OPTOELECTRONICS LETTERS Vol.11 No.1, 1 January 2015

Luminescence and energy transfer of Ce^{3+}-Eu^{2+} in $Ca_9Al(PO_4)_7$*

MENG Xiang-yu (孟祥雨)[1], JIE Xi (节喜)[1], ZHANG Yue-dong (张月冬)[1], WANG Di (王迪)[1], WANG Ying-bin (王迎彬)[1], LI Pan-lai (李盼来)[1], WANG Zhi-jun (王志军)[1], PANG Li-bin (庞立斌)[2]**, and GAO Shao-jie (高少杰)[2]****

1. College of Physics Science & Technology, Hebei University, Baoding 071002, China

2. Department of Foreign Language Teaching and Research, Hebei University, Baoding 071002, China

(Received 27 October 2014)

A series of Ce^{3+}, Eu^{2+} and Ce^{3+}-Eu^{2+} doped $Ca_9Al(PO_4)_7$ phosphors are synthesized by a high temperature solid-state method. Under 291 nm excitation, $Ca_9Al(PO_4)_7$:Ce^{3+} has one emission band at 356 nm, which is attributed to $4f^05d^1 \rightarrow 4f^1$ transition of Ce^{3+}. Under 305 nm excitation, $Ca_9Al(PO_4)_7$:Eu^{2+} presents one emission band at 445 nm, which is assigned to $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+}. Energy transfer from Ce^{3+} to Eu^{2+} in $Ca_9Al(PO_4)_7$ is validated and proved to be a resonant type via a quadrupole-quadrupole interaction. Critical distance (R_c) of Ce^{3+} to Eu^{2+} in $Ca_9Al(PO_4)_7$ is calculated to be 1.264 nm. Moreover, the emission intensity of $Ca_9Al(PO_4)_7$:Ce^{3+}, Eu^{2+} can be tuned by properly adjusting the relative doping composition of Ce^{3+}/Eu^{2+}.

Document code: A **Article ID:** 1673-1905(2015)01-0045-4

DOI 10.1007/s11801-015-4198-8

The resonant energy transfer among impurity ions in the phosphor material has been a considerable subject during recent decades[1-3]. The interest in this field arises because the energy transfer from a donor to an acceptor can improve the luminescence of phosphor[4-7]. Luminescence and energy transfer of Ce^{3+}-Eu^{2+} in $Ba_{1.3}Ca_{0.7}SiO_4$ have been explored[8]. And the similar type of energy transfer between Ce^{3+} and Eu^{2+} was observed in $SrSi_2O_2N_2$ and $CaSi_2O_2N_2$, respectively[9,10]. For the phosphate compound, such as $Sr_3Gd(PO_4)_3$ and $Ca_9Y(PO_4)_7$, the effective energy transfer between Ce^{3+} and Eu^{2+} widely exists[11,12]. However, to the best of our knowledge, there is no report about the energy transfer between Ce^{3+} and Eu^{2+} in $Ca_9Al(PO_4)_7$. In this paper, $Ca_9Al(PO_4)_7$:Ce^{3+}, Eu^{2+} is synthesized by solid state method, and energy transfer and luminescence of $Ca_9Al(PO_4)_7$:Ce^{3+}, Eu^{2+} are investigated.

$Ca_9Al(PO_4)_7$:xCe^{3+}, yEu^{2+} phosphors are synthesized by a high temperature solid-state method, where x and y are molar concentrations of Ce^{3+} and Eu^{2+}, respectively. The initial materials $CaCO_3$(A.R.), Al_2O_3(A.R.), $NH_4H_2PO_4$(A.R.), CeO_2(99.99%) and Eu_2O_3(99.99%) were weighed in stoichiometric proportion, thoroughly mixed and ground by an agate mortar and pestle for more than 30 min till they were uniformly distributed. The obtained mixtures were heated at 1 200 °C for 10 h in crucibles along with a reducing atmosphere (5%H_2/95%N_2), and then were naturally cooled to room temperature. In order to measure the characteristics of phosphors, the samples were ground into powder.

