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Emission analysis of Pr^{3+} & Ho^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphors

B. Vengala Rao · S. Buddhudu

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Abstract Emission spectral results of Pr^{3+} & Ho^{3+} ions doped $Ca_4GdO(BO_3)_3$ powder phosphors are reported here. XRD, SEM and FTIR measurements have been carried out for them. The emission spectrum of Pr^{3+}: $Ca_4GdO(BO_3)_3$ has shown an emission transition $^1D_2 \rightarrow {}^3H_4$ at 606 nm with λ_{exci} = 480 nm ($^3H_4 \rightarrow {}^3P_0$) and Ho^{3+}: $Ca_4GdO(BO_3)_3$ phosphor has shown an emission transition $^5S_2 \rightarrow {}^5I_8$ at 549 nm with λ_{exci} = 447 nm ($^5I_8 \rightarrow {}^5F_1$). Emission performances of these two phosphors have been explained in terms of energy level diagrams.

Introduction

Luminescent materials containing rare-earth or transition metal ions have become popular in the progress of optical materials of significant importance [1–5]. Commercial powder phosphors are usually based on the host matrices of borates, aluminates, vanadates, phosphates, silicates and tungstates etc [6–10]. Among them, all the borate based phosphors have three structural units, namely $(BO_3)^{3-}$, $(B_3O_6)^{3-}$, $(B_3O_7)^{5-}$ anion groups. We have mainly investigated the borate based materials with $(BO_3)^{3-}$ groups, since the electronic delocalization in the planer borate anions could be exhibiting NLO (Non Linear Optical) properties [11]. A large number of borate compounds are polyfunctional materials with non-linear optical, piezo-electrical and acousto electrical properties. In addition to that borate compounds are known to be transparent over a wide spectral range from VUV to IR region, large band gaps, low cost of materials with good chemical stability [12–14]. Recently, the borate host matrix $Ca_4GdO(BO_3)_3$ has attracted a great deal of attention as a potential optical material based on its stable crystalline structure, non-hygroscopic, versatility and chemical stability [15–17]. Alkaline earth lanthanide oxy-borates doped with rare-earth ions are of more interesting luminescent materials. Earlier, we have made an attempt to analyze the luminescence properties of $Eu^{3+}(4f^6)$ [18], $Tb^{3+}(4f^8)$ [19] and $Sm^{3+}(4f^5)$ [20] ions doped in $Ca_4GdO(BO_3)_3$ powder phosphors. These three rare-earth ions have prominent emissions (red, green and reddish orange) in the visible region. In the present work, we report on the emission properties of $Pr^{3+}(4f^2)$ & $(Ho^{3+}(4f^{10})$: $Ca_4GdO(BO_3)_3$ powder phosphors.

Experimental studies

$Ca_4GdO(BO_3)_3$: Pr^{3+} & Ho^{3+} powder phosphors were prepared by employing a solid state reaction method. The chemical equation can be expressed as follows

$$\begin{aligned}&8CaCO_3 + 6H_3BO_3 + (1-x)Gd_2O_3\\&\quad + x\,RE_2O_3\ (RE = Pr, Ho) \rightarrow 2Ca_4Gd_{(1-x)}O(BO_3)_3 :\\&\quad RE^{3+}(= Pr,\ Ho) + 9H_2O + 8CO_2\end{aligned}$$

The starting reagents Gd_2O_3 (99.9%), Pr_2O_3 (99.9%) and Ho_2O_3 (99.9%), $CaCO_3$ and H_3BO_3 (Analar grade) were used in the samples preparation. They were weighed on stoichiometric ratio and powdered finely by using an agate mortar. In order to mix the raw chemicals homogenously, small amount of acetone was added and those powder mixtures were collected into an alumina

B. Vengala Rao · S. Buddhudu (✉)
Department of Physics, Sri Venkateswara University,
Tirupati 517502, India
e-mail: drsb99@hotmail.com

crucible for heating. The temperature was gradually raised from the room temperature to 900 °C, where the mixture was kept for 10 h in an ambient atmosphere with an intermediate grinding.

