Accepted Manuscript

NIR emission IN Ba₂SiO₄:Eu²⁺, Nd³⁺ phosphors with near UV/violet excitation

Arpita Vyas, C.P. Joshi, P.D. Sahare, S.V. Moharil

PII: S0925-8388(18)30128-2

DOI: 10.1016/j.jallcom.2018.01.127

Reference: JALCOM 44591

To appear in: Journal of Alloys and Compounds

Received Date: 19 November 2017

Revised Date: 8 January 2018

Accepted Date: 9 January 2018

Please cite this article as: A. Vyas, C.P. Joshi, P.D. Sahare, S.V. Moharil, NIR emission IN Ba₂SiO₄:Eu²⁺, Nd³⁺ phosphors with near UV/violet excitation, *Journal of Alloys and Compounds* (2018), doi: 10.1016/j.jallcom.2018.01.127.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.





NIR EMISSION IN Ba₂SiO₄:Eu²⁺, Nd³⁺ PHOSPHORS WITH NEAR UV/VIOLET EXCITATION

Arpita Vyas¹, C.P. Joshi¹, P.D.Sahare² and S.V. Moharil³

1 Physics Department, Shri Ramdeobaba College of Engineering and Management, Katol Road, Nagpur 440013, India

2 Department of Physics and Astrophysics, University Of Delhi, North Campus, New Delhi 110007, India

3 Department of Physics, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur 440010, India

ABSTRACT

New results on NIR emission in Ba₂SiO₄:Eu²⁺, Nd³⁺ phosphors are reported. Though excitation for Eu²⁺ emission is in predominantly near UV (nUV) region, that for the Nd³⁺ emission around 1067 nm extends into visible region covering violet and blue part of the spectrum. These results are highly significant for applications where NIR emission with nUV/blue excitation is required, e.g. for improving efficiency of c-Si solar cell, for designing NIR sources using efficient blue LEDs, etc. Energy transfer efficiencies for Eu²⁺ \rightarrow Nd³⁺ energy transfer are estimated by measuring reduction of Eu²⁺ emission lifetime, and are close to 80 %. Possible mechanisms for Eu²⁺ \rightarrow Nd³⁺ energy transfer are suggested. These involve down shifting or quantum cutting.

Key Words: photoluminescence; NIR emission; silicate; Quantum Cutting; $Eu^{2+} \rightarrow Nd^{3+}$ energy transfer

*arpvyas@gmail.com

1. Introduction

In the system BaO-SiO₂ as many as thirteen phases are known [1]. Luminescence has been studied in some of them and important phosphors have been discovered. Eu^{2+} activated BaSi₂O₅ [2], Ba₂Si₃O₈ [3], and Ba₃SiO₅ [4] are green emitting phosphors and have applications in devices such as white-light-emitting diodes (W-LEDs). Pb-doped BaSi₂O₅ is a phosphor for black-light lamp [5], whereas Ce³⁺ and Eu²⁺ doped BaSiO₃ [6] generate blue-violet to yellow light; a proper ratio leading to white light generation. Eu²⁺ and Dy³⁺ doped Ba₃Si₅O₁₃ and Ba₅Si₈O₂₁ are stable even in water and exhibit long lasting phosphorescence (LLP) by exposure to sunlight [7].

Barry [8] and Blasse et al [9] were the first to study Ba₂SiO₄:Eu phosphors. They observed a broad emission band covering blue and green regions of the spectrum. Excitation spectrum was also very broad; spread over almost entire UV region and extending into violet part of the spectrum. Later, Poort et al [10] reported finer features of the PL spectra, e.g. presence of two overlapping bands in the emission spectra which are responsible for the observed large width. They attempted explanation of these specific features on the basis of the crystal structure. They tried to resolve emission from Eu^{2+} at two crystallographically nonequivalent sites on the basis of decay constants [11]. Grinberg et al [12] used high-pressure spectroscopy for characterizing these sites. Zhang et al [13 14] suggested a method for improving the stability of this phosphor. More recently, Lin et al [15] suggested use of this phosphor as a scintillator. Broad excitation spanning 350-430 nm makes this phosphor suitable for applications requiring near UV/blue excitation, such as solid state lighting [16-20]. Wang et al [21] observed green long lasting phosphorescence (LLP) in this phosphor after nitrogen doping. Xiaoye et al [22] observed significant increase in emission intensity by La^{3+}/Y^{3+} codoping. This has been attributed to the defects introduced by the incorporation of trivalent ions. Similar effects have been observed by Gd^{3+ [23]}, Li^{+ [24]}, Er^{3+ [25]}, Pr³⁺, Yb^{3+ [26]} co-doping. This has been attributed to the defects introduced by the incorporation of aliovalent ions. Doping with Zn has also resulted in enhanced emission intensity. However, this could be due to formation on BaZnSi₂O₇ phase[27]. In contrast to this, luminescence enhancement by direct energy transfer to Eu²⁺ is observed in Ba₂SiO₄: Ce, Eu [28]. Theoretical calculations have been made to estimate effects of nitrogen [29] and Mn[30] co-doping on Ba₂SiO₄:Eu optical absorption. However, these estimates are far off from the experimental values. Apart from Eu^{2+} , intense emission from Eu^{3+} has also been reported in Ba₂SiO₄ host [31].

