



Luminescence studies on lanthanide ions (Eu^{3+} , Dy^{3+} and Tb^{3+}) doped YAG:Ce nano-phosphors

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ABSTRACT

Yttrium aluminum garnet nanoparticles both undoped and doped with lanthanide ions (Ce^{3+} , Eu^{3+} , Dy^{3+} and Tb^{3+}) having average size around $30 (\pm 3)$ nm were prepared by glycine nitrate combustion method followed by annealing at a relatively low temperature of 800°C . Increase in the annealing temperature has been found to improve the luminescence intensity and for 1200°C heated samples there exists strong energy transfer from Tb^{3+} to Ce^{3+} ions in YAG:Ce(2%),Tb(2%) nanoparticles as revealed by luminescence studies. Co-doping the YAG:Ce nanoparticles with Eu^{3+} results in significant decrease in the emission intensity of both Ce^{3+} and Eu^{3+} ions and this has been attributed to the oxidation of Ce^{3+} to Ce^{4+} and reduction of Eu^{3+} to Eu^{2+} ions. Dy^{3+} co-doping did not have any effect on the Ce^{3+} emission as there is no energy transfer between Dy^{3+} and Ce^{3+} ions.

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1. Introduction

Lanthanide ions doped yttrium aluminum garnet (YAG) is an efficient phosphor material and has got potential application as an active material in cathode ray tubes (CRTs) field emission and vacuum fluorescent displays (FEDs and VFDs) [1–3]. Ce^{3+} doped YAG is a yellow light emitting phosphor with absorption in the blue region [4]. Hence mixing YAG:Ce phosphor with blue light emitting materials such as GaN or ZnS:Ag, Cl [5,6] can give rise to white light emitting materials. Yellow light emission from YAG:Ce phosphor arises due to $5d \rightarrow 4f$ transition of Ce^{3+} . This transition is very sensitive to presence of other lanthanide ions in the host and conditions employed for their synthesis [7–10]. For example co-doping bulk YAG:Ce with Eu^{3+} and Mn^{2+} ions results in a significant decrease in luminescence intensity of $5d \rightarrow 4f$ transition of Ce^{3+} ions [8]. Energy transfer from the excited state of Ce^{3+} ions to Mn^{2+} or Eu^{3+} levels is the reason for observed decrease in intensity of Ce^{3+} emission from these samples. Unlike this, increase in concentration of Tb^{3+} ions in the bulk YAG:Ce host has been found to increase the luminescence intensity corresponding to $5d \rightarrow 4f$ transition of Ce^{3+} and authors have attributed this to energy transfer from Tb^{3+} to Ce^{3+} levels in the sample [9]. In the above study, samples were excited in the vacuum ultraviolet region (173 nm) and it is quite possible that both Tb^{3+} and Ce^{3+} can get excited by this process and hence energy transfer from Tb^{3+} to Ce^{3+} cannot be confirmed by this study.

There are also reports regarding the change in peak position corresponding to $5d \rightarrow 4f$ transition of Ce^{3+} brought about by Tb^{3+} co-doping in YAG:Ce phosphor. Jang et al. [11] have observed that partial replacement of Ce^{3+} by Tb^{3+} in bulk YAG:Ce phosphor results in shifting of $5d \rightarrow 4f$ transition of Ce^{3+} to longer wavelengths. This has been attributed to the distortion of dodecahedral symmetry around Ce^{3+} ions brought about by Tb^{3+} substitution and subsequent lowering of $5d$ energy level due to the large crystal field splitting. This results in the lowering of energy gap between $5d$ and $4f$ levels, thereby leading to red shift of emission and excitation peaks [11].

Energy transfer from Ce^{3+} to Tb^{3+} or Tb^{3+} to Ce^{3+} also depends on the nature and crystal structure of the host. For example in lanthanide phosphate-based nano-phosphors containing Ce^{3+} and other lanthanide ion dopants like Tb^{3+} and Dy^{3+} , it is observed that strong energy transfer occurs from Ce^{3+} to dopant lanthanide ions [12,13]. In the present study we investigate the aspect of energy transfer between Ce^{3+} and ions like Tb^{3+} , Eu^{3+} and Dy^{3+} , when doped in nanoparticles of YAG host. Energy transfer has been found to take place only from Tb^{3+} to Ce^{3+} ions, leading strong yellow emission along with emission characteristic of Tb^{3+} ions. To the best of authors' knowledge, such an aspect has not been addressed previously for lanthanide ions doped YAG nanoparticles which are potential candidates for developing multi-colour displays.

