.

As per literature, it is clear lanthanide ions doped luminescent materials have interested candidate in the field of lighting due to their amazing characteristics such as long lifespan, good color quality, great luminescence ability, high efficiency, environment friendly nature, etc. A present numerous lanthanide ion doped luminescent materials are deeply examined to expand the abilities of the existing materials. In the present work, we are focused to develop single color emitting potential luminescent materials for their applicability in generating white light and in this regard we have synthesized Sm³⁺ and Tb³⁺ ions doped K₃Ca₂(SO₄)₃Cl phosphors, which are exhibit red and green emissions based on their 4f-4f or 5d-4f transitions[16, 17]. Among the different activators, Sm³⁺ acts as a powerful emitting center due to the structure of its energy level and high luminescence efficiency, when it is doped into suitable host matrix. Also, Sm³⁺ ion is widely used as an activator of reddish-orange emission due to its 4G₅/₂→6H₃ (J = 5/2, 7/2, 9/2 and 11/2) transitions[18–22]. On the other hand, Tb³⁺ is also considered to be of great interest due to stimulated green emission through the 5D₄→7F₅ (545nm) transition. Due to the large energy difference (14663 cm⁻¹) between 7F₉/₂ to multiplet levels and 5D₄ emitting level, the luminescence property of Tb³⁺ has been proven to be useful in characterizing the energy level structure and optical transition mechanism[23–26].

In the present work, we have mainly focused on the formation of Tb³⁺ and Sm³⁺ activated K₃Ca₂(SO₄)₃Cl phosphors. In this work, samples have been synthesized through the wet chemical reaction method. The obtained samples have been analyzed through X-ray diffraction and microscopic techniques, as published in the previously reported papers. In the present work, photoluminescence emission and excitation spectra have been evaluated to study the optical behavior of samples. The results of this research indicated that synthesized samples have potential applications for solid-state light.

2. Experimental
Preparation of K₃Ca₂(SO₄)₃Cl
Tb³⁺ and Sm³⁺ activated K₃Ca₂(SO₄)₃Cl phosphors have been successfully prepared by wet chemical method. According to older studies, the wet chemical method is an important method for the synthesis of inorganic phosphors. In the present work, high purity K₂SO₄, CaCl₂, Ca(NO₃)₂, (NH₄)₂SO₄, Tb₂O₃ and Sm₂O₃ (all AR grades, 99.99% purity; E Merck) was used as starting raw materials for the synthesis of Tb³⁺ and Sm³⁺ activated K₃Ca₂(SO₄)₃Cl phosphors. The doping concentration of Tb³⁺ and Sm³⁺ were varied, ranging from 0.05 to 1.0 mol% and 0.1 to 1.5 mol%, respectively, with respect to host ions. Each initial raw material is weighed using a high-precision electronic weighing machine. Tb³⁺ and Sm³⁺ were dissolved in concentrated HNO₃ to convert to nitrate. Later, nitrate solutions of the obtained Tb³⁺ and Sm³⁺ were mixed with the host. Subsequently, the obtained solutions were filtered and dried in an oven at 80°C for 10–12
hours. The dried samples were then finely crushed to particles. The re-grounded sample was then placed in a crucible and heated at 800°C for 24 hours in a muffle furnace. The resulting powder was used for further characterization.

3. Results and Discussion:

3.1 XRD pattern and Particle size

XRD pattern represents phase confirmation and the crystallinity of prepared phosphor and Scanning Electron Microscope (SEM) represents particle size and morphological behavior of prepared sample. Figure 1 represents XRD pattern of un-doped K₃Ca₂(SO₄)₃Cl phosphor. In XRD pattern shows a good crystalline nature. Standard JCPDS data for this composition does not exist. The results indicate that the final product is highly crystalline in nature. This XRD structure is typical of the apatite group. SEM images of K₃Ca₂(SO₄)₃Cl phosphors were recently published[15]. SEM images of K₃Ca₂(SO₄)₃Cl phosphor were observed at different magnifications. The SEM images show that the phosphor consists of a porous clustered structure of micro-particles. The particle size ranges from 2 to 5μm. The particles seem to have distorted elongated structure[15].

