Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Journal of Solid State Chemistry 179 (2006) 4047–4051
JOURNAL OF SOLID STATE CHEMISTRY
www.elsevier.com/locate/jssc

Rapid communication

UV–VUV-excited photoluminescence of *RE*-activated $CaLaP_3O_{10}$ ($RE = $ Eu,Tb)

Chunfang Wu, Yuhua Wang*, Wenjing Liu

Department of Materials Science, Institute of Functional and Environmental Materials, School of Physical Science and Technology, Lanzhou University, Lanzhou, Gansu Province 730000, PR China

Received 17 June 2006; received in revised form 17 July 2006; accepted 18 July 2006
Available online 24 July 2006

Abstract

Monazite-type polyphosphate $CaLaP_3O_{10}$ was synthesized by solid-state reaction at 1000 °C and their photoluminescence of Eu^{3+} and Tb^{3+} in $CaLaP_3O_{10}$ under ultraviolet (UV) and vacuum-ultraviolet (VUV) excitation were evaluated for the first time. The emission spectra of $CaLaP_3O_{10}$:Eu^{3+}showed that Eu^{3+} are in a site with inversion symmetry because the magnetic dipole transition $^5D_0$–$^7F_1$ was the strongest both upon 254 and 147 nm excitation. Monitored at 621 nm the excitation spectra consisted of host absorption bands, charge transfer band of Eu–O and the intraconfiguration $4f^6$ transition of Eu^{3+}. Green phosphor $CaLaP_3O_{10}$:Tb^{3+}exhibited better color purity when excited by 147 nm than that excited by 254 nm. With monitored at 542 nm the host absorption bands of $CaLaP_3O_{10}$:Tb^{3+} were also observed. Besides the host absorption bands there were strong *f–d* and weak *f–f* transitions of Tb^{3+}.

PACS: 78.55.−m

Keywords: VUV; Phosphor; Polyphosphate

1. Introduction

Plasma display panels (PDPs) is the most promising technique for the large-sized flat panel displays [1,2]. Phosphors in the PDP are excited by vacuum-ultraviolet (VUV) light consisting of the Xe resonance emission line (147 nm) and/or the Xe_2 molecular emission band (172 nm). In the VUV range, most of the photos are absorbed by the host crystal then the energy is transferred from host to rare earth ions and allows the rare earth ions emit visible light. So the host absorption efficiency and the energy transfer efficiency are very important for phosphors applied in PDPs. Eu,Tb-doped orthophosphate phosphors [3–5] have been extensively studied because the anion PO_4^{3-} group can effectively absorb the energy in the range of 124–177 nm and transfer the energy to emitting centers. Different polyphosphate can be constructed from PO_4^{3-} tetrahedra linked at each corer. $CaLaP_3O_{10}$ is one of the complex polyphosphate with a general composition of ABP_3O_{10}, where *A* is an alkaline earth anion, *B* is a trivalent rare earth element. $P_3O_{10}^{5-}$ anion group is formed by three PO_4^{3-} group sharing oxygen between two adjacent PO_4^{3-}. Ravindran Nair [6] reported $CaLaP_3O_{10}$ and $LnPO_4$ ($Ln = $ La, Gd) [7] are isostructural with monazite-type structure having a monoclinic unit cell. Therefore, $CaLaP_3O_{10}$ is expected to be a good host matrix like orthophosphate for VUV phosphors. The radius of La^{3+} are similar to Eu^{3+} and Tb^{3+}, so Eu^{3+} and Tb^{3+}can be doped into $CaLaP_3O_{10}$ and prefer to locate in La^{3+} site. On the other hand, Eu^{3+} and Tb^{3+} also probably substitute partial Ca^{2+} sites as the radius difference between Eu^{3+}(95 pm), Tb^{3+}(92.3 pm) and Ca^{2+}(99 pm) [8] is small. As a probe to investigate the structure of a new compound, the luminescent properties of Eu^{3+} and Tb^{3+} in $CaLaP_3O_{10}$ can provide useful information about the structure of $CaLaP_3O_{10}$. So the study of emission and excitation properties of $CaLaP_3O_{10}$:*RE* (*RE* = Eu,Tb) in UV and VUV range will provide not only fundamental research data but also potential application in Hg-free lamps, PDPs and back lighting source.

