

PL Characterization of Efficient $K_3Ca_2(SO_4)F:X, Y$ ($X=Ce$ and $Y=Dy$ or Mn) by Co-Precipitation Method

¹ Anuradha Poddar, ²V.M. Pendsey

¹Associate Professor, ² Associate Professor

¹Department of Physics,

¹DRB Sindhu Mahavidyalaya, Nagpur, - 440017, India.

Abstract: In the present work, X-ray powder diffraction (XRD), Photoluminescence (PL) properties of co-doped $K_3Ca_2(SO_4)_3F:Ce^{3+}, Dy^{3+}$ and $K_3Ca_2(SO_4)_3F:Ce^{3+}, Mn^{2+}$ have been investigated and discussed at various concentrations of Ce, Dy and Ce, Mn. Investigated material has been synthesized by co-precipitation method. The energy transfer from Ce^{3+} to Dy^{3+} is discussed based on the excitation and emission spectra, which transfers energy. $K_3Ca_2(SO_4)_3F:Ce^{3+}, Dy^{3+}$ have two peaks in PL emission spectra at 484nm and 576nm by UV excitation at 264nm

PL emission spectra of $K_3Ca_2(SO_4)_3F:Ce^{3+}, Mn^{2+}$ is efficient for $Ce^{3+}-Mn^{2+}$ energy transfer. The Mn^{2+} in this system can be effectively excited in a wide UV; it gives an intense emission peak at 585 nm and at 655nm after quenching the material. The phosphors in this system may be chosen as the orange or red component in the tri-colour system and can be applied in red-LEDs.

Index Terms—Co-precipitation, co-doped, Photoluminescence, Radiative.

I. INTRODUCTION

Light-emitting diodes (LEDs) have attracted much attention in recent years due to their advantages in luminous efficiency, reliability, energy-saving, maintenance, long lifetime, etc. [1]. The most commonly used approach to generate white light relies on the combination of blue LED with yellow phosphor (YAG:Ce³⁺) [2]. However, this approach has several deficiencies [3], such as low colour rendering index because of the lack of sufficient red component, yellow-halo effect, as well as poor thermal stability. Therefore, their applications have been limited in some fields, e.g., architectural and medical lighting [4]. To overcome these deficiencies, a combination of UVLED with red-green-blue (RGB) phosphors has been suggested [5].

A new concept of energy transfer (ET) sensitization is developed, based on nearly resonant energy migration through a RE ion by a single-step transfer towards the emission centers created by Ce³⁺ or Dy³⁺. Rare earths are especially suitable for energy transfer because of their well-defined and narrow electronic levels, to which absorption occurs and from which fluorescence is observed.

Transition metal ions generally have larger oscillator strengths than rare-earth ions and can therefore absorb more energy. Thus sensitized luminescence with high emission efficiency can be observed from luminescent matrix co-doped with transition metal ions. This sensitized luminescence is very important for the research and application of luminescent materials.

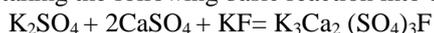
Mixed sulphates are also known to be good PL materials. $CaF_2:Mn$ does not give any fluorescence under the UV excitation, while $CaF_2:Ce$ gives a characteristic Ce³⁺ fluorescence emission with UV light excitation. The combination of Ce and Mn in the CaF_2 lattice [6], however, gives brilliant Mn²⁺ fluorescence emission in addition to that of Ce³⁺ on UV excitation, due to energy transfer from Ce³⁺ to Mn²⁺ ions. Similar enhancement in the fluorescence efficiency of Dy and Mn ions was reported in $CaSO_4:Ce, Dy$ and $CaSO_4:Ce, Mn$ [7]. However, the application of a similar energy transfer mechanism leads to enhanced sensitivity in the case of PL and thermoluminescence (TL) and during the course of investigation on TL in sulphate-based phosphors, many have reported several sulphate phosphors possessing properties useful to TL dosimetry of ionizing radiations [8-14]. Recently Gedam et al have reported PL characterization of $KZnSO_4Cl:Ce^{3+}, Dy^{3+}$ and $KZnSO_4Cl:Ce^{3+}, Mn^{2+}$ halo-sulphate phosphors [15].