In majority of works, conventional solid state reaction had been used for preparing Ba₂SiO₄:Eu²⁺ phosphor. Han et al [32] suggested hydrothermal route for preparation of this phosphor and claimed this to be simpler than the conventional solid state reaction. During recent years different novel techniques have been used. These include sol–gel/Pechini [33], sol–gel [34], co-precipitation [35 36], solution combustion [37], gas-solid phase hybrid synthesis method [38], etc.

Broad nUV/blue excitation of $Ba_2SiO_4:Eu^{2+}$ has been discussed in context of solid state lighting. Apart from solid state lighting, such excitation is relevant for other applications like modification of solar spectrum, luminescent solar concentrators (LSC) [39 40] photoluminescence liquid crystal displays (PLLCD), etc. First two applications involve near infrared (NIR) emission. c-Si solar cell is to date the most successfully commercialized solar cell. One of the factors which limits efficiency of c-Si solar cell is the "spectral mismatch", that is spectral response curve for c-Si solar cell differs from solar spectrum. The mismatch can be removed to some extent by converting the near UV and blue region of the spectrum, where solar cell response is poor, to NIR region (around 1000 nm) by using suitable phosphors [41]. Trupke et al predicted that if the light in the region 300-500 nm is converted to NIR using quantum cutting, then the Shockley-Queisser limit for c-Si will be pushed from 29.5 to 39.6 % [42]. With such efficiencies, cost of solar energy will be at par with the conventional energy sources.

There are not many, if any, reports on NIR luminescence in Ba₂SiO₄ host. For obtaining NIR emission Yb³⁺ and Nd³⁺ ions are considered to be most suitable. Yb³⁺ has a simple energy level diagram. There are only 2 levels; ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$, separated by about 10150 cm⁻¹. It is thus most suitable for luminescence processes in NIR region around 985 nm. Since there are only two levels there is no branching, all the emission must come through ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition. However, ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ transition of Yb³⁺ ion is forbidden and hence very weak. CT band of Yb³⁺ is also usually at very high energies [43]. A sensitizer is needed for obtaining efficient NIR emission. Paucity of energy levels often makes cooperative energy transfer as the only possible process for sensitization. In contrast, owing to presence of large number of levels, sensitization of Nd³⁺ is easily achievable. NIR emission in Nd³⁺ is very well known [44]. In fact, YAG:Nd is one of the most important laser working in NIR region. For these reasons we attempted to obtain

NIR emission using Yb³⁺ and Nd³⁺ dopants. In this work we report for the first time, NIR emission in Ba₂SiO₄ resulting from efficient Eu²⁺ \rightarrow Nd³⁺ energy transfer.

2. Experimental

Ba₂SiO₄ phosphors doped with Eu²⁺, and Nd³⁺ or Yb³⁺ were prepared by solid state reaction between barium carbonate and silicic acid (GR Loba, India). NH₄Cl (2 wt %) was used as a flux. BaCO₃ was thoroughly mixed with stoichiometric amount of silicic acid. Eu/Nd/Yb nitrate solutions in desired quantities were sprinkled on this mixture and then it was heated in the furnace in 2 steps of 700 C for 4 hours, 1250 C for 6 hours. It was then slowly cooled to room temperature. Eu/Nd/Yb nitrate solutions were obtained by dissolving europium oxide/neodymium oxide (Indian Rare earths, 99.99 % pure)/ Yb₂O₃ (99.99 % pure, Rare Metals, China) in dilute nitric acid. Samples prepared at 1250 C in air do not show Eu²⁺ luminescence. For reducing europium to divalent form, the powders were heated in reducing atmosphere provided by burning charcoal at 950 C for 2 hrs. This treatment was found adequate for obtaining efficient PL.