2. Experimental

For the preparation of undoped and Eu^{3+} doped YAG nanoparticles, stoichiometric amounts of solid oxides of yttrium and

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europium along with $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in aqueous nitric acid. Required amount of glycine was added by keeping the nitrate to glycine ratio 1.2. The solution was slowly heated at 100°C on a hot plate to get a colourless gel. Temperature was then raised to 200°C so that combustion reaction took place to form a white fluffy powder. The powder was initially heated to 600°C followed by heating to 800 and 1200°C for 4 h each. For preparing Ce^{3+} and Tb^{3+} co-doped as well as Ce^{3+} and Dy^{3+} co-doped samples, $\text{Ce}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Tb_4O_7 and Dy_2O_3 were taken as the starting materials. The remaining procedure was exactly same as that for preparing the Eu^{3+} doped samples. All dopant concentrations are maintained at 2 at%. X-ray diffraction studies were carried out using a Philips X-ray diffractometer with nickel filtered $\text{Cu-K}\alpha$ radiation. The average crystallite size was calculated from the diffraction line width based on Scherrer relation $D = 0.9\lambda/\beta \cos \theta$, where D is the average particles size, λ is the wavelength of X-rays and β is full-width at half-maximum (FWHM) obtained after the correction of instrumental broadening. All luminescence measurements were carried out at room temperature using Hittachi F-4500 instrument with a resolution of 5 nm.

3. Results and discussion

Fig. 1 shows the XRD pattern of the product obtained after combustion reaction followed by heat treatment at 600 and 800°C . Samples annealed at 600°C are found to be amorphous. However on heating to 800°C , crystalline nanoparticles with YAG structure are formed. From the line width of the XRD peaks average crystallite size is calculated and found to be $\sim 30\text{ nm}$ ($\pm 3\text{ nm}$). Fig. 2 shows XRD patterns corresponding to YAG and 2 at% Eu^{3+} doped YAG samples heated at 1200°C . In YAG lattice, Y^{3+} ions are having an eight coordinated dodecahedral symmetry [14] and Eu^{3+} ions when incorporated in the lattice goes and occupy the Y^{3+} sites. Lattice parameters were calculated from the least square fitting of the XRD peaks and are found to be $12.035(3)\text{ \AA}$ for undoped YAG and $12.062(2)\text{ \AA}$ for Eu^{3+} doped YAG nanoparticles. The increase in lattice parameter for the Eu^{3+} doped samples compared to the undoped one has been attributed to increase in ionic radii of Eu^{3+} (1.07 \AA) compared to Y^{3+} ions (1.02 \AA) [15]. Ce^{3+} , Tb^{3+} and Dy^{3+} doped samples also gave higher

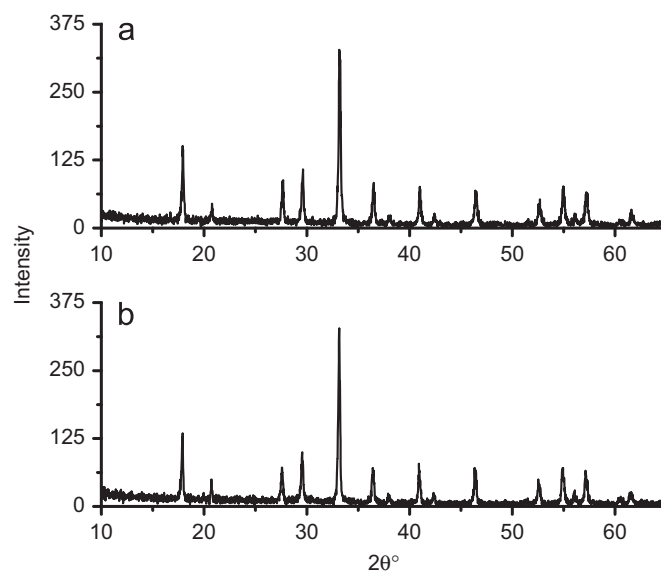


Fig. 2. XRD patterns corresponding to (a) undoped and (b) 2 at% Eu^{3+} doped YAG nanoparticles heated at 1200°C .