Energy transfer between pairs of rare earth ions at dilution levels below the self-quenching limits has been known to take place generally through multi-polar interactions like dipole-dipole interactions or dipole-quadrupole interactions [16]. Much work has been done on the energy transfer from Ce³⁺ to different activator ions in different host lattices [17-19]. In the field of luminescence, scope of study of mixed halo-sulphate phosphor is wide open. Considering lot of scope to study new material $K_3Ca_2(SO_4)_3F$, a choice of synthesis of fluoride based mixed halo-sulphate phosphor co-doped by RE and RE with transition metal is made.

We have already studied crystal structure, PL, TL, TL response, fading and reusability by doping RE and transition metals and energy transfer from Ce³⁺→Eu²⁺→Eu³⁺ in $K_3Ca_2(SO_4)_3F$ [20-22]. In this paper, we are presenting detailed study of PL of $K_3Ca_2(SO_4)_3F$ by co-doping Ce, Dy and Eu, Mn.

II. EXPERIMENTAL

The sample $K_3Ca_2(SO_4)_3F$, $K_3Ca_2(SO_4)_3F:Ce^{3+}, Dy^{3+}$ and $K_3Ca_2(SO_4)_3F:Ce^{3+}, Mn^{2+}$ were prepared by co-precipitation method, taking the following basic reaction into consideration:



In the co-precipitation method salts of different materials are used to precipitate together from a common solution. The precipitate then consists of an intimate mixture of two salts or solid solution. Salts of required materials are usually dissolved in water medium. They are co-precipitated either by concentrating the solution or by adding precipitating reagent. Water soluble

materials K_2SO_4 and KF (Merk make) were taken in a stoichiometric ratio and dissolved separately in double-distilled de-ionized water. $CaSO_4$ was washed several times at constant temperature with distilled water, filtered and then it was added, resulting in the solution of $K_3Ca_2(SO_4)_3F$. Water-soluble sulphate salt of Cerium and Dysprosium was added to get the solution of $K_3Ca_2(SO_4)_3F: Ce^{3+}, Dy^{3+}$. Similarly water-soluble sulphate salt of Cerium and Manganese was added to the solution of $K_3Ca_2(SO_4)_3F$ to get $K_3Ca_2(SO_4)_3F: Ce^{3+}, Mn^{2+}$ in liquid form in the proper ratio. The solution was stirred for an hour with the help of magnetic stirrer and then it was kept in oven for 12 hrs. at 80 °C. The resultant polycrystalline mass was crushed to fine particle in a crucible and powder was used in further study. The formation of pure compound was confirmed by taking the X-ray diffraction (XRD). The photoluminescence (PL) emission spectra of the samples were recorded using Fluorescence spectrophotometer (Shimadzu RF-5301 PC) fitted with a sensitive photomultiplier. Emission and excitation spectra in the 250–450nm and 350–650 nm range were recorded respectively for different concentration of Dy and Mn with same amount of Ce of 5mol%. The same amount of sample was used in each case. The spectral slit width of spectrophotometer was kept at 1.5 nm.

III. RESULTS AND DISCUSSION

3.1 X- Ray Diffraction (XRD)

XRD of $K_3Ca_2(SO_4)_3F$ (Figure 1) pattern did not indicate presence of the constituents K_2SO_4 , $CaSO_4$, KF and other likely phases. The results indicate that the final product was formed in homogeneous form.