---

*Corresponding author. Fax: +86 931 891 3554.
E-mail address: wyh@lzu.edu.cn (Y. Wang).

0022-4596/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2006.07.026

Up to now, there is no report about the photoluminescence of $CaLaP_3O_{10}$:$RE(RE=$ Eu,Tb) under ultraviolet (UV) and VUV excitation. In this paper, the phosphors $CaLaP_3O_{10}$:$RE(RE=$ Eu,Tb) were synthesized by traditional solid state method. The UV and VUV optical properties were investigated in details.

2. Experimental

La_2O_3 (99.99%), Tb_4O_7(99.99%), Eu_2O_3(99.99%), $CaCO_3$($\geqslant$99%) and $(NH_4)_2HPO_4$ ($\geqslant$98.5%) were employed as raw materials. The appropriate amount of raw materials were weighed and transferred to an agate mortar for mixing. After intimately mixing these powders with ethanol, the mixtures were calcined at 1000 °C for 4 h in air, then quenched to room temperature.

The samples were characterized by Rigaku D/max 2400 X-ray powder diffractometer (XRD). The excitation and emission spectra were measured at room temperature by FLS920T spectrophotometer equipped with VM504 vacuum monochromator using Xe-lamp and Deuterium lamp as light sources, respectively, and the VUV excitation spectra were corrected by the sodium salicylate at the same measurement conditions.

3. Results and discussion

The powders of $CaLaP_3O_{10}$ and Eu^{3+}- and Tb^{3+}-doped $CaLaP_3O_{10}$ are all white colored. The XRD pattern of the as-synthesized compound $CaLaP_3O_{10}$ is presented in Fig. 1. The XRD pattern is found to be very similar to the XRD pattern reported $CaLaP_3O_{10}$ [6]. All the peaks of as prepared samples are indexed to the monazite-type structure with $a=0.6842(5)$ nm, $b=0.7085(1)$ nm, $c=0.6516(7)$ nm and $\beta=103.23(2)°$. Therefore, it is assumed that $CaLaP_3O_{10}$ prepared here have the monoclinic monazite-type structure. Meanwhile Eu^{3+}- and Tb^{3+}-doped $CaLaP_3O_{10}$ are also characterized as single phase with monoclinic structure.

The emission spectra of $CaLaP_3O_{10}$ doped with Eu^{3+} excited with 147 and 254 nm are similar except for the emission intensity, so only the typical emission spectrum of $CaLa_{0.85}P_3O_{10}$:0.15 Eu^{3+}under 147 nm excitation is given in Fig. 2.The characteristic $^5D_0$–^7F_J ($J=1$, 2, 3) emission of Eu^{3+} (as labeled in Fig. 2) are observed. Among them, the $^5D_0$–$^7F_1$ transition is the strongest. According to the Judd–Ofelt theory [9,10] in the $CaLaP_3O_{10}$ host, Eu^{3+} ions prefer to occupy the lattice sites with inversion centro-symmetry. The $^5D_0$–^7F_J ($J=1$, 2) emission of Eu^{3+} are split. The splitting of Eu^{3+} emission in several host such as (Y,Gd)AlO_3, YPO_4 and Mg_2GeO_4 [11–13] have been observed, but the reason were not discussed. The reason why the splitting of Eu^{3+} emission occurred in $ZnGaO_4$ [14] and SrY_2O_4 [15] are explained as that the Eu^{3+} ions at least occupied two sites. We have point out that Eu^{3+} ions probably occupy both Ca^{2+} site and La^{3+} site for their similar ionic radius. So the reason about the splitting of Eu^{3+} emission mentioned in Refs. [14,15] can be applied in our work.

