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Synthesis and photoluminescence property of RE^{3+} activated $Na_2CaP_2O_7$ phosphor

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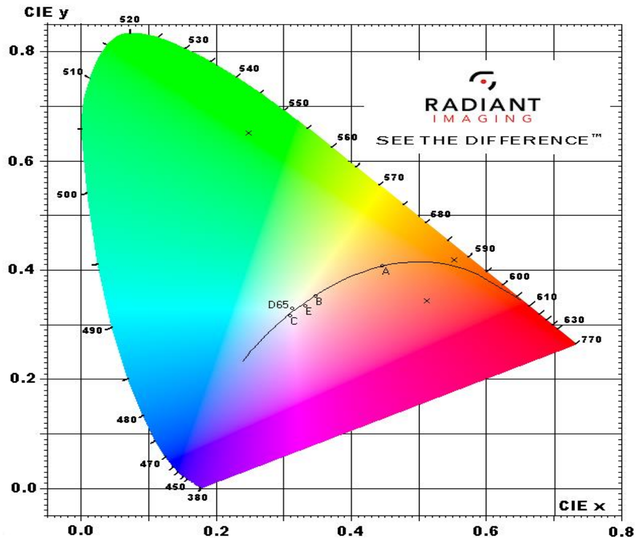
ABSTRACT

As host materials, phosphate compounds offer great potential for lanthanides to display luminescence characteristics. In this work luminescence behaviour of $Na_2CaP_2O_7$:RE^{3+} are presented for the first time. $Na_2CaP_2O_7$ novel phosphors activated with the trivalent rare earth ions ((RE = Ce, Eu, Tb, Sm) were synthesized by solid state diffusion method. Phosphors were characterized for phase purity and luminescent properties. The emission and excitation spectra were followed to explore the luminescence attributes. The as prepared powders of Ce^{3+}, Eu^{3+},Tb^{3+} and Sm^{3+} doped $Na_2CaP_2O_7$ emit near-uv, red, green and orange reddish light as result of f-d and f-f transitions respectively. The study is novel as no such luminescence data are available for this compound. The results are promising in view of the requirement for pc-white LEDs for solid state lighting applications.

Keywords: Sodium calcium pyrophosphate; luminescence; phosphors; solid state lighting.

Graphical abstract



Chromaticity diagram of $Na_2CaP_2O_7$:RE^{3+} (RE = Eu, Tb, Sm) phosphors. The three crosses in the figure show chromaticity values corresponding to $Na_2CaP_2O_7$:Eu^{3+}, $Na_2CaP_2O_7$:Tb^{3+} and $Na_2CaP_2O_7$:Sm^{3+} phosphors, respectively.

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Introduction

With increase in cognizance among people are searching for novel technologies to minimize consumption of global electrical energy and render environment-friendly illumination and display devices **[1]**. As an ideal energy preserving, potential and eco-benign candidate for general lighting, white light-emitting diodes (w-LEDs) have drawn considerable attention due to their high efficiency, compactness, long functional lifetime, and relatively highly energy saving and are gradually substituting traditional light sources **[2]**. The maximum efficiency of a commercial high-power white LED is currently about 30% (100 lm W^{-1} efficacy), which is six times greater than the efficiency of a filament light bulb and 50% better than that of a compact fluorescent lamp. Nowadays, the most widely followed method to have white light emission is the coupling of a blue InGaN LED chip and a yellow phosphor (YAG: Ce^{3+}). Even though the approach is cost-effective and efficient, it is accompanied by poor color rendering index (CRI) and insufficient color temperature in illumination applications. Now this di-chromatic (yellow-blue) approach white LED has been developed to a tri-chromatic white LED by coupling the near-ultraviolet (n-UV) or ultraviolet (UV) LED with blue and yellow phosphors with more red components or the red, green, and blue (RGB) multi-phased phosphors, to achieve higher CRI and color tenability **[3-5]**. However, it is a bit hard to get a requisite red inorganic phosphor for tri-chromatic white LEDs, for the generally employed red emitting phosphor for white LEDs is $Y_2O_2S:Eu^{3+}$ This phosphor is chemically unsound and its fluorescent efficiency is grimmer than that of the $BaMgAl_{10}O_{17}:Eu^{2+}$ and ZnS: Cu+, Al^{3+} (green-emitting) phosphors. Red phosphors based on nitride family have exhibited high stability and therefore have got attraction but due to costly preparation conditions of high temperatures, high nitrogen pressure and the synthesis method is limited **[6, 7]**. In flat panel displays, field emission displays (FEDs) have received sound attention due to their unique advantages, such as thin panel thickness, self emission, distortion-free images, wide viewing angle, quick response and low power consumption. Moreover, tri-chromatic white LEDs and tricolor phosphors are also regarded as essential constituents in FEDs. In spite of the fact that the traditional red sulfide-based phosphors Y_2O_2S: Eu^{3+} have been used as potential low voltage phosphor for FEDs, the excitability of sulfur makes the cathodes to degenerate and as a result reduce the luminous efficiency, which restricts their practical use in FEDs. Thus, in order to enhance the working capability of FEDs and white LEDs, it is imperative to produce novel red-emitting phosphors with excellent physical and chemical stabilities, and higher efficiencies **[8, 9]**.