![XRD pattern of undoped K₃Ca₂(SO₄)₃Cl phosphor](image)

Figure 1. XRD pattern of undoped K₃Ca₂(SO₄)₃Cl phosphor

3.2 Photoluminescence properties

3.2.1 K₃Ca₂(SO₄)₃Cl: Tb³⁺ phosphor

Figure 2 shows the PL excitation spectra of K₃Ca₂(SO₄)₃Cl phosphor, which is recorded between the 240 - 400 nm wavelength range. The excitation spectrum consisted of sharp bands situated at 257 nm, 353 nm, 372 nm, and 380 nm, respectively. The excitation spectrum was observed under 546nm (⁵D₄→⁷F₅) emission wavelength of Tb³⁺ ion in K₃Ca₂(SO₄)₃Cl host compound. Some weak excitation bands observed around at 250-350nm along with relatively strong ones (350-400nm) were observed for Tb³⁺ ions in the K₃Ca₂(SO₄)₃Cl compound. Figure 2 represents highest excitation intensity at 380nm excitation wavelength, which is observed due to ⁷F₅ → ⁵G₆ transition of Tb³⁺ ions. Thus, we find that this phosphor can be efficiently excitable by NUV (380nm) LED chips, and thus, may have possible applications in solid-state lighting. The PL excitation spectra revealed weak excitation bands in the range of 280nm to 375nm, these bands are originated due to transitions between ⁷F₅ and different excited states related to the f⁸ electronic configuration of Tb³⁺ ions. A strong excitation band due to spin allowed (4f⁸→4f⁷d¹) transition and a relatively weak band at a lower energy position due to spin forbidden transition (4f⁸→4f⁷5d¹) have been
earlier reported for Tb$^{3+}$ ions[27]. The excitation bands in 200–300 nm region and the relatively weak band at 257nm in K$_3$Ca$_2$(SO$_4$)$_3$Cl are due to the spin allowed and the spin forbidden transitions of Tb$^{3+}$ ions involving 4f$^8$ and 4f$^7$5d electronic configurations in the ground and excited states respectively.

Figure 2. Excitation spectra of K$_3$Ca$_2$(SO$_4$)$_3$Cl:Tb$^{3+}$ phosphor

Figure 3 illustrates the emission spectra for K$_3$Ca$_2$(SO$_4$)$_3$Cl compound in 400–750 nm range obtained at 380 nm excitation wavelength. The PL emission spectra demonstrate that the several emission bands which are located around at 417 nm, 437 nm, 491nm and 546 nm, 588 nm, 624 nm. These emissions bands are attributed to $^5$D$_3$$\rightarrow$$^7$F$_5$ (417nm), $^5$D$_3$$→$^7F$_4$ (437nm), $^5$D$_4$$→$^7F$_6$ (491nm) and $^5$D$_4$$→$^7F$_5$ (546nm), $^5$D$_4$$→$$^7$F$_4$ (588nm), $^5$D$_4$$→$^7F$_3$ (624nm) transitions of Tb$^{3+}$ ions[28]. The strongest peak appears at 546 nm, which lies in the green region of the visible spectrum. Figure 4 displays the variation of intensity with the increase in Tb$^{3+}$ion concentration; the intensity first decreases and then again increases monotonously with the increase of concentration Tb$^{3+}$ ions. It is also found that the growth rate of emission intensity corresponding to the transition of $^5$D$_4$$→$^7F$_6$(491 nm) is much slower than that of $^5$D$_4$$→$^7F$_5$(546 nm). The possible reason is that the radius of Tb$^{3+}$ ion is smaller than that of Ca$^{2+}$ ions. The incorporation of Tb$^{3+}$ ions forCa$^{2+}$ sites may lead to unitcell volume shrinkage of K$_3$Ca$_2$(SO$_4$)$_3$Cl host. Thus, the crystal field may be expanding with the increase of Tb$^{3+}$ ions concentration. This provides bigger possibility for electrons and phonons coupling, resulting in the energy loss of excited Tb$^{3+}$ ions through non-radioactive relaxation. As a result, the emission intensity of $^5$D$_4$$→$$^7$F$_5$ transition has increased faster than that of $^5$D$_4$$→$^7F$_6$. We find that for the 1 mol% Tb$^{3+}$ activated K$_3$Ca$_2$(SO$_4$)$_3$Cl phosphor, the green emission band at 545 nm is the most intense one, and $^5$D$_3$$→$^7F$_3$ transitions (green emission), which generally depends on the doping concentration of Tb$^{3+}$ cations, are comparatively less intense. This is due to the cross relaxation process between two adjacent Tb$^{3+}$ cation pairs. In the present host, the intensity of blue emission arising from $^5$D$_3$$→$^7F$_5$ is very less (partially quenched) compared to the intensity of green emission arising from $^5$D$_4$$→$^7F$_3$. Figure 5 shows the schematic energy level diagram for Tb$^{3+}$ ion displaying the transitions that produce emission in the visible region.
3.2.2 $K_3Ca_2(SO_4)_3Cl:Sm^{3+}$