lattice parameter compared to undoped YAG sample and this again has been attributed to their higher ionic radii compared to Y^{3+} ions. Further, lattice parameter for the YAG nanoparticles prepared in the present study is found to be more than that of bulk YAG sample ($a = 12.001\text{ \AA}$). For 1200°C heated samples average crystallite size is calculated and found to be around 40 nm ($\pm 3\text{ nm}$).

Fig. 3 shows the emission spectrum corresponding to YAG:Eu(2%) and YAG:Ce(2%), Eu(2%) nanoparticles heated at 1200°C . YAG:Eu nanoparticles after excitation at 240 nm showed an intense emission peak around 592 nm characteristic of the magnetic dipole allowed $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition along with a relatively weak emission around 609 nm characteristic of the electric dipole allowed $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. In the Eu^{3+} doped YAG nanoparticles, Eu^{3+} ions are having D_2 symmetry and this leads to observation of both electric and magnetic dipole transitions. Excitation spectrum corresponding to 591 nm emission for the sample is shown as an inset in Fig. 3. In addition to very weak peaks characteristic of the intra $4f$ transitions of Eu^{3+} , a broad peak centered around 240 nm can be clearly seen from the spectrum. The broad peak is characteristic of the O^{2-} to Eu^{3+} charge transfer process. Co-doping YAG:Eu nanoparticles with Ce^{3+} leads to significant reduction in the intensity of Eu^{3+} emission as can be seen from Fig. 3(b). Further no Ce^{3+} emission is observed from the sample. The reason for this can be that when Ce^{3+} and Eu^{3+} ions co-exist in the matrix, Ce^{3+} can undergo easy oxidation to Ce^{4+} during heating, the electron released during the oxidation is used to convert Eu^{3+} to Eu^{2+} species. If this mechanism is the reason for reduction in the Eu^{3+} and Ce^{3+} luminescence, then Eu^{2+} emission should be observed from the sample. It is reported that Eu^{2+} species in YAG nanocrystals is characterised by a broad emission around 480 nm [16]. However in the present study, a clear emission around 480 nm is not observed. Probably, it might have got buried under broad background over the range of $365\text{--}550\text{ nm}$, as can be seen from the inset of Fig. 3(b). Formation of Ce^{4+} in CePO_4 nanoparticles containing other lanthanide ions and its strong quenching effect on lanthanide ion luminescence is previously reported by Riwotzki et al. [17]. Further easy oxidation of Ce^{3+} to Ce^{4+} in CePO_4 nanoparticles is recently reported by Li et al. [12]. Poor luminescence intensity of Eu^{3+} ions in Ce^{3+} compound is also observed by Blasse et al. [18] and it is suggested that quenching

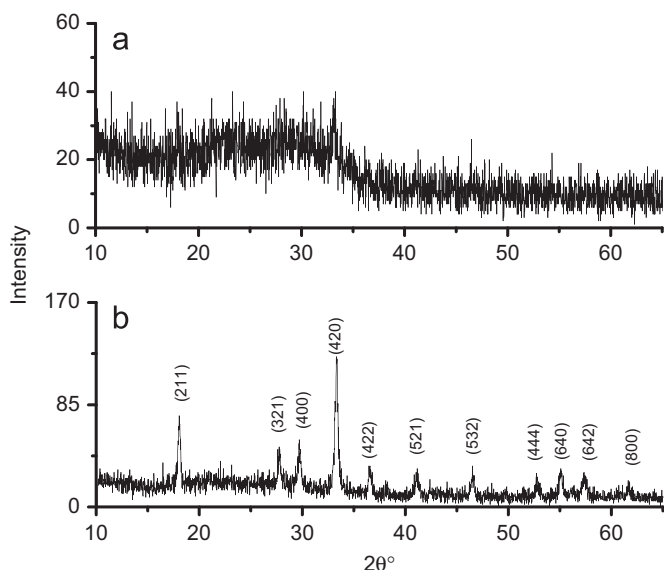


Fig. 1. XRD patterns of YAG nanoparticles prepared by combustion method followed by annealing at (a) 600°C and (b) 800°C .