The crystalline phases of the synthesized samples were identified by x-ray diffraction (XRD) analysis. The XRD patterns were recorded on XPERT-PRO diffractometer using Cu K_{α} (λ =1.54059 Å) radiation. The NIR photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured by a Photon Technology International QM-51 NIR spectrophotometer. PL in visible range were recorded on Hitachi F-7000 spectro-fluorimeter. Reflectance spectra were also recorded on the same instrument by using "synchronous" mode. BaSO₄ was used as a reference standard. Lifetime measurements were obtained on Horiba-JY Fluromax 4- equipped with Time Correlated Single Photon Counting system using 379 nm LED as excitation source.

3. Results and discussion

Formation of Ba₂SiO₄ host following the solid state reaction was confirmed by XRD. Fig.1 shows comparison of the XRD pattern recorded for the synthesized Ba₂SiO₄ (undoped) with ICDD file 70-2113. Excellent match is seen. Indexing is same as in the ICDD file and hence not marked in Fig.1 to preserve clarity. For a BaO-SiO₂ system, there are various phases depending on the Ba/Si ratio. Three common phases are BaSiO₃ [45], Ba₂SiO₄ [46], and Ba₃SiO₅ [47]. In the XRD pattern for the synthesized compound, lines at angles 24.118 and 36.464 which distinguish BaSiO₃ (ICDD 70-2112), and Ba₃SiO₅ (ICDD 26-0180) respectively, are missing. Phase pure Ba₂SiO₄ is thus formed. XRD patterns of doped samples were also similar and no change in the structure was noticed.

Fig. 2 shows reflectance spectra for various samples. For Ba₂SiO₄, nearly 85% reflectance is observed in the wavelength range of 500–600 nm, and then the reflectance starts to decrease rapidly at shorter wavelengths. Two broad bands around 280 and 370 nm are due to Eu²⁺. The host absorption edge is around 280 nm. These results are in good agreement with those reported earlier [12]. After Nd co-doping, the graph remains almost similar. There is additional absorption around 587 nm which can be assigned to ${}^{4}I_{9/2}$ --> ${}^{4}G_{5/2}$, ${}^{2}H_{11/2}$ transitions of Nd³⁺.

Fig.3 shows PL spectra for Ba_{1.94}Eu_{0.06}SiO₄. From literature, it was found that maximum PL intensity is observed for 3% Eu and concentration quenching occurs for higher doping concentration, hence this composition was chosen. Emission spectrum (Fig.3, curve a) consists of a broad band peaking around 500 nm. The band is broad because it is superposition of two bands as first mentioned by Poort et al [10]. Two bands arise from two types of Eu^{2+} centres. In Ba₂SiO₄, Eu²⁺ will obviously occupy Ba substitutional site. Ba₂SiO₄ crystallizes in orthorhombic system. There are two crystallographically non-equivalent sites. Fig. 4 shows unit cell of Ba₂SiO₄ drawn using VESTA 3 software for three-dimensional visualization of crystal, volumetric and morphology data [48]. Ba1 is ten coordinated while Ba2 nine [41]. Thus the coordination of the Eu(I) and Eu(II) centres are ten and nine, respectively. According to Park et al [49], the bond length of Eu(II)–O is shorter than that of Eu(I)–O, so the nephelauxetic effect and the crystal field strength surrounding Eu(II) sites is greater than in the surrounding Eu(I). Consequently, the Eu(I) and Eu(II) sites are responsible for emissions at the short (500 nm) and long wavelengths (520 nm), respectively. Poort et al [10], on the other hand, argued on the basis of second neighbor distances that the emission at shorter wavelengths can be expected from Eu²⁺ on Ba(II) site. It is difficult to decide between these two arguments, as in the recorded spectra only one maximum can be observed. Two bands can be conjectured only after deconvolution [49]. In the excitation spectrum (Fig.3, curve b), there is an intense band around 378 nm with a shoulder around 280 nm. All these results are in good agreement with the literature.

Fig.5 shows PL spectra for Ba₂SiO₄:Eu²⁺ (3.0 mol %), Nd³⁺ (3.0 mol %) and Ba₂SiO₄: Nd³⁺ (3.0 mol %) in NIR region. For doubly doped phosphor, a prominent emission is seen for 400 nm excitation (curve a) around 1067 nm corresponding to transition ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$. There are also weaker emission lines around 1010, 995, $({}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2})$, 915, 909, 900, $({}^{2}P_{1/2} \rightarrow {}^{4}F_{5/2})$, 887 nm $({}^{2}D_{5/2} \rightarrow {}^{4}F_{5/2}, {}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2})$.