The excitation spectra of $CaLa_{0.85}P_3O_{10}$:0.15Eu^{3+} are exhibited in Fig. 3. The excitation spectrum monitored at 620 nm has a broad peak at about 257 nm, which is consistent with the observed charge transfer band (CTB) band of Eu–O in $LaPO_4$ with a small difference (about 1 nm) [16]. So it can be attributed to the charge transfer of Eu–O resulting from an electron transfer from the ligand $O^{2-}(2p^6)$ orbitals to empty states of $4f^6$ for Eu^{3+} configuration [17]. Further, it was found that with the Eu concentration increasing the CTB of Eu–O became broad gradually. Generally, when $CaLaP_3O_{10}$ is doped by Eu, Eu^{3+} prefers to substitute La^{3+} site due to their similar ionic radius. Considering the ionic radius difference between $Eu^{3+}$and Ca^{2+} is also small, Eu^{3+} probably also

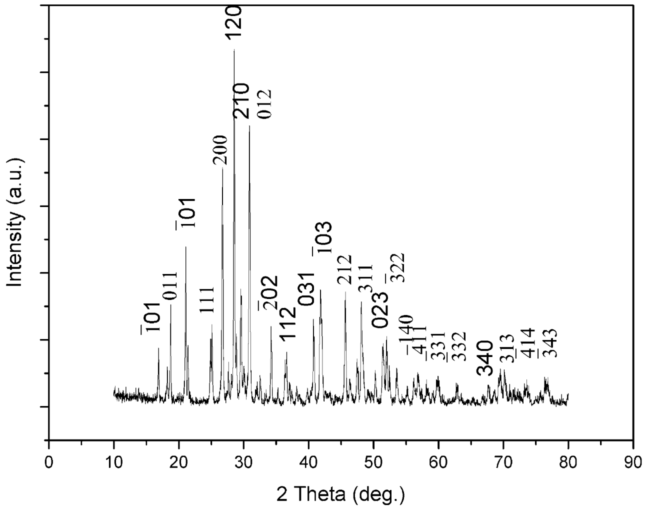

Fig. 1. XRD pattern of $CaLaP_3O_{10}$.

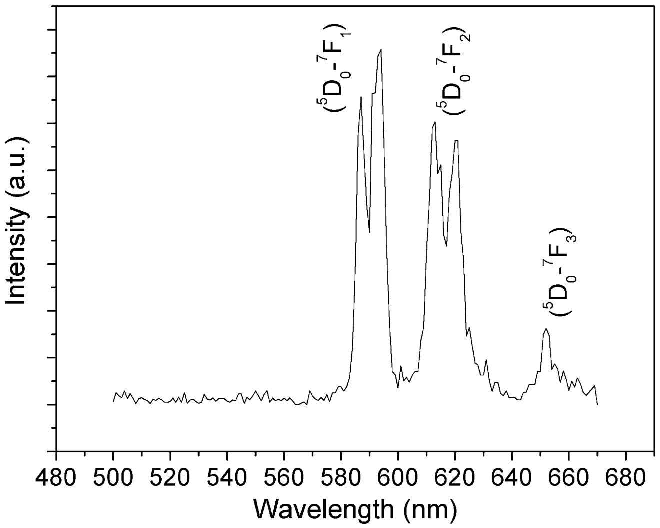

Fig. 2. Emission spectra of $CaLa_{0.85}P_3O_{10}$:0.15Eu^{3+} excited by 147 nm radiation.

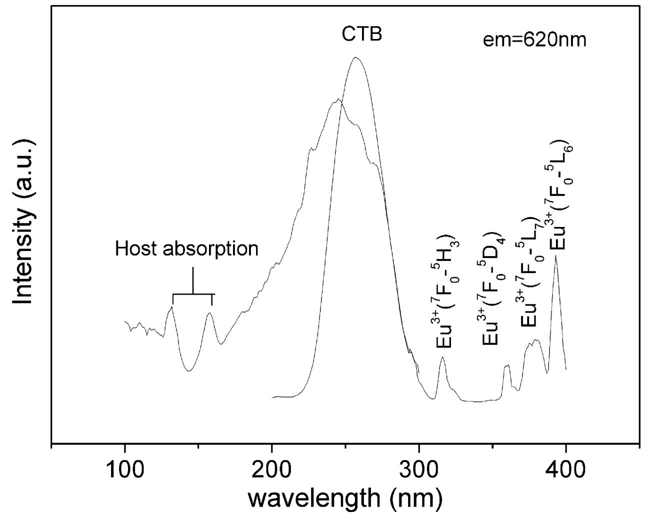

Fig. 3. Excitation spectra of $CaLa_{0.85}P_3O_{10}$:0.15Eu^{3+} ($\lambda_{em} = 620$ nm).