Owing to the excellent thermal stabilities, good charge stabilities and low sintering temperature phosphate compounds have gained very much attention in luminescent materials. Rare earth activated phosphates usually have wide luminescent properties, typically, $LaPO_4$: Ce^{3+}, Tb^{3+} ;(Y, Gd) (P, V)O_4: Eu^{3+} ; $Sr_5(PO_4)_2Cl$: Eu^{2+} etc., find extensive use as commercial phosphor materials in solid state lighting. It is well known that beta phased $Ca_3(PO_4)_2$ and its derivatives are important phosphates that have been widely studied for their potential applications including their ferroelectric properties, ionic solid electrolyte conductivity bioceramics thermally stimulated luminescence (TSL) or thermoluminescent dosimeters (TLD) for X-rays and potential phosphors for w-LEDs. Trivalent rare-earth ions such as cerium (Ce^{3+}), europium (Eu^{3+}), samarium (Sm^{3+}) and terbium(Tb^{3+}) have been realized as potential activators in many good phosphors due to their $4f^15d^0 \rightarrow 4f5d^1$, ${}^5D_0 \rightarrow {}^7F_{J(J\,=\,0,1,2,3,4)}$, ${}^4G_{5/2} \rightarrow {}^6H_{J\ (J\,=5/2,\ 7/2,\ 9/2)}$ and ${}^5D_4 \rightarrow {}^7F_{J(J\,=\,5,6)}$ transitions respectively. The Ce^{3+} ion has the [Xe] $4f^1$ configuration, which results in only two $4f^1$ energy levels: the ${}^2F_{5/2}$ and ${}^2F_{7/2}$ state. These energy levels are approximately 2000 cm^{-1} apart. At higher energy, the $4f^05d^1$ bands can be found. The energy of the bands is strongly dependent on the host lattice. The photoluminescence emission of europium ion is highly affected by the site symmetry occupied by the Eu^{3+} in the crystal structure. In many luminescent materials, when it is located at a noncentrosymmetric site, Eu^{3+} can generate high quality red emission corresponding to the ${}^5D_0$–${}^7F_2$ transition. Terbium (Tb^{3+}) ions are important Ln^{3+} ions for their characteristic green emission, which is most often initiated by UV excitation. For instance, as a result of strong absorption in ultraviolet region, YPO_4: Tb^{3+} has been found to be a suitable phosphor for PDP applications. Sm^{3+} luminescence is generally known by three main emissions viz 562nm (${}^4G_{5/2} \rightarrow {}^6H_{5/2}$), 600nm (${}^4G_{5/2} \rightarrow {}^6H_{7/2}$), 650nm (${}^4G_{5/2} \rightarrow {}^6H_{9/2}$) and there is another small peak at

706nm ($^4G_{5/2} \rightarrow {}^6H_{11/2}$) respectively **[10-13]**. Hence keeping the above attributes of RE^{3+} ions in focus, in this work we therefore report on Ce, Eu, Tb and Sm activated $Na_2CaP_2O_7$ phosphors. The work is novel because no such study on this compound existed before. The photoluminescence properties of $Na_2CaP_2O_7$:RE^{3+} suggest that this phosphor could turn out to be a useful component for white LEDs in solid state lighting applications.

Experimental

Na_2CO_3 (Qualigens Excel R), $CaCO_3$ (Qualigens Excel R), (NH_4) H_2PO_4 (Qualigens Excel R) $(NH_4)_2Ce(NO_3)_6$(Merck GR), Tb_4O_7 (Loba 99.99%), Sm_2O_3(Loba 99.99%) and Eu_2O_3 (Loba 99.99%). Na_2CO_3, Na_2CO_3, $CaCO_3$, (NH_4) H_2PO_4, $(NH_4)_2Ce(NO_3)_6$, Tb_4O_7, $Sm_2O_3$and Eu_2O_3 were used as the starting precursors. The $Na_2CaP_2O_7$: RE^{3+} (RE = Ce, Tb, Eu, Sm) phosphors were prepared by the high temperature solid state reaction. The reactants were mixed stoichiometrically. The raw materials were ground for more than half an hour, using agate mortar and pestle. Finally, the crushed mixtures were fired at 750 °C for 12 hours followed by slow cooling to room temperature. The samples at room temperature were taken out and used for characterizations such as powder X-ray diffraction and photoluminescence measurements. For brevity m% is written for mole% (mole percent).