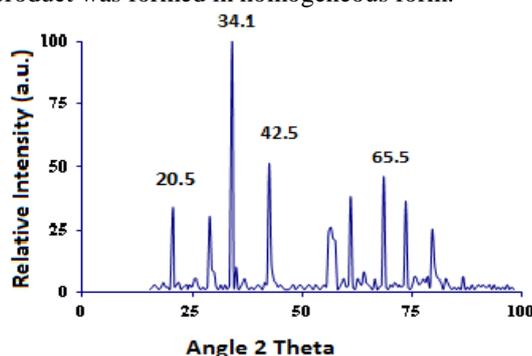


Figure 1: XRD of $K_3Ca_2(SO_4)_3F$

3.2 PHOTOLUMINESCENCE (PL) IN $K_3Ca_2(SO_4)_3F$

3.2.1 Ce^{3+}, Dy^{3+} emission in $K_3Ca_2(SO_4)_3F$

Wang et al. have given the coordination environments for the two crystallographic sites of Ca^{2+} ions in the $KNaCa_2(PO_4)_2$ host calculated by the van Uiter formula: eight and six coordination centers [23]. In the $K_3Ca_2(SO_4)_3F$ crystallite, Ce^{3+} ions are expected to replace Ca^{2+} sites. However, it would be difficult to maintain a charge balance in the samples. Therefore, univalent ions K^+ were added as charge compensators in order to keep the charge balance. It is worth mentioning that the charge compensators K^+ for Ce^{3+} -doped $K_3Ca_2(SO_4)_3F$ samples also substitute the Ca^{2+} site. The radius of the K^+ ion is closer to that of the Ca^{2+} ion.

We have reported Excitation spectra of $K_3Ca_2(SO_4)_3F: Ce^{3+}$ phosphor shows broadband at 278nm. PL emission spectra of Ce^{3+} ions under excitation of 278nm wavelength of light is at 334nm, which are assigned to the 5d-4f transition of Ce^{3+} ions. [24-25] With increasing concentration of Ce^{3+} ions, the peak intensity of 334nm increases and maximum intensity is observed for 10mol%

The emission spectrum of Dy^{3+} has two groups of emissions located at 481 and 574nm, which correspond to the transitions from ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ (blue) and ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow) respectively. In this sample, the blue emission (${}^4F_{9/2} \rightarrow {}^6H_{15/2}$) at 481 nm was stronger than the yellow emission (${}^4F_{9/2} \rightarrow {}^6H_{13/2}$) at 574 nm, which demonstrate that the Dy^{3+} ions occupied a high-symmetry site in this $K_3Ca_2(SO_4)_3F$ host. The emission intensity has increased with the increase of Dy^{3+} concentration and reached a maximum value for 0.5mol% of Dy.

The excitation spectra of $K_3Ca_2(SO_4)_3F: Ce, Dy$ show the peak in UV region of spectrum containing excitation of Ce^{3+} at 264 nm at emission wavelength of 334nm. (Figure 2) Peaks of Dy^{3+} emission at 484nm and 576nm are observed at excitation wavelength of 264nm shown in figure 3 The PL emission intensity has increased with the increase of Dy^{3+} concentration from (a) 0.1 to (b) 0.2 to (c) 0.5 and (d) 1mol% and reached a maximum value for 1 mol% of Dy and the concentration of Ce is kept constant at 5mol%. The transfer of energy from Ce^{3+} to Dy^{3+} ions in $K_3Ca_2(SO_4)_3F$ lattice brings Ce^{3+} to the ground state and Dy^{3+} to the excited state. The emission in Dy^{3+} comes via a non-radiative transition to the ${}^4F_{9/2}$ level, followed by radiative transitions to ${}^6H_{15/2}$ and ${}^6H_{13/2}$ levels. Schematic energy-level diagram of energy transfer in $K_3Ca_2(SO_4)_3F: Ce^{3+}, Dy^{3+}$ is shown in figure 4 Due to the matching energy levels of Ce^{3+} and Dy^{3+} during de-excitation, while Ce^{3+} comes to the ground state, Dy^{3+} moves to the excited state. Finally, Dy^{3+} comes to the ground state via a series of non-radiative and radiative transitions.

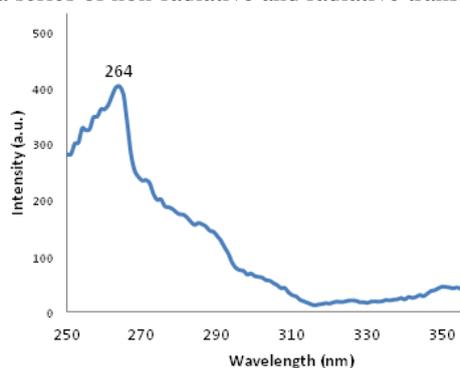


Figure 2: Excitation spectra of $K_3Ca_2(SO_4)_3F: Ce^{3+}, Dy^{3+}$ at emission wavelength of 334nm.