Fig.5 (curve b) shows excitation spectrum monitored at 1067 nm. A broad band peaking at 400 nm, which is quite similar to Eu^{2+} excitation, but shifted slightly to longer wavelengths, is again seen. This indicates energy transfer from Eu^{2+} to Nd^{3+} . In addition to this, there are several intense excitation lines attributable to f-f transitions of Nd^{3+} around 896,883,869 (${}^{4}F_{3/2} \rightarrow {}^{2}G_{9/2}$) 825, (${}^{4}I_{9/2} \rightarrow {}^{4}F_{3/2}$), 809,799 (${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$, ${}^{2}H_{11/2}$), 765, 754 (${}^{4}I_{9/2} \rightarrow {}^{4}F_{5/2}$, ${}^{2}H_{9/2}$), 743, (${}^{4}I_{9/2} \rightarrow {}^{4}F_{7/2}$), 722,725 (${}^{4}I_{9/2} \rightarrow {}^{4}S_{3/2}$), 673 (${}^{4}I_{9/2} \rightarrow {}^{4}F_{9/2}$), 601 (${}^{4}I_{9/2} \rightarrow {}^{2}K_{15/2}$), 587,576, (${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$, ${}^{2}H_{11/2}$), 529, (${}^{4}I_{9/2} \rightarrow {}^{2}K_{13/2}$, ${}^{4}G_{7/2}$), 516, (${}^{4}I_{9/2} \rightarrow {}^{4}G_{9/2}$) and 490 nm (${}^{4}I_{9/2} \rightarrow {}^{2}K_{11/2}$). Due to f-f excitation lines at shorter wavelengths, which overlap with Eu^{2+} broad band excitation, the latter becomes broader and shifts slightly to longer wavelength side (Fig.6). It is also quite likely that addition of Nd^{3+} causes small perturbations in Eu^{2+} levels. There is change in the physical appearance of the samples after Nd^{3+} codoping. Nd^{3+} codoped samples present a richer hue. This is due to more effective absorption in the visible region due to red shift of the excitation. For Ba₂SiO₄: Nd^{3+} (3.0 mol %), only f-f lines are seen in the excitation spectrum, the broad band around 400 nm is absent (Fig.5, curve e).

Inset to Fig.5 shows variation of intensities with Nd^{3+} concentration. PL intensity of Nd^{3+} emission is highest for 3 mol. %. Concentration quenching is observed for higher concentrations. From this the critical distance for Nd^{3+} - Nd^{3+} energy transfer can be calculated using the formula [50].

$Rc = 2 (3V/4\pi x_c N)^{1/3}$

where x_c is the critical concentration (.03), N is the number of Ba sites in the unit cell (8), and V is the volume of the unit cell (445.5 Å³). Rc comes out to be 15.250 Å.

PL intensity of $Eu^{2+} 500$ nm emission goes on decreasing continuously with Nd³⁺ concentration. This indicates that $Eu^{2+} \rightarrow Nd^{3+}$ energy transfer is not affected by concentration quenching. However, Nd³⁺ emission is quenched beyond Nd³⁺ concentration of 3 mol. % due to Nd³⁺ $\rightarrow Nd^{3+}$ energy transfer. Efficiency for $Eu^{2+} \rightarrow Nd^{3+}$ energy transfer can be estimated from the formula [51]-

$$\eta_{ETE} = 1 - \frac{I_{Eu}}{I_{Eu,Nd}}$$

where I_{Eu} is the intensity of the Eu²⁺ emission without co-doping, and $I_{Eu,Nd}$ is the intensity after co-doping with Nd³⁺. For Nd³⁺ concentration of 3 mol. %, where maximum Nd³⁺ emission is observed η_{ETE} comes out to be about 50%.

Efficiency for Eu²⁺ \rightarrow Nd³⁺ energy transfer can also be estimated by measuring the lifetime of Eu²⁺ emission with and without Nd³⁺ co-doping using a similar equation [47] $\eta_{ETE} = 1 - \frac{\tau_x}{\tau_0}$

where τ_0 is the lifetime of the Eu²⁺ emission without co-doping, and τ_x is the lifetime after codoping with Nd³⁺.