The phase purity and phase structure of powder samples were characterized from the X-ray powder diffraction (XRD) patterns, using a HLG4/B-PC X-ray diffractometer with CuK_α radiation (1.54060 Å) and a graphite monochromator at the room temperature. The morphology of the powder phosphor has been observed using JEOL JSM 840A Scanning Electron Microscope. The samples were gold coated using the sputter coater polaron SC7610 system. The FTIR absorption spectrum of the sample was recorded on a Nicolet IR-200 spectrometer using KBr pellet technique in the wave number range of 400–4,000 cm^{-1}. Both the excitation and emission spectra of the Pr^{3+} & Ho^{3+}: $Ca_4GdO(BO_3)_3$ phosphors were measured on a Spex Fluorolog-2 Fluorimeter with a Datamax software to acquire the data with a Xe-arc lamp (150 W) as the excitation source. A Xe-flash lamp (25 W) with a phosphorimeter attachment was used to measure the lifetimes of the emission transitions of these powder phosphors.

Results and discussion

Figure 1 shows the X-ray diffraction patterns of (a) $Ca_4GdO(BO_3)_3$, (b) Pr^{3+}: $Ca_4GdO(BO_3)_3$, (c) Ho^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphors. The standard XRD pattern for $Ca_4GdO(BO_3)_3$ is also shown as a reference. It can be seen clearly that all the diffraction peaks of the synthesized $Ca_4GdO(BO_3)_3$: RE^{3+} (=Pr^{3+}, Ho^{3+}) phosphors are in good agreement with those of standard of $Ca_4GdO(BO_3)_3$. These powder phosphors belong to a monoclinic structure with a space group Cm ($a = 8.078$; $b = 15.98$; $c = 3.55$; $\beta = 101.26$ Å). On comparing these XRD patterns, it is found that the Pr^{3+} & Ho^{3+} ions could easily be substituted (in the place of Gd^{3+}) in the host matrix without any change in the host matrix structure [21–23]. All the diffraction peaks of $Ca_4GdO(BO_3)_3$: RE^{3+}(=Pr^{3+}, Ho^{3+}) could be indexed according to those of $Ca_4GdO(BO_3)_3$, as shown in Fig. 1. Figure 2 shows the SEM micrograph of the $Ca_4GdO(BO_3)_3$ doped with Pr^{3+} & Ho^{3+} powder phosphors to understand their morphology and from Fig. 2 we have found that the particles are agglomerated in the phosphor powders studied. Figure 3 shows the FTIR spectra of $Ca_4GdO(BO_3)_3$: Pr^{3+} & Ho^{3+} ions doped powder phosphors and were assigned to vibrational transitions of the host lattice $Ca_4GdO(BO_3)_3$. FTIR patterns of those samples have similarities. The fundamental vibrations occur below 1,500 cm^{-1}, and are associated with parent three coordinated boron modes at 1,450–1,150 cm^{-1} (v_3, B–O antisymmetric stretch), 950–910 cm^{-1} (v_1, B–O symmetric stretch), 795–710 cm^{-1} (v_2, B–O–B bend). The v_3 mode is an intense one whereas v_1 is a weak as shown in Fig. 3. The strong features between 340 and 525 cm^{-1} correspond to Gd–O stretching modes [24, 25].

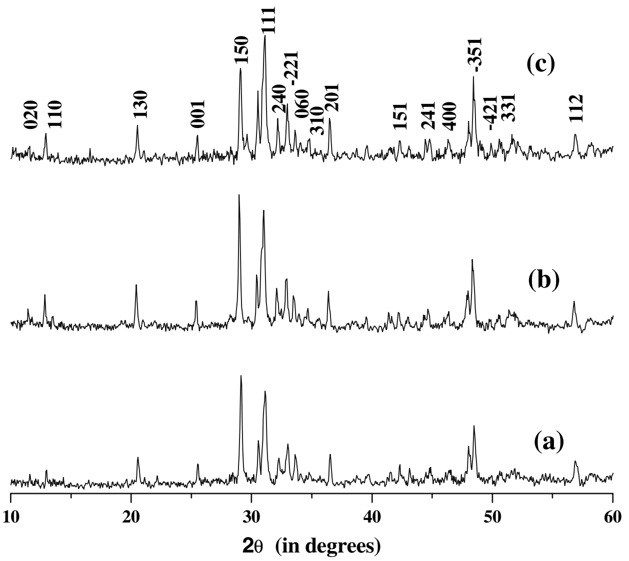

Fig. 1 XRD patterns of (**a**) $Ca_4GdO(BO_3)_3$, (**b**) Pr^{3+}: $Ca_4GdO(BO_3)_3$, (**c**) Ho^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphors