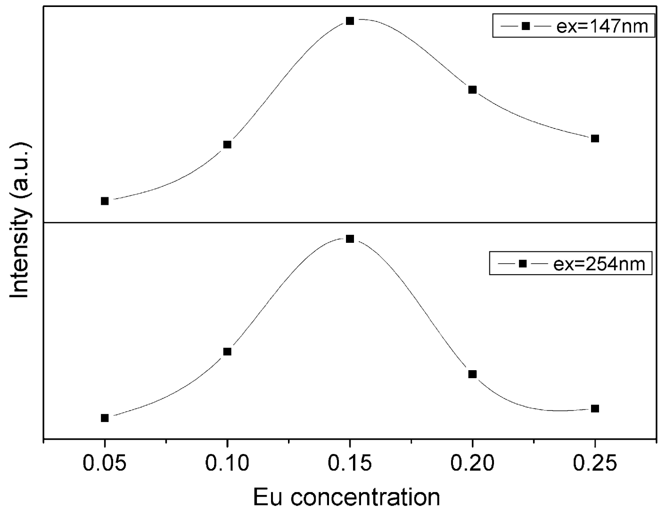

Fig. 4. Concentration dependence of relative emission ($^5D_0$–$^7F_2$) intensity for $CaLaP_3O_{10}$:Eu^{3+} excited by 147 and 254 nm radiation.

occupy Ca^{2+} site. That is to say with the increasing of Eu^{3+}, Eu^{3+} will occupy two different sites La^{3+} and Ca^{2+}, which leads to the broadening of CTB of Eu–O. The excitation peaks in the range 300–400 nm are due to the intraconfiguration $4f^6$ excitation peaks of Eu^{3+} which has been observed in many other borate and phosphate phosphors [18,19]. In VUV region, two small absorption peaks of $CaLaP_3O_{10}$ host lattice are located at about 131 and 158 nm, respectively.

Various emission intensities of $CaLaP_3O_{10}$:Eu^{3+} under 147 and 254 nm excitation are shown in Fig. 4 plotted against the concentration of Eu^{3+}. As we could see from this figure, the most intense peak is observed at concentration of 0.15 in spite of the different excitation wavelength, then the intensities decrease gradually owing to the energy transfer between the neighboring Eu^{3+}, which is corresponding to the quench of the emission of Eu^{3+} [20]. The concentration quench theory of phosphor under VUV excitation is not very clear and is under investigation.

The emission spectra of $CaLa_{0.85}P_3O_{10}$:0.15Tb and $CaLa_{0.65}P_3O_{10}$:0.35Tb (Fig. 5) excited with 147 and 254 nm show four peaks which center at about 487, 543, 583 and 621 nm which are consistent with Tb^{3+} emission properties in other matrix [16,18] and they are attributed to the transition of $^5D_4$–^7F_J ($J = 6, 5, 4, 3$), respectively. The $^5D_4$–$^7F_5$ transition is the strongest emission, but the ration of the green emission results from $^5D_4$–$^7F_5$ to other emission of $^5D_4$–^7F_J ($J = 6, 4, 3$) is higher when sample excited by 147 nm than that excited by 254 nm. It indicates that the green phosphors $CaLa_{0.85}P_3O_{10}$:0.15Tb have better color purity excited by 147 nm than $CaLa_{0.65}P_3O_{10}$:0.35Tb excited by 254 nm. The calculated CIE (Commission Internationale De L'Eclairage) coordination x, y values for $CaLa_{0.85}P_3O_{10}$:0.15Tb and $CaLa_{0.65}P_3O_{10}$:0.35Tb under 147 and 254 nm excitation are (0.298, 0.674) and (0.331,0.564), respectively. The luminescent chromaticity coordinates of National Television Standards Committee (NTSC) for green are $x = 0.21$, $y = 0.71$.