Phase purity of the host compound was identified by powder X-ray diffraction (XRD) (X'-pert. Pro Analytical X-ray Diffractometer with Cu Kα = 1.5406 Å). Excitation and emission spectra were measured using RF-5301PC Shimadzu Spectrofluorophotometer with slit width 1.5 nm. All measurements were performed at room temperature.

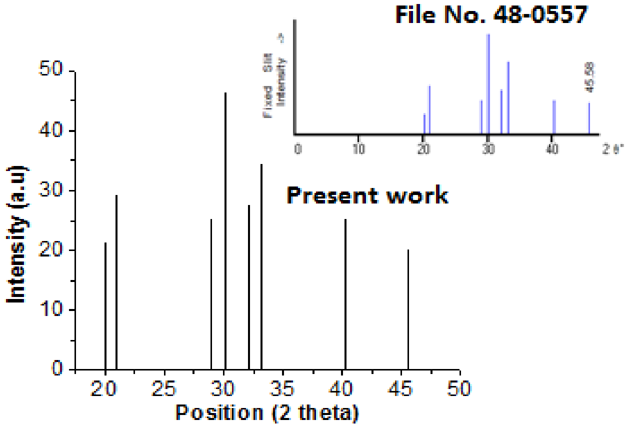

Fig. 1. X--ray powder diffraction pattern of $Na_2CaP_2O_7$ and JCPDS standard card No.48-0557.

Results and discussion

XRD analysis

To analyse the crystalline nature and phase purity and to specify whether the compound has any identical data available so that its complete formation can be affirmed, powder X-ray diffraction of $Na_2CaP_2O_7$ was carried out. The XRD pattern of $Na_2CaP_2O_7$ along with JCPDS file is shown in **Fig. 1**. Well match between the as prepared compound and the JCPDS data (file no. 48-0557) was observed.

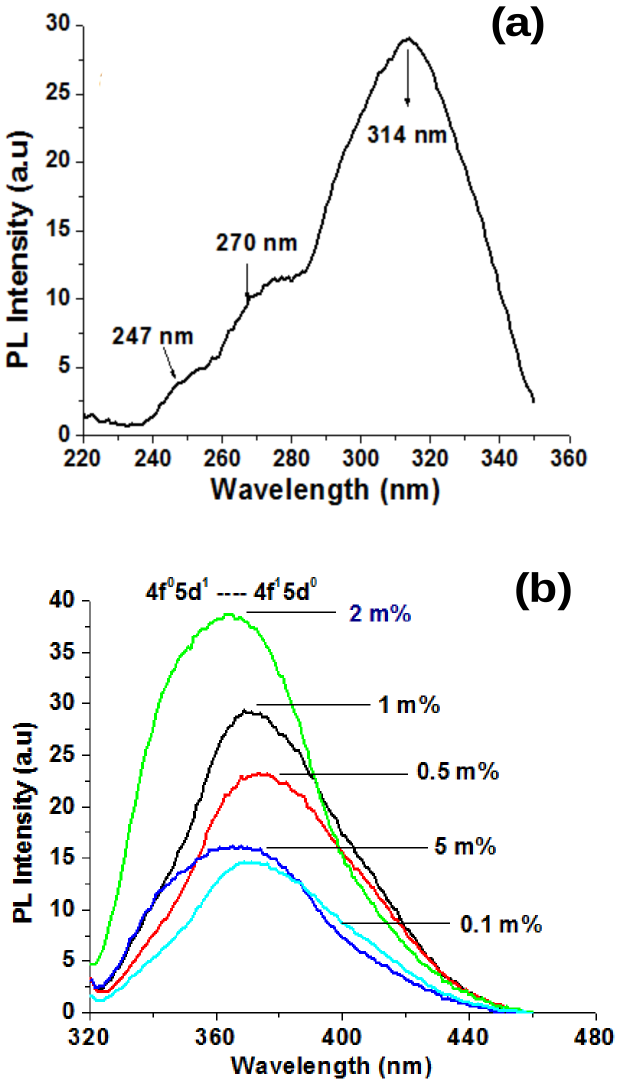

Fig. 2. PL excitation (a) and PL emission (b) spectra of $Na_2CaP_2O_7$:Ce^{3+} phosphor.

Optical properties

The Ce^{3+} ion has the [Xe] $4f^1$ configuration, which results in only two $4f^1$ energy levels: the $^2F_{5/2}$ and $^2F_{7/2}$ state. These energy levels are approximately 2000 cm^{-1} apart. At higher energy, the $4f^05d^1$ bands can be found. The energy of the bands is strongly dependent on the host lattice.