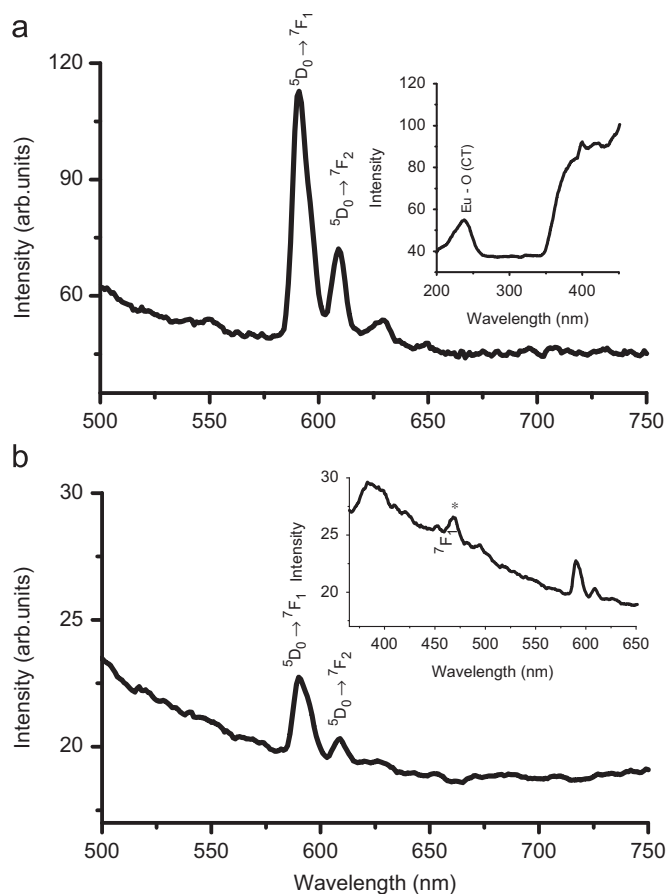


Fig. 3. Emission spectrum corresponding to (a) YAG:Eu and (b) YAG:Ce,Eu nanoparticles. The samples were excited at 240 nm. Inset in (a) shows the excitation spectrum corresponding to 591 nm emission and that in (b) shows broad background in the emission spectrum wherein the Eu^{2+} emission might have got buried. Peak marked “*” is an artifact.

occurs via a low-energy charge transfer state ($\text{Ce}^{4+} + \text{Eu}^{2+}$) existing in such compounds. Recently, Saladino et al. [19] have also observed that Ce^{3+} ions in YAG host have got a tendency to undergo oxidation to Ce^{4+} and phase separate as CeO_2 on heat treatment.

The other possibility is the Ce–Eu pair formation. In this case excited 5d level of Ce^{3+} is having comparable energy with the excited $5D_0$, $5D_1$, $5D_2$ and $5D_3$ levels of Eu^{3+} [20]. Hence the excited states of Ce^{3+} and Eu^{3+} can interact non-radiatively leading to energy transfer between them. If the energy transfer takes place, it should lead to improvement in the luminescence intensity of either Ce^{3+} or Eu^{3+} ions, which is not observed in the present study. Energy transfer from Ce^{3+} to Eu^{3+} ions has been reported in YAlO_3 host [21]. Similar energy transfer is also observed in Ce–Tb pairs formed in Ce^{3+} , Tb^{3+} -doped zinc meta-phosphate glasses [22], wherein, the pair formation is associated with increase in Tb^{3+} luminescence intensity. Based on our results and that reported previously, it has been inferred that there is no energy transfer between Ce^{3+} and Eu^{3+} ions in YAG host and the reduction in the luminescence intensity of both Ce^{3+} and Eu^{3+} ions is only due to the conversion of Ce^{3+} to Ce^{4+} and Eu^{3+} to Eu^{2+} ions.