As per literature, various Sm$^{3+}$ activated luminescent materials demonstrate orange and red emission due to the transition from $^4G_{5/2}$ to $^6H_j$ ($j=7/2, 9/2, & 11/2$). Sm$^{3+}$ activated luminescent materials are widely applied in the various fields such as visible solid state lasers, temperature sensors, various fluorescent devices, color display, optical storage, etc [29]. Figure 6 shows the excitation spectra of $K_3Ca_2(SO_4)_3Cl:Sm^{3+}$ phosphor monitored under 598nm emission wavelength. The PL excitation spectrum revealed several excitation peaks in the range of 350 to 500nm, which are observed under maximum emission intensity peak at 404nm. In most cases, the Sm$^{3+}$-activated phosphors show charge transfer absorption from Sm$^{3+}$-$O_2^{-}$.
interaction in the UV region. In our current work, we observed no such charge transfer absorption, but only direct excitation of Sm$^{3+}$ ions. Thus, the interaction of Sm$^{3+}$ with the host lattice is very weak.

**Figure 6.** Excitation spectra of K$_3$Ca$_2$(SO$_4$)$_3$Cl:1mol%Sm$^{3+}$ phosphor ($\lambda_{em}$=598nm)

The emission spectra of K$_3$Ca$_2$(SO$_4$)$_3$Cl: Sm$^{3+}$ monitored under 404nm excitation wavelength, as shown in **Figure 7.** It consists three sharp emission peaks in the range extending from 550 to 750 nm with two low intensity peaks, which are characteristic of Sm$^{3+}$ ions. The emission peaks observed at 565 nm, 598 nm, 645nm and 706nm, which are attributed due to $^4G_{5/2} \rightarrow ^6H_j$ ($j = 5/2, 7/2, 9/2, 11/2$) transitions of Sm$^{3+}$ ions respectively[30,31]. **Figure 8** shows variation of intensity with concentration of Sm$^{3+}$ ions. It is clear from the figure emission intensity increases with increasing the concentration of dopant up to 1.5mol% after that PL emission intensity decreased due to concentration quenching mechanism.

**Figure 7.** Emission spectra of K$_3$Ca$_2$(SO$_4$)$_3$Cl: Sm$^{3+}$ phosphor

**Figure 8.** Variation of emission intensity with concentration of Sm$^{3+}$ in K$_3$Ca$_2$(SO$_4$)$_3$Cl phosphor.
3.3 Photometric Characterization