Fig.7 shows decay curves for 500 nm Eu^{2+} emission in Ba₂SiO₄:Eu²⁺,Nd³⁺ phosphors. 379 nm LED was used for excitation. For Ba₂SiO₄:Eu²⁺, lifetime of 0.52 µs is observed. After co-doping with Nd³⁺ another fast decay component with lifetime of about 110 ns is induced. This component becomes more and more dominant with increasing Nd³⁺ concentration. For the composition Ba_{1.88}Eu_{0.06}Nd_{0.06}SiO₄ the decay is almost exponential showing only this component. Using this data η_{ETE} comes out to be about 78.9%.

There is thus huge discrepancy in η_{ETE} value when computed by two different methods. The value obtained from intensity comparison can be much lower due to following reason. When trivalent Nd³⁺ is added to Ba₂SiO₄:Eu²⁺, there can be two effects on Eu²⁺ emission intensity. There will be obvious decrease due to energy transfer to Nd³⁺. However, substitution of trivalent ions at Ba²⁺ sites also leads to formation of defects. These defects lead to increase in Eu²⁺ emission. Considerable increase in Eu²⁺ emission following co-doping by trivalent lanthanide ions have been observed by several workers [22 23 25 26]. The apparent decrease in Eu²⁺ emission after Eu²⁺ \rightarrow Nd³⁺ energy transfer will be thus much less than the actual, which will lead to much smaller value of η_{ETE} .

A possible mechanism of $Eu^{2+} \rightarrow Nd^{3+}$ energy transfer will be now discussed. Nd^{3+} has several energy levels. Some of them (e.g. ${}^{4}I_{9/2} - {}^{+}G_{7/2}$) overlap with Eu^{2+} emission. Thus, there are several channels for energy transfer from Eu^{2+} to Nd^{3+} . ${}^{4}G_{j}$ levels of Nd^{3+} are populated by energy transfer from Eu^{2+} . Nd^{3+} can then relax to ${}^{4}F_{3/2}$ state by emitting phonons in several steps (Fig.8). NIR emission is obtained by transitions from ${}^{4}F_{3/2}$ state to lower lying ${}^{4}I_{j}$ states. Another possibility is that energy transfer takes place directly from excited state of Eu^{2+} to higher ${}^{4}G_{j}$ states (${}^{4}G_{11/2}$, ${}^{4}G_{9/2}$). From there Nd^{3+} can de-excite to ${}^{4}F_{3/2}$ level by cross relaxation (Fig.9), taking a nearby Nd^{3+} ion to excited state. Subsequent de-excitation to ground state leads

to emission of second photon. Thus, in this case two NIR photons will be obtained by quantum cutting.

Apart from Nd³⁺, Yb³⁺ also can yield NIR emission. Yb³⁺emission is at relatively shorter wavelengths and unlike Nd³⁺ there is no branching. Hence, we attempted Ba₂SiO₄:Eu²⁺,Yb³⁺ phosphor for obtaining NIR emission. However, no such emission was observed. Yb³⁺ has only two energy levels with separation of about 10150 cm⁻¹. CT band of Yb³⁺ is also usually at very high energies, usually below 250 nm [43]. The only way energy in nUV region can be transferred to Yb³⁺ is by cooperative energy transfer (CET), which is a less probable phenomenon compared to energy transfer (ET). Apparently, no CET is taking place in Ba₂SiO₄:Eu²⁺,Yb³⁺. In the past Nd³⁺-Yb³⁺ energy transfer had been reported [52-54]. Hence, we studied triply doped Ba₂SiO₄:Eu²⁺,Nd³⁺,Yb³⁺ phosphor also. However, no Nd³⁺→Yb³⁺ energy transfer was observed.

It will be interesting to measure the quantum efficiencies for NIR emission. However, in this case the excitation is in nUV region and emission in NIR. A wide range spectrofluorimeter that will enable seamless measurements of incident, reflected and emitted light is needed for this purpose. Such experiments will be carried out in future and the results will be presented in due course.

NIR emission in Ba₂SiO₄:Eu²⁺,Nd³⁺ phosphor with nUV/blue excitation can be useful in several applications, solar photovoltaics being at the forefront. Ba₂SiO₄:Eu²⁺,Nd³⁺ phosphor appears suitable for modification of solar spectrum. This is illustrated in Fig.10. As can be seen, c-Si solar cell response decreases rapidly below 500 nm (Fig.10, curve b). If this part of the spectrum (shown by yellow shaded region) is converted by quantum cutting to about 1000 nm, efficiency of photovoltaic conversion will obviously increase. There is good overlap between the solar spectrum suitable for quantum cutting, and Eu²⁺ absorption. More than 50% of the spectrum available for quantum cutting will be converted by Ba₂SiO₄:Eu²⁺,Nd³⁺ phosphor to Nd³⁺ emission that is close to the maxima in the response curve of c-Si.