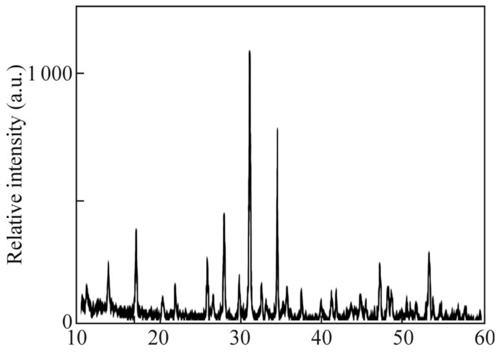
The phase formation was determined by X-ray diffraction (XRD) in a Bruker AXS D8 advanced automatic diffractometer (Bruker Co., German) with Ni-filtered Cu Kα1 radiation (λ=0.154 06 nm), and a scan rate of 0.02°/s was applied to record the patterns in the 2θ range from 10° to 60°. The steady time-resolved photoluminescence spectra and the excitation and emission spectra were detected by a fluorescence spectrophotometer (Hitachi F-4600), and the exciting source was a 450 W Xe lamp. The Commission International de I'Eclairage (CIE) chromaticity coordinates of the samples were measured by a PMS-80 spectra analysis system. All measurements were carried out at room temperature.

Fig.1 shows the representative XRD patterns of as-prepared Eu^{2+} and Ce^{3+} doped $Ca_9Al(PO_4)_7$, such as $Ca_9Al(PO_4)_7$:0.05Ce^{3+}, $Ca_9Al(PO_4)_7$:0.01Eu^{2+} and $Ca_9Al(PO_4)_7$:0.05Ce^{3+}, 0.01Eu^{2+}. It is obvious that the diffraction peaks of all these samples can be exactly assigned to the pure phase of $Ca_9Al(PO_4)_7$ according to XRD pattern of standard JCPDS card (No.48-1192). The uniform diffraction pattern means that the phase formation of $Ca_9Al(PO_4)_7$ is not influenced by a little amount of Ce^{3+}, Eu^{2+} or Ce^{3+}-Eu^{2+}. $Ca_9Al(PO_4)_7$ has a β-$Ca_3(PO_4)_2$ structure with a space group of R3c (No.161) [2,6].

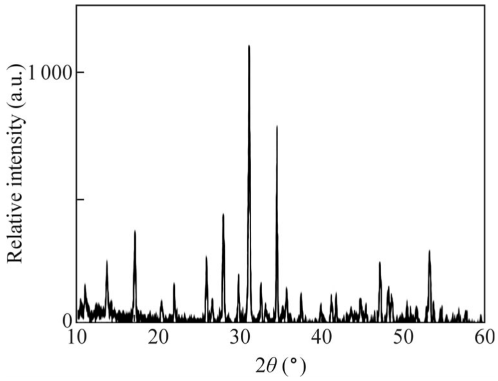
---

* This work has been supported by the National Natural Science Foundation of China (No.50902042), and the Natural Science Foundation of Hebei Province in China (Nos.A2014201035 and E2014201037), and the Education Office Research Foundation of Hebei Province in China (Nos.ZD2014036 and QN2014085).