Fig. 4(a) shows the emission spectrum corresponding to YAG:Ce,Tb nanoparticles excited at 460 nm. Unlike YAG:Ce,Eu nanoparticles, strong emission has been observed around 520 nm characteristic of the $5d \rightarrow 4f$ transition of Ce^{3+} ion. Excitation spectrum corresponding to this emission is shown as an inset in Fig. 4(a). Broad peaks centered around 460 and 344 nm are characteristic of transitions between $4f^1$ ground state ($^2F_{5/2}$ and

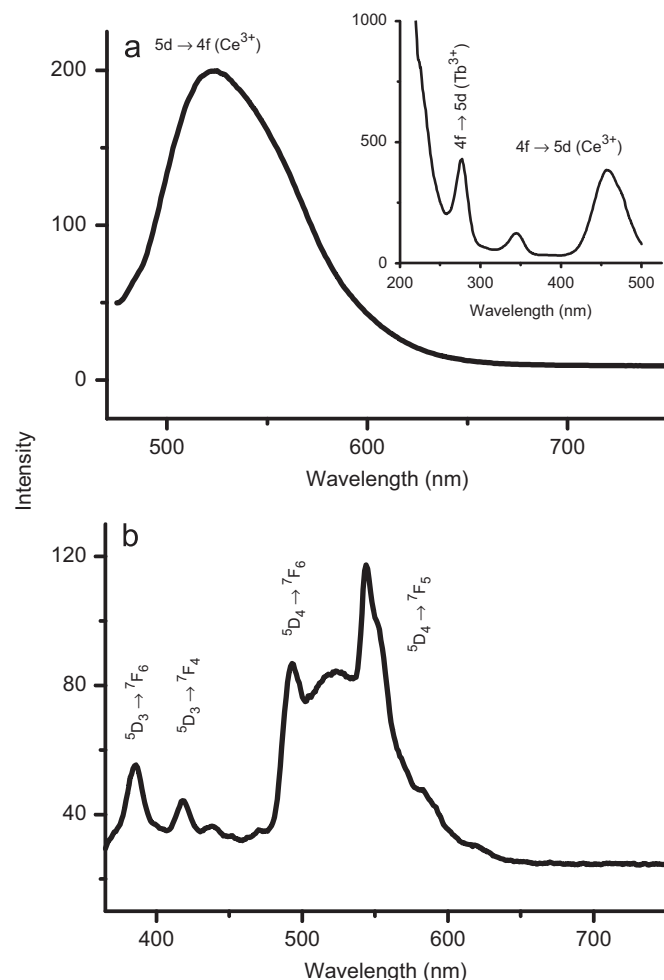


Fig. 4. Emission spectrum corresponding to YAG:Ce,Tb nanoparticles after (a) 460 nm excitation and (b) 277 nm excitation. The inset of (a) shows the excitation spectrum corresponding to 520 nm emission.

$^2F_{7/2}$ levels) to two lower energy crystal field split 5d states of Ce^{3+} ions. The difference in energy between the two excited states matches well with that reported for Ce^{3+} ions in YAG host [9,10]. Further the pattern also consists of a relatively sharp peak around 277 nm. The peak around 277 nm, seen only for Tb^{3+} -doped sample is arising due to $4f \rightarrow 5d$ transition of Tb^{3+} in the nanoparticles. Observation of both Ce^{3+} and Tb^{3+} excitation peaks in the excitation spectrum monitored at 520 nm emission very clearly demonstrates that there exists energy transfer between Ce^{3+} and Tb^{3+} ions. On excitation at 277 nm strong emission peaks characteristic of Tb^{3+} superimposed over broad emission around 520 nm (Fig. 4(b)). Taking into consideration of energy levels of both Ce^{3+} and Tb^{3+} ions as well as corresponding emission and excitation patterns, it is inferred that the energy transfer is taking place from Tb^{3+} to Ce^{3+} ions. Unlike this no emission characteristic of Tb^{3+} is observed on exciting the samples at 460 and 340 nm which are excitation peaks corresponding to Ce^{3+} ions, further establishing the fact that energy transfer is taking place only from Tb^{3+} to Ce^{3+} ions and not the vice versa. These results are in conformity with that reported by Yang et al. [23], who observed that the energy transfer is taking place only from Tb^{3+} to Ce^{3+} in Tb^{3+} co-doped YAG:Ce nanocrystalline phosphors prepared by using a modified polyol method.