Apart from solar photovoltaics, $Ba_2SiO_4:Eu^{2+},Nd^{3+}$ phosphor could be useful for obtaining compact NIR light sources. Efficient blue LEDs are commercially available. $Ba_2SiO_4:Eu^{2+}, Nd^{3+}$ phosphor shows appreciable excitation around 450 nm. By coating it on blue LED, compact, intense and efficient LED emitting in NIR region can be constructed.

8

4. Conclusions:-

New results on luminescence of Ba₂SiO₄:Eu²⁺,Nd³⁺ are reported. Efficient energy transfer from Eu²⁺ \rightarrow Nd³⁺ has been observed. Critical distance for Nd³⁺ \rightarrow Nd³⁺ energy transfer is 15.25 Å. Lifetime of Eu²⁺ emission decreases from 0.52 µs to 0.11 µs following Nd³⁺co-doping. Efficiency for Eu²⁺ \rightarrow Nd³⁺ energy transfer is close to 80 %. By virtue of this energy transfer it is possible to convert nUV-blue light around 350-450 nm to NIR around 1067 nm. This phosphor thus holds a great potential for application as a solar spectrum modifier. In contrast to Eu²⁺ \rightarrow Nd³⁺ pair, no energy transfer is observed for Eu²⁺ \rightarrow Yb³⁺ or Nd³⁺ \rightarrow Yb³⁺ pairs.

-REFERENCES-

- [1] Liudmila A.Gorelova, RimmaS.Bubnova, Sergey V.Krivovichev, Maria
- G.Krzhizhanovskaya, Stanislav K.Filatov J. Solid State Chem. 235 (2016) 76
 - [2] J.H.Park, J.S.Kim and J.T.Kim J.Opt.Soc. Korea 18 (2014) 45
 - [3] F.Xiao, Y.Xue and Q.Zhang, Spectro chim.Acta A:Mol. Biomol.Spectrosc.74 (2009) 758
- [4] J.Park, M.Lim, K.Choi and C.Kim, J.Mater.Sci.40 (2005) 2069
- [5] J.W.Chung, H.K.Yang, B.K.Moon, B.C.Choi and J.H.Jeong, J.Korean Phys. Soc. 55 (2009) 1965
- [6] C.Guo, Y.Xu, Z.Ren and J.Bai, J.Electrochem.Soc.158 (2011) J373
- [7] P.Wang, X.Xu, D.Zhou, X.Yu and J.Qiu, Inorg.Chem.54 (2015) 1690
- [8] T.L. Barry, J. Electrochem. Soc. 115 (1968) 1181
- [9] G. Blasse, W.L. Wanmaker, J.W. Tervrugt and A. Bril, Philips Res. Rep. 23 (1968) 189
- [10] S.H.M. Poort, W. Janssen, G. Blasse, J. Alloys Compd. 260 (1997) 93
- [11] S.H.M. Poort, A.Meyerink and G. Blasse J.Phys. Chem. Solids 58 (1997) 1451
- [12] M.Grinberg, J. Barzowska, A. Baran, and B. Kuklínski, Materials Science- Poland, 29(2011) 272
- [13] B.Zhang, J.W. Zhang, H. Zhong, L.Y.Hao, X. Xu, S. Agathopoulos, C.M. Wang and L.J.Yin, Mater. Res. Bull., 92 (2017) 46
- [14] B.Zhang, J.W. Zhang, H. Zhong, L.Y.Hao, X. Xu, S. Agathopoulos, C.M. Wang and L.J.Yin, J. Phys. Chem. C, 121 (2017)11616
- [15] Litian Lin, Xiaoxiao Huang, Rui Shi, Weijie Zhou, Yan Huang, Jiuping Zhong, Ye Tao,Jun Chen, Lixin Ning and Hongbin Liang RSC Adv. 7 (2017) 25685
- [16] M. Venkataravanappa, H. Nagabhushana, G.P. Darshan, S.C. Sharma, K.V. Archana, R.B.Basavaraj and B.D.Prasad, Mater. Res. Bull.97, (2018) 281
- [17] J.S. Kim, Y.H. Park, S.M. Kim, J.C. Choi and H.L. Park Solid State Commun., 133 (2005) 445.
- [18] J.S. Kim, P.E. Jeon, J.C. Choi and H.L. Park Solid State Commun., 133(2005) 187.
- [19] M. Zhang, J. Wang, Q. Zhang, W. Ding and Q. Su, Mater. Res. Bull. 42 (2007) 33
- [20] Z. Wang, S. Guo, Q. Li, X. Zhang, T. Li, P. Li, Z. Yang, Q. Guo, Physica B: Condensed Matter, 411 (2013) 110