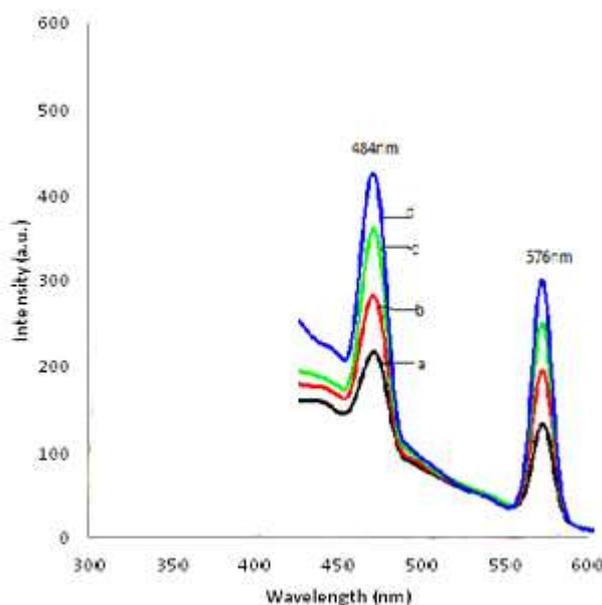


Figure 3: Emission spectra of $K_3Ca_2(SO_4)_3F:Ce^{3+},Dy^{3+}$ at excitation wavelength of 264nm

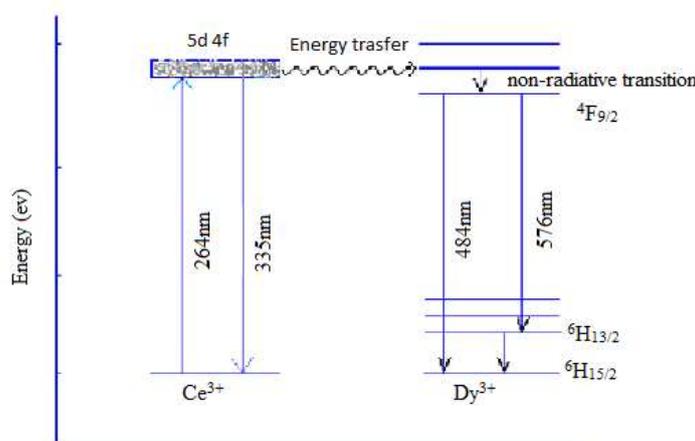


Figure 4: Schematic energy-level diagram showing energy transfer in $K_3Ca_2(SO_4)_3F:Ce^{3+},Dy^{3+}$

3.2.1 Ce^{3+},Mn^{2+} emission in $K_3Ca_2(SO_4)_3F$

In some hosts, Mn^{2+} can give the luminescence from orange to red, thus choosing Mn^{2+} as the activator is another way to design UVLED red phosphors [26]. We didn't observe any PL emission in $K_3Ca_2(SO_4)_3F$ when doped by Mn by UV excitation. In the present experiment, when $K_3Ca_2(SO_4)_3F$ is co-doped with Ce and Mn, strong Mn^{2+} emission is observed at 585 nm when excited at 278nm due to transition of ${}^4T_1-{}^6A_1$ of Mn^{2+} ion in $K_3Ca_2(SO_4)_3F$ materials (Figures 5 and 6). After quenching the material, $K_3Ca_2(SO_4)_3F:Ce^{3+},Mn^{2+}$ shows Mn^{2+} broad emission spectrum at 655 nm when excited at 278nm. (Figures 7). The PL emission intensity has been observed by varied concentration of Mn with fixed concentration for Ce to 5mol%. Emission intensity increases with the increase in Mn^{2+} concentration from (a) 0.01 to (b) 0.02 and (c) 0.05 mol% and reached a maximum value for 0.05mol%. The Ce^{3+} ions can act as an efficient sensitizer by transferring its excitation energy to co-activators. [27-29] In the $K_3Ca_2(SO_4)_3F:Ce^{3+},Mn^{2+}$ system, the Ce^{3+} ions can serve as an effective sensitizer for Mn^{2+} , which not only help Mn^{2+} ions to emit efficiently but also tune the emission colour of the co-doped samples. The variation of Mn^{2+} peak intensity in $K_3Ca_2(SO_4)_3F$ lattice is shown in figure 6 and figure7. Generally, Mn^{2+} activated phosphors are divided into two classes, viz. green emission and orange to red emission [30-31]. In octahedral surroundings with large crystal field, the emission is usually red, while in tetrahedral surroundings with a much smaller crystal field, the emission is green. Another possibility to obtain a green Mn^{2+} emission is to choose a lattice in which Mn^{2+} is on a site, which is considerably larger than the Mn^{2+} radius. The requirement is met in compounds like $SrB_6O_{10}:Mn^{2+}$, in which the Mn^{2+} emission is at 512 nm [32].