Fig. 2a represents excitation spectrum of $Na_2CaP_2O_7$: Ce monitored at 369 nm. Two peaks 270 nm and 314 nm can be seen due to f-d transition. Excitation spectrum is broad through transition of electron from one subshell to different subshell. The concentration of cerium activator was varied between 0.1m% and 5m% and the highest PL emission intensity was observed at 2m% (**Fig. 2b**). As shown in **Fig. 3 (b)**, the PL emission spectra show an orange-red emission bands peaking at 592 and 615nm under 257 and 395 nm excitations. The PL excitation spectrum (**Fig. 3(a)**) shows a broad peak spanning from 246 to 280 nm, which can be attributed to charge transition between $Eu^{3+} \rightarrow O^{2-}$ ions. Whilst sharp lines from 320 to

500 nm are due f→f transitions of Eu^{3+} ions. The excitation spectrum was monitored at 615 nm. The intensity ratio between magnetic dipole transition and electric dipole transition seems to be identical thereby indicating that Eu^{3+} ion has occupied both the centrosymmetric as well as non-centrosymmetric sites in the $Na_2CaP_2O_7$ lattice. Other deep red emission corresponding to $^5D_0 \rightarrow {}^7F_{J\ (J=4,\ 5,\ 6)}$ transitions could also be seen. No concentration quenching of photoluminescence was seen as the population of Eu^{3+} impurity in $Na_2CaP_2O_7$ host changed **[14-19]**.

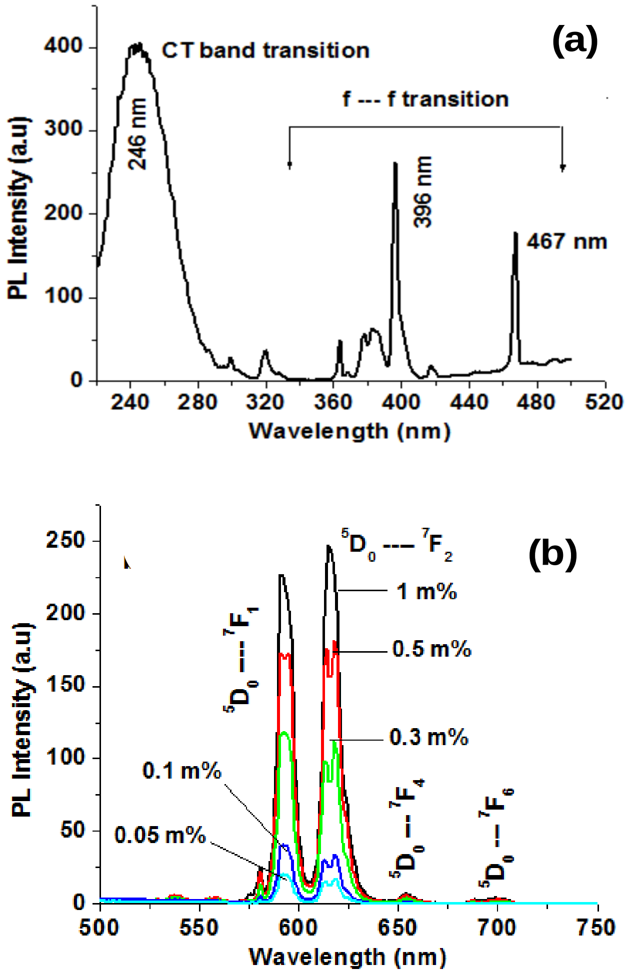

Fig. 3. PL excitation (a) and PL emission (b) spectra of $Na_2CaP_2O_7$:Eu^{3+} phosphor.

As depicted in **Fig. 4(a)**, UV excitation spectrum observed at 546 nm emission wavelength of $Na_2CaP_2O_7$ doped withTb^{3+} consisting of a broad band as well as some sharp lines. The broad band is due to f-d interaction while sharp lines are due to f-f transitions. The emission spectrum (**Fig. 4 (b)**) has sharp lines on account of f–f transition of Tb^{3+} ions. The emission spectrum usually has major contribution from $^5D_4$–^{7}FJ (J= 6, 5, 4, 3) but a weak peak around 434 nm due to $^5D_3$–$^7F_{J(J=\ 6,\ 5,\ 4,\ 3)}$ can also be seen. The nature of $^5D_4 \rightarrow {}^7F_J$ transitions is governed by the selection rule ΔJ = ±1 for electric dipole and ΔJ = 0, ±2 for magnetic dipole transitions respectively. As depicted in **Fig. 4(b)**, the emission intensity of $^5D_3$ level is very weak and weakens further with increasing Tb^{3+} concentration, followed by the enhancement of the emission from the $^5D_4$ level. This occurs due to non-radiative cross-relaxation via the resonant energy transfer process between $^5D_3$ and $^5D_4$ levels. As the concentration of Tb^{3+} is changed, the cross-relaxation effect becomes stronger, which enhances the intensity of green emission at 545 nm.