[21] M.Wang, X. Z.Hang, Z.Hao, X.Ren, Y.Luo, X.Wang and J. Zhang, Opt. Mater. 32 (2010)1042

- [22] H. Xiaoye, L. Zhenhua, X. Xin and L. Yongxiu, J. Rare Earths 27 (2009) 47
- [23] X. Li, Y. Liang, F. Yang, Z. Xia, W.Huang and Y. Li, J. Mater. Science: Materials in Electronics, 24 (2013) 3199
- [24] D. Kim, K.W. Jeon, J.S. Jin, S.G. Kang, D.K. Seo and J.C. Park, RSC Advances, 5 (2015) 105339
- [25] L.L. Luo, K. Tang, D.C. Zhu, T. Han and C. Zhao, Acta Physica Sinica, 62 (2013) 157802
- [26] D. Zhong, X.Hu, Z. Li and Y.J. Li, Chinese Rare Earth Soc., 27 (2009) 36
- [27]Y. X. Pan and G. K. Liu Spectroscopy Letters, 44 (2011) 1
- [28] H.L.Liu, D.W. He and F. Shen, Spectroscopy and Spectral Analysis, 26 (2006) 1790
- [29] H.Chen, X.Huang, W.Huang and W. Wang, Optik, 134(2017)78
- [30] H.Chen, X.Huang and W.Huang Chinese J. Physics, 54 (2016) 931
- [31]A.M.Pires, M.R.Davolos and O.L.Malta, J. Lumin. 72-74 (1997) 244
- [32] J.K. Han, M.E. Hannah, A. Piquette, J.B. Talbot, K.C. Mishra and J. McKittrick, J. Lumin. 161 (2015) 20
- [33] J. K. Han, M. E. Hannah, A. Piquette, J. Micone, G. A. Hirata, J. B.Talbot, K. C. Mishra and J. Mckittrick, J. Lumin. 133 (2013) 184
- [34] A. Birkel, N. A. DeCino, N. C. George, K. A. Hazelton, B.-C. Hong and R. Seshadri, Solid State Sci. 19 (2013) 51
- [35] J. K. Han, M. E. Hannah, A. Piquette, J. B. Talbot, K. C. Mishra and J. Mckittrick, ECS J. Solid State Sci. Technol. 1 (2012) R98
- [36] J. S. Lee and Y. J. Kim Ceram. Int. 39 S555 (2013)
- [37] Huayna Cerqueira Streit, Jennifer Kramer, Markus Suta and Claudia Wickleder Materials,6 (2013) 3079
- [38] Tatsuya Sakamoto, Kazuyoshi Uematsu, Tadashi Ishigaki Kenji Toda and Mineo Sato Key Engineering Materials 485 (2011) 325
- [39] W.G.J.H.M.van Sark, etal. Optics Express 16 (2008) 21773
- [40] C.J. Barrows, P. Chakraborty, L.M. Kornowske and D.R. Gamelin ACS Nano 10 (2016) 910

[41] M.B. de la Mora, O. Amelines-Sarria, B.M. Monroy, C.D. Hernandez-Perez and J.E. Lugo Solar Energy Mater. Solar Cells 165 (2017) 59

[42] T. Trupke, M. A. Green and P. Wurfel J. Appl. Phys. 92(2002) 1668

[43] L. van Pieterson, M. Heeroma, E. de Heer and A. Meijerink, J.Lumin 91 (2000) 177

[44] K. Lemanskin, M.Babij, M.Ptak and P.J.Deren J. Lumin. 184(2017)130

[45] H. P. Grosse and E. Tillmanns, Cryst. Struct. Commun. 3 (1974) 603

[46] H.P. Grosse and E. Tillmanns, Cryst. Struct. Commun. 3 (1974) 599

[47] E. Tillmanns and H. P. Grosse Acta Cryst. B34 (1978) 649

[48] K. Momma and F. Izumi: J. Appl. Crystallogr. 44 (2011) 1272

[49] Jung Hye Park, Wonsik Ahn and Young Jin Kim J. Nanosci. Nanotechnol.15 (2015) 8155