In order to substantiate the fact that Ce^{3+} and Tb^{3+} emission observed from YAG:Ce,Tb nanoparticles after excitation at 277 nm, is not because of the energy transfer from the YAG host to

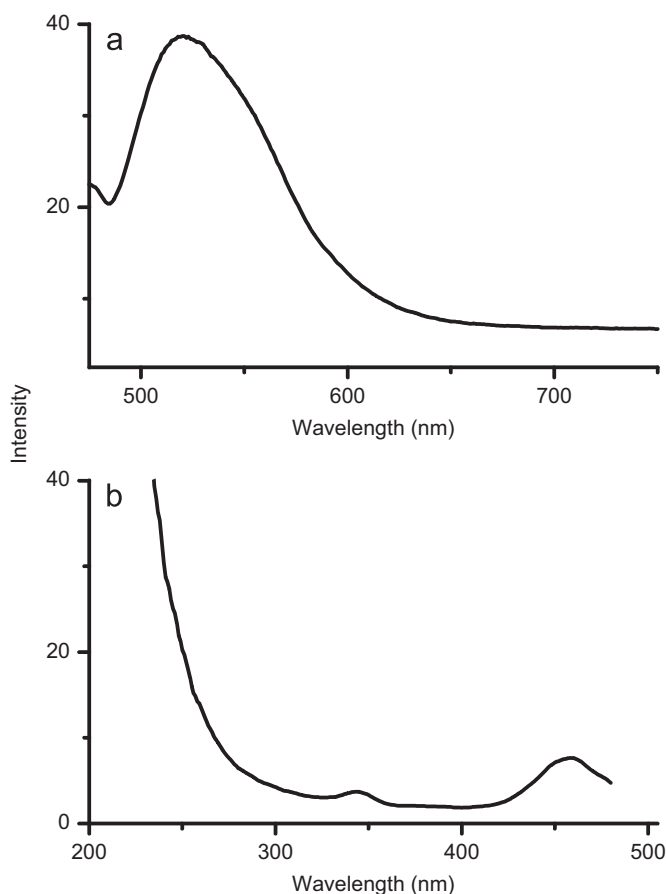


Fig. 5. Emission spectrum after excitation at 460 nm (a) and excitation spectrum after monitoring the emission at 520 nm (b) for YAG:Ce,Dy nanoparticles.

$\text{Tb}^{3+}/\text{Ce}^{3+}$ as reported by Jung et al. [24], luminescence measurements were carried out for Dy^{3+} co-doped YAG:Ce nanoparticles. Fig. 5(a) shows the emission spectrum corresponding to 460 nm excitation from Dy^{3+} co-doped YAG:Ce nanoparticles. As observed for Tb^{3+} co-doped YAG:Ce nanoparticles, strong emission characteristic of Ce^{3+} is observed from YAG:Ce,Dy nanoparticles. A similar pattern is also observed on 340 nm excitation. Other than 340 and 460 nm, under all other excitations, no emission could be seen from Ce^{3+} . Further no emission characteristic of Dy^{3+} is also observed from the sample. The excitation spectrum corresponding to 520 nm emission is shown in Fig. 5(b). Broad excitation peaks centered around 460 and 340 nm, characteristic of Ce^{3+} ions are only seen. These results very clearly demonstrate that there is no energy transfer between Dy^{3+} and Ce^{3+} ions in the

sample. Further, it is also inferred that, 277 nm excitation followed by Ce^{3+} emission observed from YAG:Ce,Tb nanoparticles is only because of the strong absorption corresponding to $4f \rightarrow 5d$ transition of Tb^{3+} ions and subsequent energy transfer to Ce^{3+} ions.