In the present case, Mn^{2+} emission is observed at 585 nm in the orange region and at 655nm red region of the spectrum by co-activator Ce^{3+} . (Figure 6 and 7 respectively) The orange emission may be due to transfer of energy from Ce^{3+} to Mn^{2+} ion in octahedral surrounding of Mn^{2+} ion in $K_3Ca_2(SO_4)_3F$ lattice. Mn^{2+} ion may be positioned and surrounded by SO_4^{2-} and Cl^- ions or SO_4^{2-} and Cl^- pair formation.

The Dy^{3+} emission in $K_3Ca_2(SO_4)_3F$ lattice may be useful for developing new TL dosimetry materials, and Mn^{2+} emission in $K_3Ca_2(SO_4)_3F$ is useful as a red phosphor for lamp industry. Figure 8 shows schematic energy-level diagram showing energy transfer in $K_3Ca_2(SO_4)_3F:Ce^{3+},Mn^{2+}$.

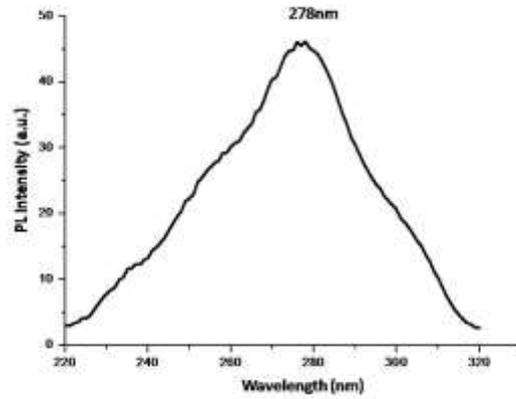


Figure 5: Excitation spectra of $K_3Ca_2(SO_4)_3F:Ce^{3+},Mn^{2+}$ at emission wavelength of 334nm.

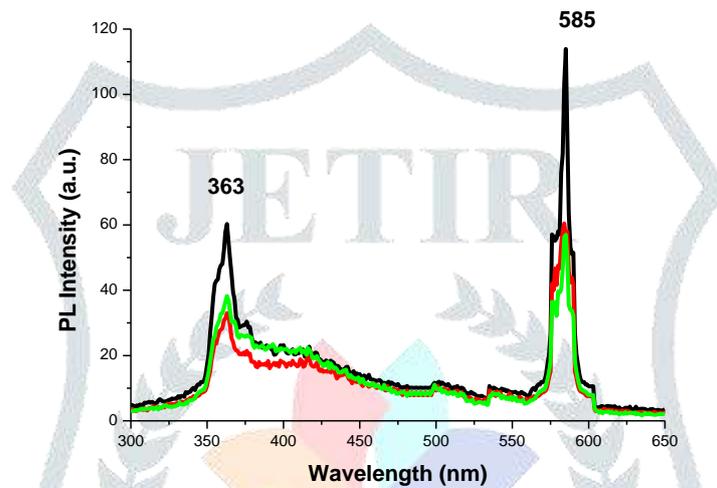


Figure 6: Emission spectra of $K_3Ca_2(SO_4)_3F:Ce^{3+},Mn^{2+}$ when excited at 278nm