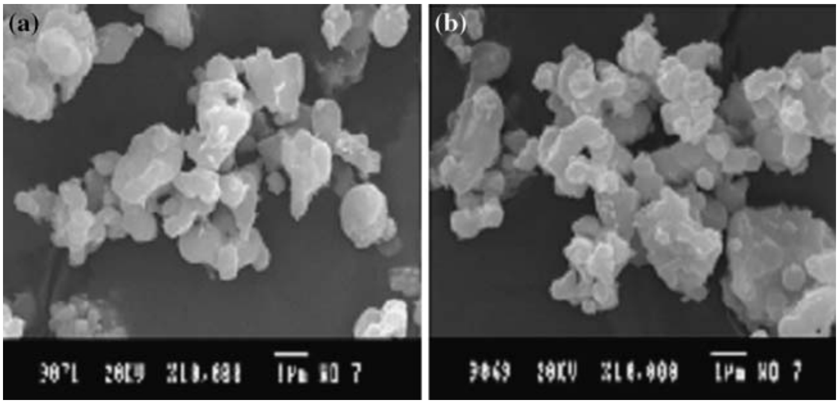

Fig. 2 SEM micrograph of (**a**) Pr^{3+}: $Ca_4GdO(BO_3)_3$, (**b**) Ho^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphors

Figure 4a shows the excitation spectrum of Pr^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphor. With the transitions from the $^3H_4$ ground state to the $^3P_0$ (480 nm), $^1I_6$ (463 nm) and $^3P_2$ (447 nm) excited states. The intense excitation wavelength is at 480 nm ($^3H_4 \rightarrow {}^3P_0$) transition and emission spectrum of Pr^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphor is shown in Fig. 4b. Under 480 nm excitation, the Pr^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphor exhibits a strong red emission ($^1D_2 \rightarrow {}^3H_4$). Due to induced relaxation by a cross-relaxation [26] and also a multiphonon relaxation [27] that could be the cause, for the non-observable of $^3P_0 \rightarrow {}^1D_2$ transition for the Pr^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphor. Figure 5a presents the decay curve of the emission band $^1D_2 \rightarrow {}^3H_4$ of Pr^{3+}: $Ca_4GdO(BO_3)_3$ phosphor with an excitation at 480 nm with a lifetime $\tau = 1.015$ ms. An energy level scheme has been given in Fig. 5b to explain the excitation and emission process in the Pr^{3+}: $Ca_4GdO(BO_3)_3$ phosphor.

The green emission from Ho^{3+} is of particular interest because it can be utilized as a green solid-state laser [28]. Figure 6a shows an excitation spectrum of Ho^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphor and excitation bands are assigned to the electronic transitions $^5I_8 \rightarrow {}^5F_1$ (447 nm), $^5I_8 \rightarrow {}^5G_6$ (454 nm), $^5I_8 \rightarrow {}^3K_8$ (461 nm) of Ho^{3+}. The emission spectrum of Ho^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphor in the wavelength range from 520 to 580 nm is shown

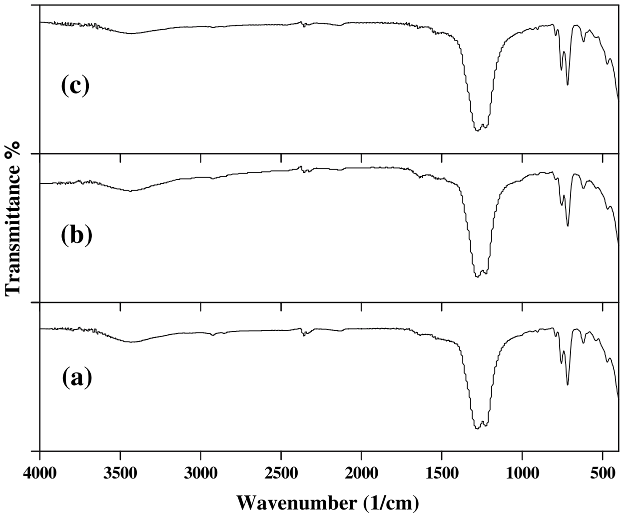

Fig. 3 FTIR spectra of (**a**) $Ca_4GdO(BO_3)_3$, (**b**) Pr^{3+}: $Ca_4GdO(BO_3)_3$, (**c**) Ho^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphors