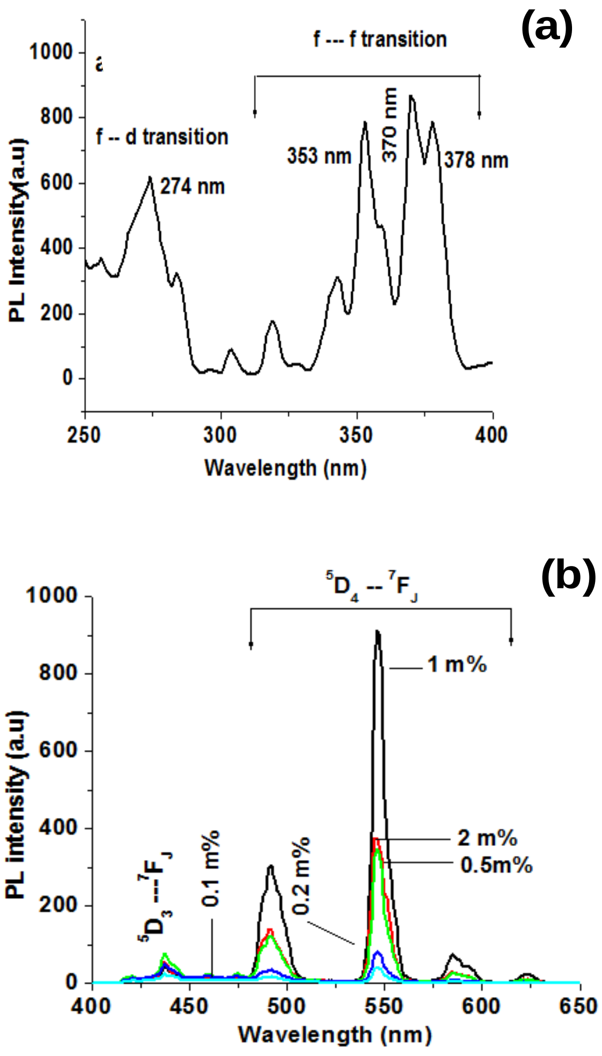

Fig. 4. PL excitation (a) and PL emission (b) spectra of $Na_2CaP_2O_7$:Tb^{3+} phosphor.

Furthermore, other reason has been assigned to weak luminescence from $^5D_3$ level is the lack of phonon energy of the host. The smaller the phonon energy of the host at diluted concentrations of terbium ions, the lower will be the $^5D_3$ emission intensity and vice versa **[20-24]**. Sm^{3+} with 4f^5 configuration has very complex energy levels and several transitions are possible between these 4f levels. Highly selective transitions between these f levels results in narrow line spectra. As shown in **Fig. 5(a)**, the excitation spectra of $Na_2CaP_2O_7$: Sm^{3+} consists of many sharp lines starting from 300 nm to 450 nm. The whole the excitation spectrum peaks can be attributed to Sm^{3+} ions. Unlike Eu^{3+}– O^{2-} interaction, no CT band corresponding to Sm^{3+}–O^{2-} interaction was observed in $Na_2CaP_2O_7$: Sm^{3+} system as can be seen in **Fig. 5(a)**.This excitation spectra was monitored at emission wavelength 600 nm. We observed that among various excitation wavelengths, Sm^{3+} doped $Na_2CaP_2O_7$ phosphors could preferentially be excited by 405 nm as it results in intense orange reddish light around 600 nm. As this excitation wavelength 405 nm is quite far away from mercury (254 nm) we assume that this phosphor will turn out to be eco-friendly.