3.3.1 CIE Diagram of K3Ca2(SO4)3Cl:Tb3+ phosphor

The CIE color coordinate is employed to analyze the color of K3Ca2(SO4)3Cl:Tb3+ samples. The CIE chromaticity diagram for K3Ca2(SO4)3Cl:Tb3+ phosphor is presented in Figure 9 and the calculated CIE coordinates are presented in Table 1 with color correlated temperature. The emission intensity of the 5D4 → 7FJ (J=6,5,4,3) transitions grow with increasing doping concentration. The CIE coordinate values grow almost linearly except at 0.2mol%, of the Tb3+ concentration. The emission color of K3Ca2(SO4)3Cl:Tb3+ shifts from blue to yellowish-green with increasing Tb3+ concentration, which means that the color of K3Ca2(SO4)3Cl:Tb3+ is tunable by simply controlling the doping concentration of Tb3+ ions.

Figure 9. CIE Chromatic diagram for K3Ca2(SO4)3Cl:Tb3+ phosphor

3.2.2 Correlated Color Temperature (CCT)

Correlated Color Temperature (CCT) is one of the important parameters for determining color appearance of light emitted by the light source. We can say that CCT is color temperature that means it is a point of planckian locus, these co-ordinates is very near to chromaticity of the illuminant point considered on the (u’, v’) CIE 1976 chromaticity diagram. We can calculate the value of (u’, v’) by using following formula [32]:

\[ u' = \frac{4x}{-2x + 12y + 3} \]  
\[ v' = \frac{9y}{-2x + 12y + 3} \]

Here (x, y) is the CIE chromaticity coordinate. By using these equations, we are calculating the value of (u’, v’). According to Mc-Camy’s approximation, the CCT value can be derived from CIE color coordinates using the third power polynomial [32, 33]:

\[ T = an^3 + bn^2 + cn + d \]  

Where \( n = (x-x_c) / (y-y_c) \). Here \((x_c, y_c) = (0.3320, 0.1858)\) and \(a = 437, b = 3601, c = 6861, d = 5514.31\). After using these values, we can calculate the value of CCT. In table we are represents CIE 1931 coordinates, CIE 1976 coordinates, CCT values. The calculated CCT values for K3Ca2(SO4)3Cl phosphors...
were found to be in the range of 1900-4200 K (Table 1). Only expect 0.05mol% CCT value all are represent suitable results for cool white.

| Concentration of Tb$^{3+}$ ion (mol%) | CIE 1931 Chromaticity (x, y) | CIE 1976 Chromaticity (u′v′) | Correlated Color Temperature (CCT) |
|--------------------------------------|------------------------------|-----------------------------|----------------------------------|
| 0.05 mol%                            | (0.2145, 0.2648)             | (0.1492, 0.4145)            | 1904.818                         |
| 0.1 mol%                             | (0.2533, 0.3972)             | (0.1395, 0.4924)            | 3453.373                         |
| 0.2 mol%                             | (0.2564, 0.3705)             | (0.1479, 0.4809)            | 3297.769                         |
| 0.5 mol%                             | (0.2464, 0.4189)             | (0.1308, 0.5004)            | 3475.276                         |
| 1.0mol%                              | (0.2629, 0.5147)             | (0.1215, 0.5354)            | 4237.202                         |

3.3.4 CIE Diagram of K$_3$Ca$_2$(SO$_4$)$_3$Cl:Sm$^{3+}$ phosphor

To analyze the luminescence color of K$_3$Ca$_2$(SO$_4$)$_3$Cl:Sm$^{3+}$ samples, the CIE color coordinates have been calculated. The CIE coordinates for 1.5mol% Sm$^{3+}$ ions in K$_3$Ca$_2$(SO$_4$)$_3$Cl host under 404nm excitation was found. From Figure 10, it is found that this point lies in the orange region. Thus, the phosphor may possibly be utilized to produce orange-colored LEDs with NUV excitation. And their CCT values are also calculated and this value represents that this is suitable for cool white light. Correlated Color Temperature (CCT) is describing how the color of the light appears from a lamp, it is measured in kelvin (K). Cool White light is found in the range of 4000K. Cool white lighting is most suited in areas where you may require more brightness and a livelier feel in a space. It is often used in bathrooms, makeup, or shaving, kitchens, laundries, garages, and study rooms as it provides a brighter, clearer light making it easier to see. Table: 2 represent CIE coordinate and CCT values of K$_3$Ca$_2$(SO$_4$)$_3$Cl:Sm$^{3+}$ phosphor.