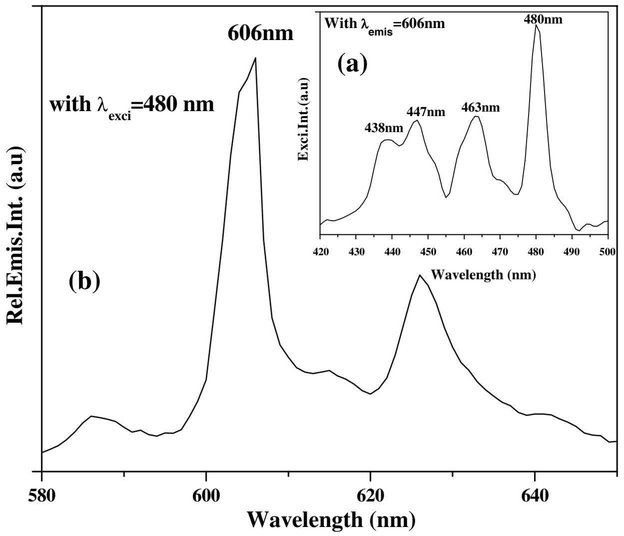

Fig. 4 (**a**) Excitation and (**b**) emission spectra of Pr^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphor

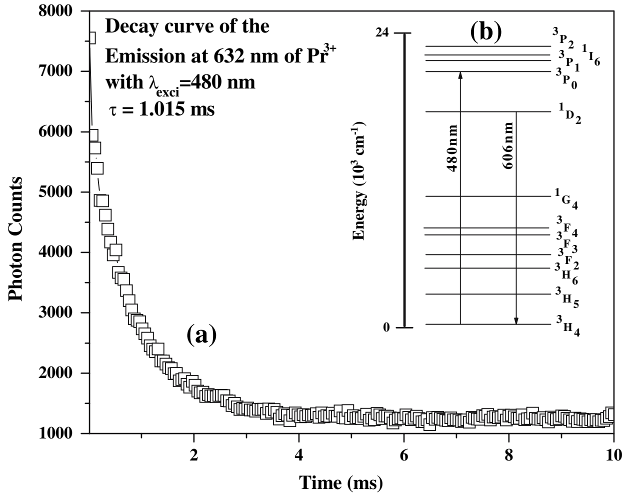

Fig. 5 (**a**) Decay curve and (**b**) energy level scheme of Pr^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphor

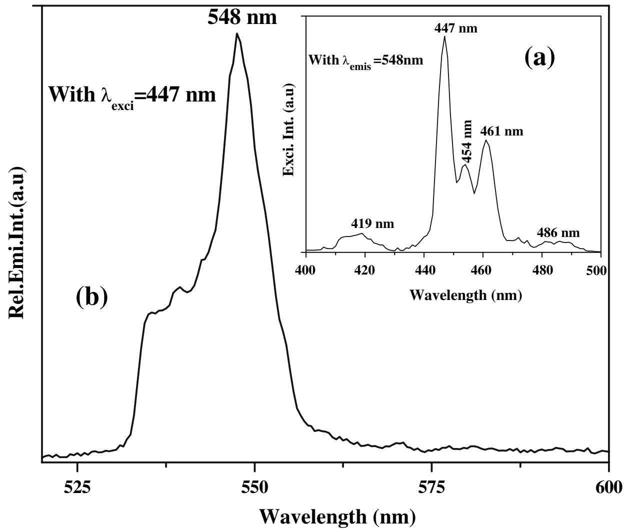

Fig. 6 (**a**) Excitation and (**b**) emission spectra of Ho^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphor

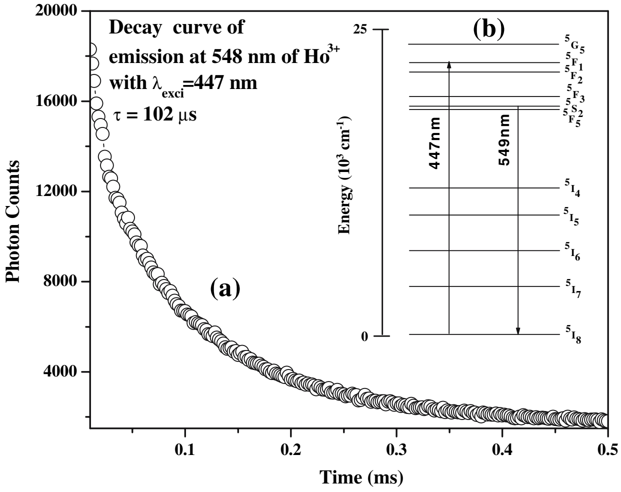

Fig. 7 (**a**) Decay curve and (**b**) energy level scheme of Ho^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphor

in Fig. 6b. The emission spectrum of Ho^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphor, shows an emission band of $^5S_2 \rightarrow {}^5I_8$ transition [29]. Figure 7a presents the decay curve of the emission band $^5S_2 \rightarrow {}^5I_8$ of Ho^{3+}: $Ca_4GdO(BO_3)_3$ phosphor with an excitation at 447 nm with a lifetime is $\tau = 102$ µs. An energy level scheme is given in Fig. 7b to explain the excitation and emission process in powder phosphor.