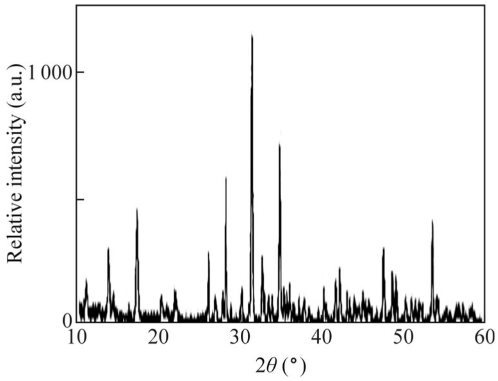
** E-mails: wangzj1998@sohu.com; lizhibin268@sohu.com; lipanlai@sohu.com



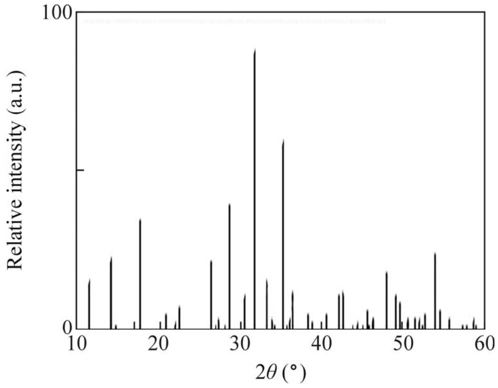
(a) $Ca_9Al(PO_4)_7$:0.05Ce^{3+}, 0.01Eu^{2+}



(b) $Ca_9Al(PO_4)_7$:0.01Eu^{2+}



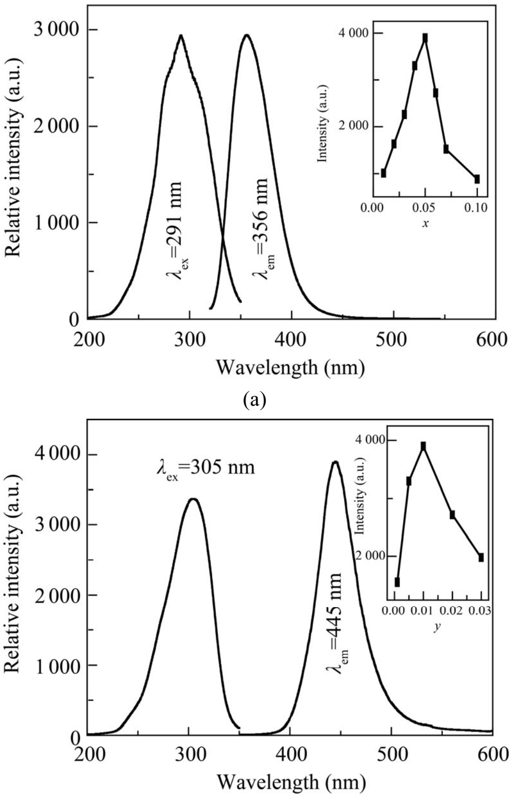
(c) $Ca_9Al(PO_4)_7$:0.05Ce^{3+}



(d) JCPDS No.48-1192

Fig.1 XRD patterns of (a) $Ca_9Al(PO_4)_7$:0.05Ce^{3+}, 0.01Eu^{2+}, (b) $Ca_9Al(PO_4)_7$:0.01Eu^{2+}, (c) $Ca_9Al(PO_4)_7$:0.05Ce^{3+}, and (d) $Ca_9Al(PO_4)_7$ (standard JCPDS No.48-1192)