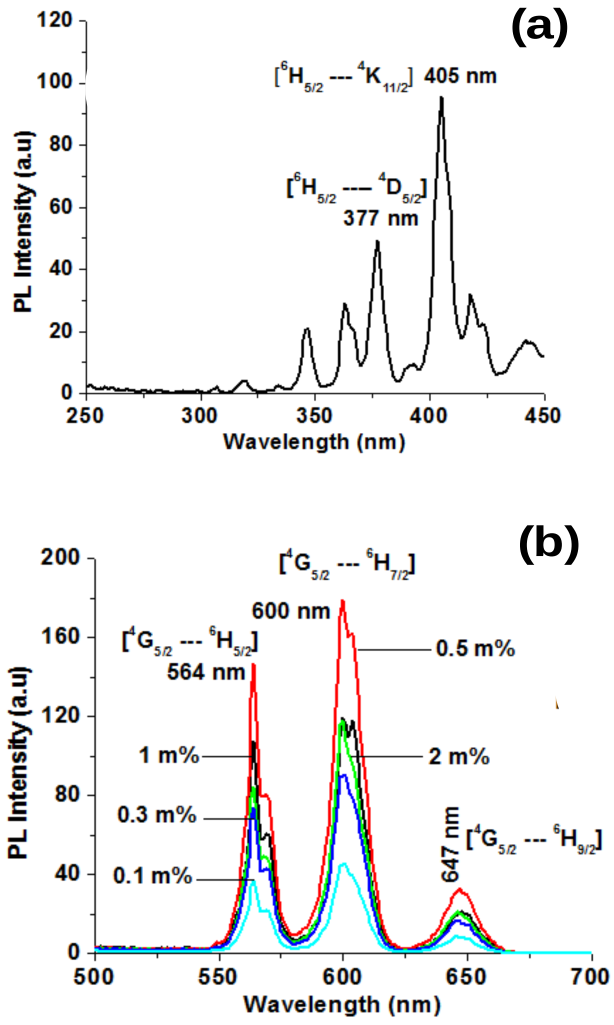

Fig. 5. PL excitation (a) and PL emission (b) spectra of $Na_2CaP_2O_7:Sm^{3+}$ phosphor.

Intense absorption at 405 nm also indicates that $Na_2CaP_2O_7$: Sm^{3+} phosphors can be effectively excited by near UV LEDs. The excitation wavelength 405 nm corresponds to $^6H_{5/2} \rightarrow {}^4K_{11/2}$ transition of Sm^{3+} ions. The reddish orange light of Sm^{3+} possesses three emission peaks (**Fig. 5(b)**) in the visible region near 564, 600, and 647 nm, which are associated to the intra f-f subshell transitions from the excited level $^4G_{5/2}$ to ground levels $^6H_{5/2}$, $^6H_{7/2}$, and $^6H_{9/2}$, respectively. The first one at 564 nm ($^4G_{5/2} \rightarrow {}^6H_{5/2}$) is a magnetic-dipole transition, the second at 600 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$) is a partly magnetic and partly a forced electric-dipole transition, and the other at 650 nm ($^4G_{5/2} \rightarrow {}^6H_{9/2}$) is purely electric dipole transition which is sensitive to the crystal field **[25-29]**. Therefore, it suggests that the $Na_2CaP_2O_7:RE^{3+}$ (RE = Ce^{3+}, Eu^{3+}, Tb^{3+}, Sm^{3+}) phosphors can be efficiency excited by UVLEDs (350–400 nm). In order to see how much promising the photoluminescence characteristics of $Na_2CaP_2O_7$: RE^{3+} phosphors are in view of the CIE (Commission Internationaldel'E´ clairage (CIE) 1931) Chromaticity diagram **(Fig. 6)**.

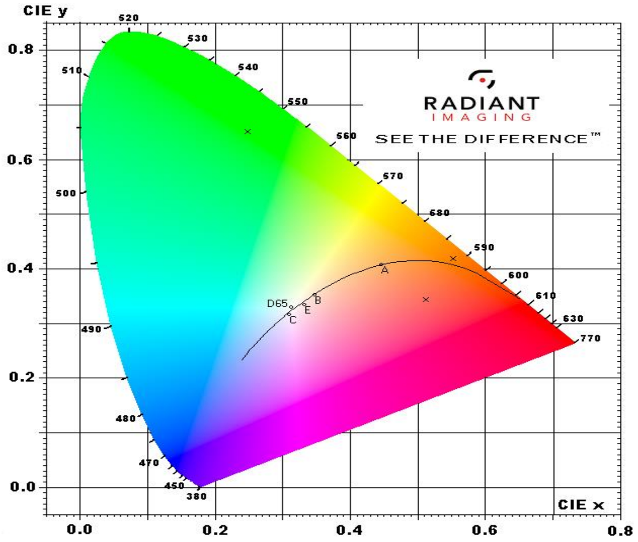

Fig. 6. CIE diagram for $Na_2CaP_2O_7:RE^{3+}$ (RE = Eu, Tb, Sm) phosphors. Note the three crosses in the Fig. show chromaticity values corresponding to $Na_2CaP_2O_7:Eu^{3+}$, $Na_2CaP_2O_7:Tb^{3+}$ and $Na_2CaP_2O_7:Sm^{3+}$ phosphors respectively.