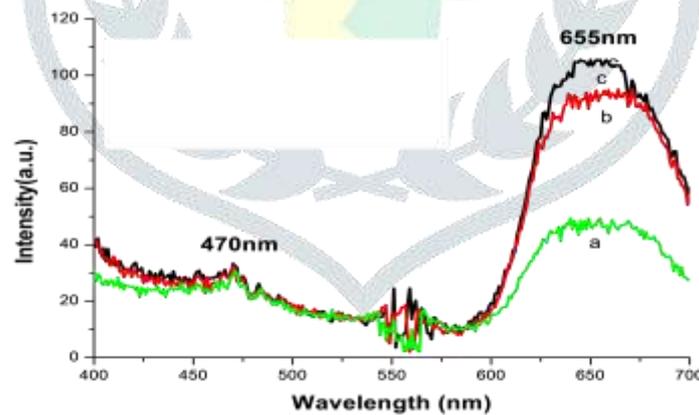


Figure 7: Emission of $K_3Ca_2(SO_4)_3F:Ce^{3+},Mn^{2+}$ after quenching when excited at 278nm

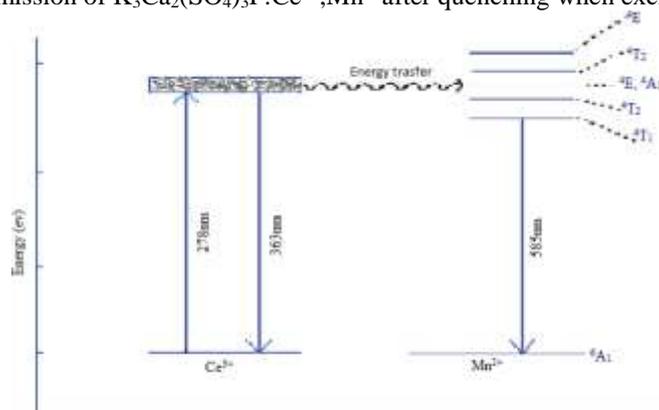


Figure 8: Schematic energy-level diagram showing energy transfer in $K_3Ca_2(SO_4)_3F:Ce^{3+},Mn^{2+}$

4. Conclusions

Co- precipitation method is the easy synthesis system for $K_3Ca_2(SO_4)_3F:Ce^{3+},Dy^{3+}$ and $K_3Ca_2(SO_4)_3F:Ce^{3+},Mn^{2+}$ halo-sulphate phosphors.

PL emission spectra of $K_3Ca_2(SO_4)_3F:Dy^{3+}$ shows very less PL intensity but when $K_3Ca_2(SO_4)_3F$ is co-doped with Ce,Dy then strong PL emissions of Dy^{3+} ions is observed at 484 and 576 nm in $KMgSO_4Cl:Ce^{3+},Dy^{3+}$ phosphor due to presence of Ce^{3+} ion as a sensitizer. Dy^{3+} emissions at 484nm and 576nm were observed due to ${}^4F_{9/2}-{}^6H_{15/2}$ and ${}^4F_{9/2}-{}^6H_{13/2}$ transitions of Dy^{3+} ions, respectively under excitation wavelength of 264 nm.

When $K_3Ca_2(SO_4)_3F$ is doped with Mn, PL emission is not observed under the excitation of UV radiation. In the present experiment, strong Mn^{2+} emission is observed at 585 nm and 655nm when quenched due to transition ${}^4T_1-{}^6A_1$ of Mn^{2+} ion. It is due to energy transfer from Ce^{3+} to Mn^{2+} ions.

The emissions of Dy^{3+} and Mn^{2+} in $K_3Ca_2(SO_4)_3F$ phosphor may be useful for TL dosimetry and lamp Industry respectively. $K_3Ca_2(SO_4)_3F:Ce^{3+},Mn^{2+}$ may be a potential candidate for UV-excited red LEDs.