| Concentration of Tb$^{3+}$ ion (mol%) | CIE 1931 Chromaticity (x, y) | CIE 1976 Chromaticity (u′v′) | Correlated Color Temperature (CCT) |
|--------------------------------------|------------------------------|-----------------------------|----------------------------------|
| 1.5 mol%                             | 404nm                        | (0.2853, 0.5324)            | (0.1294, 0.5433)                 |
4. Conclusion
In this research paper, we have reported the luminescence characteristic of Tb$^{3+}$ and Sm$^{3+}$ in K$_3$Ca$_2$(SO$_4$)$_3$Cl phosphor prepared by the wet chemical method at low temperature. The phosphors showed characteristic emission bands of Sm$^{3+}$ and Tb$^{3+}$ ions under the excitation of near UV LED. These rare earth ions have shown interesting luminescence due to the presence of their spectral bands in the range of 400–700 nm in the visible region. Also, the calculated CIE (x,y) coordinates suggested that the emission color of K$_3$Ca$_2$(SO$_4$)$_3$Cl:Tb$^{3+}$ is tunable from blue to green of the visible spectrum. The orange color emission was produced by K$_3$Ca$_2$(SO$_4$)$_3$Cl:Sm$^{3+}$phosphor. Phosphors composition presented in this article are new and there is no standard data yet to be studied in crystallography. Such a novel composition with good optical properties suggests that it may be a promising host for the lamp industry.