The Chromaticity Coordinates of $Na_2CaP_2O_7:Eu^{3+}$ phosphors were computed to be $x = 0.51$, $y = 0.34$. For $Na_2CaP_2O_7$: Tb^{3+} and $Na_2CaP_2O_7$: Sm^{3+} CIE coordinates were found to be $x = 0.24$, $y = 0.65$ and $x = 0.55$, $y = 0.42$ respectively. These parameters were estimated as per the emission spectra in $Na_2CaP_2O_7$ (λ_{exc} = 396 nm, 370 nm & 405 nm) for Eu^{3+}, Tb^{3+} & Sm^{3+} ions respectively. It was noticed that these values are almost in the vicinity of NTSC standard values ($x = 0.67$, $y = 0.33$) and some other reported data **[30]**.

Conclusion

$Na_2CaP_2O_7:RE^{3+}$ (RE = Ce^{3+}, Eu^{3+}, Tb^{3+}, Sm^{3+}) phosphors were successfully synthesized through well known solid state diffusion method. Characteristic luminescence was manifested when rare earth ions diffused into the $Na_2CaP_2O_7$ system. Ce^{3+}, Eu^{3+}, Tb^{3+} and Sm^{3+} occupy both symmetric as well as non-symmetric sites in $Na_2CaP_2O_7$ lattice. Intense absorption in NUV region for $Na_2CaP_2O_7$: RE^{3+} phosphors suggest that they could be effectively excited by LEDs emitting in the NUV region. The Chromaticity Coordinates were found to be $x = 0.51$, $y = 0.34$, $x = 0.24$, $y = 0.65$ and $x = 0.55$, $y = 0.42$ for Eu^{3+}, Tb3+ and Sm^{3+} doped $Na_2CaP_2O_7$ phosphors respectively. The CIE coordinates of $Na_2CaP_2O_7$: RE $^{3+}$ fall in the vicinity of white region. The entire photoluminescence results indicate that $Na_2CaP_2O_7$: RE^{3+} phosphors might turn out to be a vital member of pc-white LEDs for solid state lighting devices. As the excitation wavelengths (314,380, 396 nm & 405 nm) of $Na_2CaP_2O_7$: RE^{3+} are quite far away from mercury (254 nm), we assume that these phosphors will turn out to be eco-friendly.