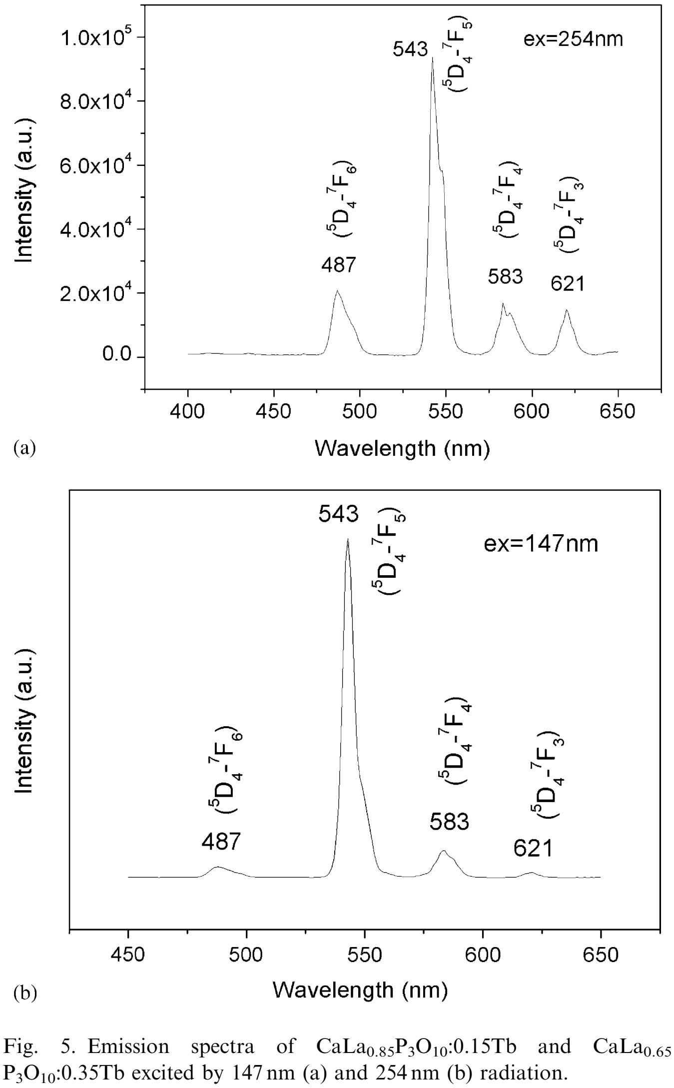

Fig. 5. Emission spectra of $CaLa_{0.85}P_3O_{10}$:0.15Tb and $CaLa_{0.65}P_3O_{10}$:0.35Tb excited by 147 nm (a) and 254 nm (b) radiation.

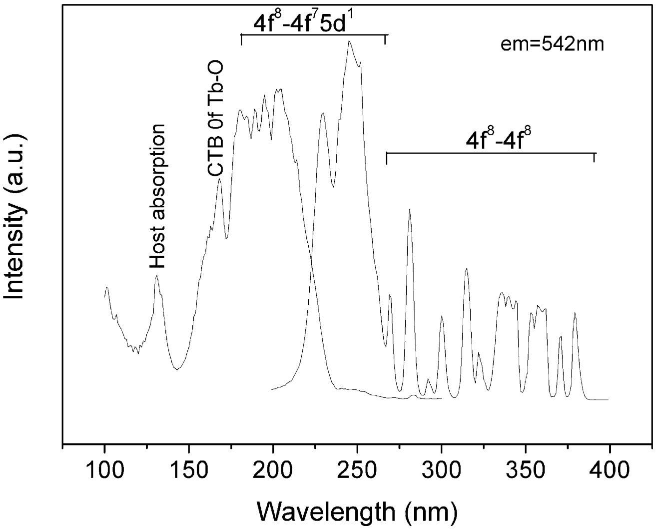

Fig. 6. Excitation spectra of $CaLa_{0.85}P_3O_{10}$:0.15Tb (λ_{em} = 542 nm).

The excitation spectra of $CaLaP_3O_{10}:Tb^{3+}$ with an emission wavelength of 542 nm are exhibited in Fig. 6.Two small peaks at 131 and 158 nm (which is overlapped by the stronger peak at 168) are observed which are similar with excitation spectra of $CaLaP_3O_{10}:Eu^{3+}$. They can be ascribed to host absorption because of the appearance of the two peaks is independent of the nature of rare earth ions. Therefore, when Tb-doped $CaLaP_3O_{10}$ is excited at wavelengths shorter than 160 nm, the excitation is absorbed first by the host and then transferred to Tb^{3+} ions, leading to an indirect excitation into Tb^{3+}. The peak at 168 nm is probably related to the CTB between Tb^{3+} and O^{2-}. The CTB position of Tb^{3+} ions can be evaluated by an empirical formula given by Jørgensen [21].