4. Conclusions

YAG nanoparticles were prepared by combustion method followed by annealing at a relatively low temperature of 800 °C. Based on steady-state luminescence studies it has been inferred that due to strong absorption corresponding to the $4f \rightarrow 5d$ transition of Tb^{3+} ions, there exist energy transfer from Tb^{3+} to Ce^{3+} ions. Poor luminescence observed from both Ce^{3+} and Eu^{3+} ions in YAG:Ce,Eu nanoparticles has been attributed to the reduction of Eu^{3+} to Eu^{2+} and oxidation of Ce^{3+} to Ce^{4+} . Lack of energy transfer between Ce^{3+} and Dy^{3+} is due to the absence of strong absorption in the UV-region corresponding to Dy^{3+} in YAG host.

References

- [1] W. Jia, H. Liu, Y. Wang, U. Hommerich, H. Eilers, K.R. Hoffman, W.M. Yen, *J. Lumin.* 60–61 (1994) 192.
- [2] D. Ravichandran, R. Roy, A.G. Chakhovakoi, C.E. Hunt, W.B. White, S. Erdei, *J. Lumin.* 71 (1997) 291.
- [3] G.W. Berkstresser, J. Shmulovich, T.C.D. Huo, G. Matulis, *J. Electrochem. Soc.* 134 (1987) 2624.
- [4] G. Blasse, A. Bril, *J. Chem. Phys.* 47 (1967) 5139.
- [5] Z. Yang, Xu, Li, Y. Yang, X. Li, *J. Lumin.* 122–123 (2007) 707.
- [6] L. Ozawa, *Cathodoluminescence: Theory and Application*, Kodansha, Tokyo, 1990.
- [7] A. Purwanto, W.N. Wang, I.W. Lenggoro, K. Okuyama, *J. Electrochem. Soc.* 154 (2007) J91.
- [8] S.H. Yang, C.Y. Lu, *J. Electrochem. Soc.* 154 (2007) J397.
- [9] Y.S. Lin, R.S. Liu, *J. Lumin.* 122–123 (2007) 580.
- [10] D. Hreniak, J. Hölsa, M. Lastusaari, W. Strek, *J. Lumin.* 122–123 (2007) 91.
- [11] H.S. Jang, W.B. Im, D.C. Lee, D.Y. Jeon, S.S. Kim, *J. Lumin.* 126 (2007) 371.
- [12] Q. Li, V.W. Yam, *Angew. Chem. Int. Ed.* 46 (2007) 3486.
- [13] A. K. Gulnar, V. Sudarsan, R. K. Vatsa, A. K. Tyagi, R. C. Hubli, U.K. Gautam, A. Vinu, A. K. Suri, unpublished results.
- [14] L. Dobrzycki, E. Bułska, D.A. Pawlak, Z. Frukacz, K. Wozniak, *Inorg. Chem.* 43 (2004) 7656.
- [15] D.R. Lide, *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 1999.
- [16] H.M.H. Fadlalla, C.C. Tang, E.M. Elssfah, F. Shi, *Mater. Chem. Phys.* 109 (2008) 436.
- [17] K. Riwotzki, H. Meyssamy, A. Kornowski, M. Haase, *J. Phys. Chem. B* 104 (2000) 2824.
- [18] G. Blasse, B.C. Grabmaier, *Luminescent Materials*, Springer, Berlin, 1994, p.88.
- [19] M. L. Saladino, E. Caponetti, D. C. Martino, S. Enzo, G. Ibba, *Opt. Mater.*, in press.
- [20] M. Nazarov, D.Y. Noh, J. Sohn, C. Yoon, *Opt. Mater.* 30 (2008) 1387.
- [21] G.C. Kim, S.I. Mho, H.L. Park, *J. Mater. Sci. Lett.* 14 (1995) 805.
- [22] U. Caldino, A. Speghini, M. Bettinelli, *J. Phys.: Condens. Matter* 18 (2006) 3499.
- [23] H. Yang, Y.S. Kim, *J. Lumin.* 128 (2008) 1570.
- [24] K.Y. Jung, H.W. Lee, *J. Lumin.* 126 (2007) 469.