5. References
[1] Kadyan S Singh S Simantilleke AMari B Singh D 2020 Optik 200 163450. https://doi.org/10.1016/j.ijleo.2019.163450
[2] Kadyan S Singh S Sheoran S Simantilleke AMari B Singh D 2020 Optik 204 164159. https://doi.org/10.1016/j.ijleo.2019.164159
[3] Kadyan S Singh S Sheoran S Simantilleke AMari B Singh D 2020 J Mater Sci Mater Electron 31 414–422. https://doi.org/10.1007/s10854-019-02544-x
[4] Feng W Zhu X Li F 2013 NPG Asia Mater 5 75-15. https://doi.org/10.1038/am.2013.63
[5] Huang X 2014 Nat Photonics 8 748–749. https://doi.org/10.1038/nphoton.2014.221
[6] Tiwari SP Kumar K Rai VK 2015 J Appl Phys 118. https://doi.org/10.1063/1.4935279
[7] Zhu P Zhu H Qin W Dantas B H Sun W Tan C K and Tansu N 2016 J Appl Phys 119. https://doi.org/10.1063/1.4944944
[8] Kumari P Manam J 2015 RSC Adv 5 107575–107584. https://doi.org/10.1039/c5ra18982a
[9] Singh D K Manam J 2018 Applied Physics A 124 261. https://doi.org/10.1007/s00339-018-1665-7
[10] Mao ZY Zhu YC Gan LZeng Y Xu F F Wang Y Tian H Li J Wang D J 2013 J Lumin 134 148–153. https://doi.org/10.1016/j.jlumin.2012.08.057
[11] Liu J Wu Z Gong M 2008 Appl Phys B Lasers Opt 93 583–587. https://doi.org/10.1007/s00340-008-3169-1
[12] Lin CC, Tang YS, Hu SF, Liu RS. 2009. *J Lumin* **129** 1682–1684. https://doi.org/10.1016/j.jlumin.2009.03.022
[13] Ding X, Zhu G, Geng W, Mikami M, Wang Y. 2015. *Mater Chem C* **2** 6676–6685. https://doi.org/10.1039/c5tc01125j
[14] Yerpude AN, Dhole SJ. 2012. *J Lumin* **132** 2975–2978. https://doi.org/10.1016/j.jlumin.2012.04.037
[15] Baig N, Dhole NS, Pawade VB, Kode N, SD. 2014. *Luminescence* **29** 695–697. https://doi.org/10.1002/bio.2586
[16] Kaynar Ü, H, Guvener E, Ayvacikli M, Dogan T, Balei–Yegen S, Ogakci M, Topaksu M, Karabulut Y, Canimoglu A, Benourdja S, Can N. 2018. *Journal of Alloys and Compounds* **764** 523–529. https://doi.org/10.1016/j.jallcom.2018.06.125.
[17] Guo N, Song Y, You H, Sun W. 2010. *Eur J Inorg Chem* **2010** (29) 4636–4642. https://doi.org/10.1002/ejic.201000392
[18] Zhou Y, Lin J, Wang S. 2003. *J Solid State Chem* **171** 391–395. https://doi.org/10.1016/S0022-4596(02)00219-0
[19] Li J, Pang R, Yu Z, Liu L, Wu H, Li H, Jiang L, Zhang S, Feng J, Li C. 2018. *Journal of Rare Earths* **36** (7) 680-686, https://doi.org/10.1016/j.jre.2017.12.005.
[20] Ju ZH, Wei RPM, Ma JX, et al. 2010. *J Alloys Compd* **507** 133–136. https://doi.org/10.1016/j.jallcom.2010.07.138
[21] Bhushana Reddy M, Nageswara Raju C, Sailaja S, et al. 2011. *J Lumin* **131** 2503–2508. https://doi.org/10.1016/j.jlumin.2011.06.015
[22] Zhai Y, Sun Q, Yang S, Liu Y, Wang J, Ren S, Ding S. 2019. *Journal of Alloys and Compounds* **781** 415-424. https://doi.org/10.1016/j.jallcom.2018.12.055.
[23] Sidike A, Saliqu RAZM, He JY, et al. 2011. *J Lumin* **131** 1840–1847. https://doi.org/10.1016/j.jlumin.2011.04.045
[24] AK Bediyal Kumar V, Sharma V, et al. 2013. *J Integr Sci Technol* **15**–8.
[25] Balaji S, Abdul Azeem P, Reddy RR. 2007. *Phys B Condens Matter* **394** 62–68. https://doi.org/10.1016/j.physb.2007.02.009
[26] Shaat S, Swart HC, Nwaechaborwa OM. 2014. *J Alloys Compd* **587** 600–605. https://doi.org/10.1016/j.jallcom.2013.11.001
[27] Zhang H, Zhang H, Liu Y, Lei B, Deng J, Liu W, R, Zeng Y, Zheng L, Zhao M. 2017. *Materials Chemistry and Physics* **193** 203-210. doi: 10.1016/j.matchemphys.2017.02.042.
[28] Dutta DP, Bandyopadhyay S, Roy AK. 2010. *AIP Adv*. https://doi.org/10.1063/1.4773443
[29] Dillip GR, Mohan Kumar P, Deva Prasad Raju B, Dhole SJ. 2013. *J Lumin* **134** 333–338. https://doi.org/10.1016/j.jlumin.2012.08.025.
[30] Wang Z, Li P, Yang Z, Guo Q. 2012. *J Lumin* **132** 1944–1948. https://doi.org/10.1016/j.jlumin.2012.03.022
[31] Shivakumara C, Saraf R, Halappa P. 2016. *Dye Pigment* **126** 154–164. https://doi.org/10.1016/j.dyepig.2015.10.032
[32] McCamy CS. 1992. *Color Res App* **17** 142–144. https://doi.org/10.1002/coll.5080170211

**Acknowledgement**

One of the authors Yatish R. Parauha is thankful to Department of Science and Technology (DST), India for financial support through INSPIRE fellowship (INSPIRE Code – IF180284). One of the authors SJD is thankful to Department of Science and Technology (DST), India (Nano Mission) (Project Ref. No. DST/NM/NS/2018/38(G), dated 16/01/2019) for financial assistance and R.T.M.Nagpur University, Nagpur for constant encouragement.