[50] G. Blasse Philips Res. Rep. 24 (1969) 131

[51] P.I. Paulose, G. Jose, V. Thomas, N.V. Unnikrishnan and M.K.R. Warrier J. Phys. Chem. Solids, 64 (2003) 841

[52] A.A. Pathak, R.A. Talewar, C.P. Joshi, S.V. Moharil Opt.Mater. 64 (2017) 217

[53] Ting Sun, Ai-Hua Li, Chao Xu, Yu-Heng Xu and Rui Wang Opt. Laser Tech.56 (2014)322

[54] Flavia Artizzu, Angela Serpe, Luciano Marchio, Michele Saba, Andrea Mura, Maria Laura Mercuri, Giovanni Bongiovanni, Paola Deplano and Francesco Quochi J.Mater.Chem. C 3(2015) 11524

-FIGURE CAPTIONS-

Figure 1 XRD pattern for Ba₂SiO₄

A good match with ICDD 70-2113 is seen. Lines at angles 24.118 and 36.464 which distinguish

BaSiO₃ (ICDD 70-2112), and Ba₃SiO₅ (ICDD 26-0180), respectively, are absent.

Figure 2 : Reflectance spectra of Ba₂SiO₄

 $a > Ba_{1.94}Eu_{0.06}SiO_4$

b> Ba_{1.88}Eu_{0.06}Nd_{0.06}SiO₄

Figure 3 : PL spectra for Ba_{1.94}Eu_{0.06}SiO₄ phosphor

a> Emission for 400 nm excitation.

b> Excitation for 500 nm emission

Figure 4 : Unit cell of Ba₂SiO₄ showing different cation coordination.

There are two types of Barium sites. Ba1 has 10 coordination while Ba2 nine.

Figure 5 : PL spectra for Ba_{1.88}Eu_{0.06}Nd_{0.06}SiO₄

a> Emission for 400 nm excitation.

b> Excitation for 1067 nm emission

Inset shows variation of Nd^{3+} emission (1067 nm, curve c) and Eu^{2+} emission (500 nm, curve d)

with Nd³⁺ concentration. Excitation was 400 nm.

For comparison, PL excitation for $Ba_{1.94}Nd_{0.06}SiO_4$ is shown (curve e).

Figure 6 : Broadening of excitation spectra after Nd³⁺ co-doping in Ba_{1.88}Eu_{0.06}Nd_{0.06}SiO₄

a> Excitation spectrum for 500 nm emission

b> Excitation spectrum for 1067 nm emission in blue region

Inset shows photographs of the samples in day light c> $Ba_{1.94}Eu_{0.06}SiO_4$ and d>

 $Ba_{1.88}Eu_{0.06}Nd_{0.06}SiO_4$, and under UV illumination $e > Ba_{1.94}Eu_{0.06}SiO_4$ and $f > Control SiO_4$ and f >

 $Ba_{1.88}Eu_{0.06}Nd_{0.06}SiO_{4}$

Figure 7 : Luminescence decay curves for $a > Ba_{1.94}Eu_{0.06}SiO_4$ and $b > Ba_{1.88}Eu_{0.06}Nd_{0.06}SiO_4$ 379 nm excitation was used.

Figure 8: Mechanism of energy transfer from Eu^{2+} to Nd^{3+} involving emission of one photon Figure 9: Mechanism of energy transfer from Eu^{2+} to Nd^{3+} involving emission of two photons Figure 10 : Modification of Solar Spectrum using $Ba_2SiO_4:Eu^{2+}$, Nd^{3+} phosphor.

a> AM1.5 solar spectrum, b> spectral response of c-Si solar cell, $c> Nd^{3+}$ excitation spectrum and d> Nd³⁺ emission spectrum

Shaded portion shows the portion of solar spectrum adequate for quantum cutting.





CER '





ACCEPTED MANUSCRIPT















CER S



CER AL



ACCEPTED MANUSCRIPT



HIGHLIGHTS

- > NIR emission at 1067 nm is reported for the first time in $Ba_2SiO_4:Eu^{2+},Nd^{3+}$
- Excitation by near ultraviolet (nUV)/violet light.
- > Energy transfer efficiencies for $Eu^{2+} \rightarrow Nd^{3+}$ energy transfer close to 80 %.
- > Attractive for application in photovoltaics based on c-Si

Chillip Mark