References

- [1] R.J. Xie, N. Hirosaki, Sci. Technol. Adv. Mater. 8 (2007) 588.
- [2] S. Nakamura, G. Fasol, in: The Blue Laser Diode: GaN Based Light Emitters and Lasers, Springer, Berlin, 1997.
- [3] R.S. Liu, Y.H. Liu, N.C. Bagkar, S.F. Hu, Appl. Phys. Lett. 91 (2007) 61119.
- [4] Y. Song, G. Jia, M. Yang, Y. Huang, H. You, H. Zhang, Appl. Phys. Lett. 94 (2009) 91902.
- [5] T. Nishida, T. Ban, N. Kobayashi, Appl. Phys. Lett. 82 (2003) 3817.
- [6] B.S.K. Nair, D. Sundar, A. Tomita, W. Hoffmann, A.R. Lakshmanan, J. Lumin. 86 (2000) 67.
- [7] A.R. Lakshmanan, Prog. Mater. Sci. 44 (1999) 1.
- [8] A.R. Lakshmanan, Prog. Mater. Sci. 44 (1999) 1.
- [9] B.T. Deshmukh, S.V. Bodade, S.V. Moharil, Phys. Status Solidi 102(1987) 381.
- [10] P.D. Sahare, S.V. Moharil, J. Phys. D 23 (1990) 567.
- [11] S.V. Moharil, P.D. Sahare, Radiat. Eff. Def. Solids 114 (1990) 167.
- [12] S.M. Dhopte, P.L. Muthal, V.K. Kondawar, S.V. Moharil, P.D. Sahare, J. Phys. D 24 (1991) 1869.
- [13] S.J. Dhoble, S.V. Moharil, S.M. Dhopte, P.L. Muthal, V.K. Kondawar, Phys. Status Solidi 135 (1993) 289.
- [14] M.S. Atone, S.J. Dhoble, S.V. Moharil, S.M. Dhopte, P.L. Muthal, V.K. Kondawar, Phys. Status Solidi 135 (1993) 299.
- [15] S.C. Gedam, S.J. Dhoble, S.V. Moharil, J. Lumin.,
- [16] X. Gong, L. Liu, W. Chen, J. Appl. Phys. 88 (7) (2000) 4389.
- [17] G. Blasse, Prog. Solid State Chem. 18 (1988) 79.
- [18] H.S. Kiliaan, J.K. Kothe, G. Blasse, J. Electrochem. Soc. 134 (1987) 2359.
- [19] J.M. Verstegen, J.L. Sommerdijk, J.G. Erriet, J. Lumin. 6 (1973) 425.
- [20] Anuradha Poddar, S.C. Gedam, S.J. Dhoble, Luminescence DOI 10.1002/bio.2839.
- [21] Anuradha Poddar, S. C. Gedam and S. J. Dhoble, Bionano frontier, 5 2(II) 2012, 63-65.
- [22] Anuradha Poddar, S.C. Gedam, S.J. Dhoble, Bionano frontier, Vol. 5, 2012, 454-456.
- [23] Wang, Z.-J.; Li, Y.; Wang, Y.; Li, P.-L.; Guo, Q.-L.; Wang, Z.-P. J. Inorg. Mater. 2011, 26, 731–734.
- [24] Birkel, A.; Denault, K. A.; George, N. C.; Doll, C. E.; Héry, B.; Mikhailovsky, A. A.; Birkel, C. S.; Hong, B.-C.; Seshadri, R. Chem. Mater. 2012, 24, 1198–1204.
- [25] Qu, X.; Yang, H.K.; Pan, G.; Chung, J.W.; Moon, B.K.; Choi, B.C.; Jeong, J.H. Inorg. Chem. 2011, 50, 3387–3393.
- [26] T. Murata, T. Tanoue, M. Iwasaki, K. Moriga, T. Hase, J. Lumin. 114 (2005) 207.
- [27] Chen, M.; Xie, L.; Li, F.; Zhou, S.; Wu, L. ACS Appl. Mater. Interfaces 2010, 2, 733–737.
- [28] Boyer, J.-C.; Gagnon, J.; Cuccia, L.A.; Capobianco, J. A. Chem. Mater. 2007, 19, 3358–3360.
- [29] Liu, Y.; Zhang, X.; Hao, Z.; Luo, Y.; Wang, X.; Zhang, J. J. Mater. Chem. 2011, 21, 16379–16384.
- [30] D.T. Palumbo, J.J. Brown Jr., J. Electrochem. Soc. 117 (1970) 1184.
- [31] D.T. Palumbo, J.J. Brown Jr., J. Electrochem. Soc. 118 (1971) 1159.
- [32] T. Koskentalo, M. Leskela, L. Niinisto, Mater. Res. Bull. 20 (1985) 265.