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Reference

1. Nizamoglu, S.; Zengin, G.; Demir, H. V.; Appl. Phys. Lett., 2008, *92*, 1
   DOI: 10.1063/1.2833693
   Tiwari, Ashutosh.; Mishra, Ajay K.; Kobayashi, Hisatoshi; Turner, Anthony, P.F.; *Intelligent Nanomaterials* Wiley-Scrivener Publishing LLC, USA, 2012, ISBN 978-04-709387-99.
2. Huang, C.H.; Chan, T.S.; Liu, W.R.; Wang, D.Y.; Chiu, Y.C.; Yeh, Y.T.; Chen, T.M.; J. Mater. Chem., 2012, *22*, 20210
   DOI: 10.1039/c2jm33160h
   Tiwari, A.; Valyukh, S. (Eds.), In Advanced Energy Materials, John Wiley & Sons, USA, **2014**.
3. Im,W. B.; George, N.; Kurzman, J.; Brinkley, S.; Mikhailovsky, A.; Hu, J.; Chmelka, B. F. S.; Baars, P.D.; Seshadri, R.; Adv. Mater. 2011, *23*, 2300
   DOI: 10.1002/adma.201003640
4. McKittrick, J.; Hannah, M. E.; Piquette, A.; Han, J. K.; Choi, J. I.; Anc, M.; Galvez, M.; Lugauer, H.; Talbot, J. B.; Mishra, K. C.; ECS. J.Sol. Sta. Sci. and Technology, 2013, *2*, 3119
   DOI: 10.1149/2.017302jss
5. Han, J. K.; Choi, J. I.; Piquette, A.; Hannah, M.; Anc ,M.; Galvez, M.; Talbot, J. B.; McKittrick, J.; ECS. J. Sol. Sta. Sci. and Technology 2013, *2*, 3138
   DOI: 10.1149/2.014302jss
6. Uheda, K.; Hirosaki, N.; Yamamoto, Y.; Naito, A.; Nakajima, T.; Yamamoto, H.; Electrochem. Solid-State Lett., 2006, *9*, H22
   DOI: 10.1143/APEX.5.062102
7. Xie, R. J.; Hirosaki, N.; Kimura, N. ; Sakuma, K.; Mitomo, M.; Appl. Phys. Lett., 2007, *90*, 191101
   DOI: 10.1063/1.2737375
8. L. Billie, A.; Holloway, P. H.; Chem. Rev., 2004, *104*, 5783
   DOI: 10.1021/cr020351r
9. Li, Y. C.; Chang, Y. H.; Lin, Y. F.; Lin, Y. J.; Chang, Y. S.; Appl. Phys. Lett., 2006, *89*, 081110
   DOI: 10.1063/1.2337275
10. Zhu, G. ; Zhipeng, Ci.; Yurong, S. .; Que, M.; Wang, Q.; Yuhua, W.; J. Mater. Chem. C, 2013, *1*, 5960
    DOI: 10.1039/c3tc31263a
11. Pierron, L.; Harari, A. K.; Viana, B.; Dorenbos, P.; Van Eijk, C.W.E.; J.Phys. Chemi. Solids 2003, *64*, 1743
    DOI: 10.1016/S0022-3697(03)00103-3
12. Vink, A.P.; Kolk, E. V.; Dorenbos, P.; van Eijk, C.W.E.; Optics Comm. 2002, *210*, 277
    DOI: 10.1016/S0030-4018(02)01758-3
13. Dorenbos, P.; Bos, A.J.J.; Poolton, N.R.J.; Opti. Materi. 2011, *33*, 1019
    DOI: 10.1016/j.optmat.2010.08.016
14. Li, Y.C.; Chang,Y.H.; Lin,Y.F.; Chang, Y.S.; Lin, Y.J. ; J. Alloy. Comp. 2007, *439*, 367
    DOI: 10.1016/j.jallcom.2006.08.269
15. L.Y. Zhou, J.S. Wei, F.Z. Gong, J.L. Huang, L.H.Yi; J. Soli. State Chem. 2008, *181*, 1337
    DOI: 10.1016/j.jssc.2008.03.005
16. Hou, J.; Yin, X.; Fang,Y.; Huang, F.; Jiang, W.; Opti. Materi. 2012, *34*, 1394
    DOI: 10.1016/j.optmat.2012.02.031
17. Shinde, K. N.; Dhoble, S. J.; Adv. Mat. Lett. 2010, *1*, 254
    DOI: 10.5185/amlett.2010.9161
18. Zhang, A.; Yang, P.; Cao, Y.; Zhu, Y.; Adv. Mat. Lett. 2011, *2*, 322
    DOI: 10.5185/amlett.2011.3042am2011
19. Deshmukh, A. D.; Dhoble, S. J.; Dhoble, N.S.; Adv. Mat. Lett. 2011, *2*, 38
    DOI: 10.5185/amlett.2010.10171
20. Nag, A.; Kutty, T.R.N.; Mater. Chemi. Physi. 2005, *91*, 524
    DOI: 10.1016/j.matchemphys.2004.12.020
21. Ratnam, B.V.; Jayasimhadri, M.; Kumar, G. B.; Jang, K.; Kim, S.S.; Lee, Y.I.; Lim, J.M. ;Shin, D.S.; Song, T.K.; J. Alloy. Comp. 2013, *564*, 100
    DOI: 10.1016/j.jallcom.2013.01.203
22. Pavitra, E.; Raju, G. S. R.; Ko, Y.H.;J. S. Yu; Phys. Chem. Chem. Phys.; 2012, *14*, 11296
    DOI: 10.1039/c2cp41722g
23. Faulkner, T. R.; Richardson, F.S.; Molecular Physics 1978, *36*, 193
    DOI: 10.1080/00268977800101511
24. Chang,Y.S.; Lin, H.J.; Li, Y.C.; Chai, Y.L.; Tsai, Y.Y.; J.Sol.State Chemi. 180 (2007) 3076
    DOI: 10.1016/j.jssc.2007.07.018
25. Sun, J.; Zhang, X.; Xia, Z.; Du, H.; J. Appl. Phy. 2012, *111*, 013101
    DOI: 10.1063/1.3673331
26. Lin, C. C.; Tang,Y.S.; Hu, S.F.: Liu, R.S.; J. Lumin. 2009, *129*, 1682
    DOI: 10.1016/j.jlumin.2009.03.022
27. Pekgozlu, I.; J. Lumin. 2013, *134*, 8
    DOI: 10.1016/j.jlumin.2012.09.031
28. Zhiping, Y.; Yue, H.; Yanchun, S.;Z. Yinhong, L. Pengfei; J. Rare Earths 2012, *30*, 1199
    DOI: 10.1016/S1002-0721(12)60205-1
29. Fangui, M.; Xinmin, Z.; Huan, L.; Seo, H.J.; J. Rare Earths. 2012, *30*, 866
    DOI: 10.1016/S1002-0721(12)60147-1
30. Cavalli, E.; Belletti, A.; Mahiou, R.; Boutinaud, P.; J.Lumin. 2010, *130*, 733
    DOI: 10.1016/j.jlumin.2009.11.038