$$E_{CT} = [\chi_{(X)} - \chi_{(M)}] \times 30{,}000\,\mathrm{cm}^{-1}.$$

Here gives the position of the CTB in cm^{-1}, $\chi_{(X)}$ the optical electronegativity of the anion, and $\chi_{(M)}$ that of central metal ion. Using $\chi_{(O)} = 3.2$ [22], $\chi_{(Tb)} = 1.2$ [23], the CTB of Tb^{3+} in oxides can be calculated as167 nm. The strongest bands from 172 to260 nm are due to parity allowed $4f^8$–$4f^7 5d$ transitions of Tb^{3+} and the result is similar with that of literature [16] reported, but it is different from the results observed in $SrGdBPO_5$:Tb [24], $Sr_3Gd\ (PO_4)_3$:Tb [25], $Sr_3(PO_4)_2$:Tb [26] and $GdCa_4O(BO_3)_3$:Tb [27]. The spin-allowed and the spin-forbidden *f–d* transitions of Tb^{3+} they reported are listed in Table 1.The *f–d* transition of Tb^{3+} in $CaLaP_3O_{10}$ and $(La,Gd)PO_4$ present a broad band shape, but that in $SrGdBPO_5$:Tb, $Sr_3Gd\ (PO_4)_3$:Tb, $Sr_3(PO_4)_2$:Tb and $GdCa_4O(BO_3)_3$:Tb are only one or two peaks, which probably is assigned as different crystal splitting of the *d*-levels of Tb [16]. The several sharp peaks between 260 and 380 nm are assigned to the $4f^8$–$4f^8$ transitions of Tb^{3+} as shown in literature [24].

Table 1
The position of *f–d* transition of Tb^{3+} in several host materials

Compound	The spin-allowed transition (nm)	The spin-forbidden *f–d* transition (nm)
$SrGdBPO_5$:Tb	220	
$Sr_3Gd\ (PO_4)_3$:Tb	224	260
$Sr_3(PO_4)_2$:Tb	229	281, 293
$GdCa_4O(BO_3)_3$:Tb	237	

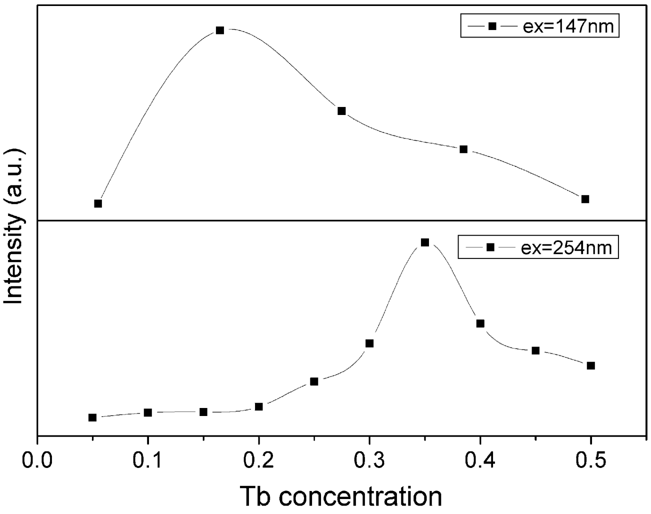

Fig. 7. Concentration dependence of relative emission ($^5D_4$–$^7F_5$) intensity for $CaLaP_3O_{10}:Tb^{3+}$ excited by 147 and 254 nm radiation.

The relative intensity of $^5D_4$–$^7F_5$ emission as functions of Tb^{3+} concentrations for $CaLaP_3O_{10}$:Tb phosphors under 147 and 254 nm excitation are shown in Fig. 7. The maximal emission intensity is obtained at 0.15 (147 nm excitation) and 0.35(254 nm excitation), respectively. The optimum Tb^{3+} concentration for $^5D_4$–$^7F_5$ emission shifts to lower concentration as the excitation varies from $4f^n$ excitation to host excitation, which is consistent with L. Ozawa's conclusion [28].