Conclusion

We have analyzed the emission characterization of Pr^{3+} & Ho^{3+}: $Ca_4GdO(BO_3)_3$ powder phosphors. Also, we have analyzed their XRD, SEM, FTIR spectral profiles to understand their structure, morphology and functional groups. Based on the results obtained in the present work, we suggest that there luminescence phosphors could be identified as novel optical materials for certain electronic display applications.

References

1. Gao H, Wang Y (2007) Mater Res Bull 42(5):921
2. Chiang CC, Tsai MS, Hon MH (2007) J Alloys Compd 431(1–2):298
3. Kim HK (2006) Appl Phys Lett 89:233504
4. Johnson JA, Schweizer S, Henke B, Chen G, Woodford J, Newman PJ, Macfarlane DR (2006) J Appl Phys 100:034701
5. Guo H (2007) J Solid State Chem 180(1):127
6. Jia D, Jia W, Jia Y (2007) J Appl Phys 101:023520
7. Nakazawa E, Murazaki Y, Saito S (2006) J Appl Phys 100:113113
8. Shen F, He D, Liu H, Xu J (2007) J Lumin 122:973
9. Yan B, Su X, Zhou K (2006) Mater Res Bull 41(1):134
10. Neeraj S, Kijima N, Cheetham AK (2004) Chem Phys Lett 387(1–3):2
11. Chen CT (1993) Laser science and technical international hand book, vol 15. Harwood Academic, New York
12. Chen CT, Bai L, Wang ZZ, Li RK (2006) J Cryst Growth 292(2):169
13. Thakare DS, Omamwar SK, Moharil SV, Dhopte SM, Muthal PL, Konawar VK (2007) Opt Mater 29:1731
14. Duan C, Ynan J, Zhao J (2005) J Solid State Chem 178(12):3698
15. Lukasiewicz T, Kityk IV, Akowska Janusik MM, Majechrowski A, Galazka Z, Kaddouri H, Mierczyk Z (2002) J Cryst Growth 237:641
16. Aka G, Mougel F, Auge F, Kahn-Harari A, Vivien D, Benitez JM, Salin F, Pelene D, Balembois F, Georges P, Brun A, Le Nain N, Jacqet M (2000) J Alloys Compd 303:401
17. Tukia M, Holsa J, Lastusaari M, Koski JN (2005) Opt Mater 27:1516
18. Vengala Rao B, Rambabu U, Buddhudu S (2006) Physica B 382:86
19. Vengala Rao B, Rambabu U, Buddhudu S (2007) Physica B 391:339
20. Vengala Rao B, Rambabu U, Buddhudu S (2007) Mater Lett 61:2868
21. Iyukhin AB, Dzhuriukii BF (1993) Russ J Inorg Chem 36:847
22. Wang Y, Endo T, Xie E, He D, Liu B (2004) Microelectron J 35:357
23. Kityk IV, Mefleh A (1999) Physica B 262:170
24. Dominiak-Dzik G, Ryba-Romnowski W, Golab S, Macalik L, Hanuza J, Pajazkowska A (2000) J Mol Struct 555:213
25. Krishnakumar V, Nagalakshmi R (2004) Spectrochim Acta Part A 60:2733
26. Van Vliet JPM, Blask G (1988) Chem Phys Lett 143:221
27. Aron A, Tigreat PY, Caramanian A, Autic-Fidancer E, Viana B, Aka G, Vivien D (2000) J Lumin 87:611
28. Sumiyoshi T, Sekita H (1998) Opt Lett 23:1837
29. Wang H, Jianfu Li, Guohna Jia, Zhenyn You, Fugui Yang, Yamping Wei, Yan Wang, Zhaojie Zhu, Xiuailu, Chaoyang Tu (2007) J Alloys Compd 431(1–2):277