4. Conclusions

Polyphosphate as a new host matrix for phosphors, luminescent properties of Tb^{3+} and Eu^{3+} in $CaLaP_3O_{10}$ were investigated in detail for their potential application in VUV region. In addition to the $4f^n$ or activator–host excitation of activators, the host absorption bands at 131 nm and 158 nm were observed both in $CaLaP_3O_{10}:Tb^{3+}$ and $CaLaP_3O_{10}:Eu^{3+}$ .It showed that under 147 nm excitation the host first absorbed the excitation energy then transfer to rare earth ions. Both excited by 254 nm or 147 nm radiation, $CaLaP_3O_{10}:Eu^{3+}$ emitted light in the orange-red spectral region, because the Eu^{3+} ion occupied an inversion symmetry site. But the emission spectra of $CaLaP_3O_{10}:Tb^{3+}$ excited by 147 nm was different from that excited by 254 nm, and under 147 nm excitation the green emission was close to the chromaticity ordinates of green National Television Standards Committee (NTSC) values.

Acknowledgments

This work was supported by Program for New Century Excellent Talents in the University of China (NCET, 04-0978), the Key Science Research Project of Ministry of Education of China (105170) and Specialized Research Fund for the Doctoral Program of Higher Education of China (SRFDP, 20040730019).

References

[1] C.R. Ronda, T. Justel, H. Nikol, J. Alloys Compds. 669 (1998) 275–277.

[2] L. Tian, B.Y. Yu, C.H. Pyun, H.L. Park, S. Mho, Solid State Commun. 129 (2004) 43.

[3] X. Wu, H. You, et al., Mater. Res. Bull. 37 (2002) 1531.

[4] R.P. Rao, J. Lumin. 113 (2005) 271.

[5] K.K. Lee, Y.C. Kang, et al., Jpn. J. Appl. Phys. 41 (2002) 5590.

[6] K. Ravindran Nair, P. Prabhakar Rao, B. Amina, M.R. Chandran, P. Koshy, Mater. Lett. 60 (2005) 1796.

[7] R.C. Ropp, J. Electrochem. Soc. 115 (1968) 841.

[8] R.C. Weast, Handbook of the Chemistry and Physics, 69th ed., CRC Press, Boca Raton, FL, 1988–1989 (P.F-164).

[9] B.R. Judd, Phys. Rev. 127 (1962) 750.

[10] G.S. Ofelt, J. Chem. Phys. 37 (1962) 511.

[11] S.D. Han, S.P. Khatkar, et al., Mater. Sci. Eng. B 127 (2006) 272.

[12] L. Tian, B.-Y. Yu, et al., Solid State Commun. 129 (2004) 43.

[13] H.-M. Yang, J.-X. Shi, et al., Mater. Sci. Eng. B 127 (2006) 276.

[14] J.S. Kim, A.K. Kwon, et al., J. Lumin., in press.

[15] L. Zhou, J. Shi, M. Gong, J. Lumin. 113 (2005) 285.

[16] X. Wu, H. You, H. Cui, et al., Mater. Res. Bull. 37 (2002) 1531.

[17] D. van der Voort, J.M.E. de Rijk, R. van Doorn, G. Blasse, Mater. Chem. Phys. 31 (1992) 333.

[18] H. Liang, Y. Tao, Q. Zeng, et al., Mater. Res. Bull. 38 (2003) 797.

[19] L. Wang, Y. Wang, J. Alloys Compds., 2006, in press.

[20] D.L. Dexter, J. Chem. Phys. 22 (1954) 1063.

[21] C.K. JØrgensen, Mol. Phys. 5 (1962) 271.

[22] L. van Piterson, S. Soverna, A. Meijerink, J. Electrochem. Soc. 147 (2000) 4688.

[23] Q. Su, in: Proceedings of the Second International Symposium on Rare Earth Spectroscopy, International Academic Publishers, Beijing, 1991, p. 765.

[24] C.-H. Lu, S.V. Godbole, V. Natarajan, Mater. Chem. Phys. 94 (2005) 73.

[25] H. Liang, Y. Tao, et al., J. Solid State Chem. 177 (2004) 901.

[26] H. Liang, Y. Tao, Q. Su, S. Wang, J. Solid State Chem. 167 (2002) 435.

[27] H.C. Yang, C.Y. Li, H. He, et al., J. Lumin. 118 (2006) 61.

[28] L. Ozawa, H. Forst, P.M. Jaffe, G. Ban, J. Electrochem. Soc. Solid State Sci. (1971) 482.