Fig.2(a) depicts that $Ca_9Al(PO_4)_7$:0.05Ce^{3+} exhibits a strong broad emission band between 320 nm and 450 nm under 291 nm excitation, and the peak locates at 356 nm due to $4f^05d^1 \rightarrow 4f^1$ transition of Ce^{3+}. The excitation spectrum shows a broad band from 200 nm to 350 nm, and the peak locates at 291 nm, which corresponds to $4f^1 \rightarrow 4f^05d^1$ transition of Ce^{3+}[7]. Fig.2(b) presents that $Ca_9Al(PO_4)_7$:Eu^{2+} has a broad emission band under 305 nm excitation, and the peak locates at 445 nm, which is typically attributed to $4f^65d^1 \rightarrow 4f^7$ electronic dipole allowed transition of Eu^{2+}. The excitation spectrum shows a broad band between 200 nm and 350 nm, and the peak locates at 305 nm, which is assigned to $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+}[7]. The inset of Fig.2(a) shows the luminescent intensities of $Ca_9Al(PO_4)_7$:$x$$Ce^{3+}$ under 291 nm excitation with doping concentration x of 0.01, 0.02, 0.03, 0.04, 0.05, 0.07 and 0.1, and it is obvious that the emission intensity can achieve the maximum for $Ca_9Al(PO_4)_7$:0.05Ce^{3+} used in our experiment. The inset of Fig.2(b) shows the emission intensities of $Ca_9Al(PO_4)_7$:$y$$Eu^{2+}$ with different contents of Eu^{2+} (y). At first, the emission intensity enhances with the increase of Eu^{2+} content (y), and achieves a maximum at y=0.01, then decreases with further increasing Eu^{2+} content because of the concentration quenching effect. So the optimum content of Eu^{2+} is 0.01. Moreover, as shown in Fig.2, based on the spectral overlap between the emission band of $Ca_9Al(PO_4)_7$:Ce^{3+} and the excitation band of $Ca_9Al(PO_4)_7$:Eu^{2+}, the effective resonant energy transfer is expected to occur from Ce^{3+} to Eu^{2+}.



(a)

(b)

Fig.2 Emission and excitation spectra of (a) $Ca_9Al(PO_4)_7$:0.05Ce^{3+} (λ_{ex}=291 nm and λ_{em}=356 nm) and (b) $Ca_9Al(PO_4)_7$:0.01Eu^{2+} (λ_{ex}=305 nm and λ_{em}=445 nm) (The insets are the emission intensities as a function of impurity Ce^{3+} (x) and Eu^{2+} (y) concentrations.)

Fig.3 presents the emission spectra of $Ca_9Al(PO_4)_7$: $0.05Ce^{3+}$, $y$$Eu^{2+}$ with different Eu^{2+} contents of 0, 0.001, 0.005, 0.01, 0.02 and 0.03. $Ca_9Al(PO_4)_7$:$0.05Ce^{3+}$, $y$$Eu^{2+}$ has two broad emission bands under 291 nm excitation, and two peaks are assigned to $4f^05d^1\rightarrow4f^1$ transition of Ce^{3+} and $4f^65d^1\rightarrow4f^7$ transition of Eu^{2+}, respectively. However, the emission intensity of Ce^{3+} decreases with the increase of Eu^{2+} content, whereas the emission intensity of Eu^{2+} increases with the increase of Eu^{2+} content, achieves the maximum at y=0.01, and then decreases. For Eu^{2+} emission intensity, the apparent decrease (y>0.01) is mainly attributed to the concentration quenching effect, which is due to the occurrence of energy reabsorption among the nearest Eu^{2+} or Ce^{3+}[7-12]. The variations in the emission intensities of Ce^{3+} and Eu^{2+} in $Ca_9Al(PO_4)_7$:$0.05Ce^{3+}$, $y$$Eu^{2+}$ strongly indicate the continuous energy transfer from the sensitizer Ce^{3+} to the activator Eu^{2+}.

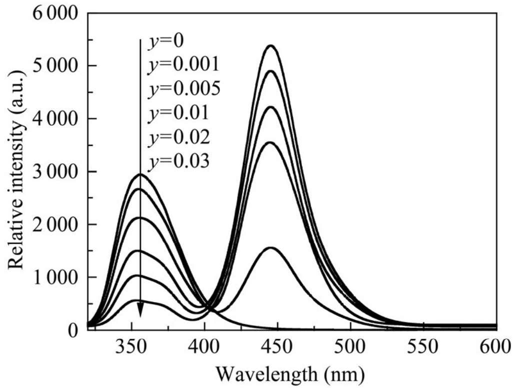


Fig.3 Emission spectra of $Ca_9Al(PO_4)_7$:$0.05Ce^{3+}$, $y$$Eu^{2+}$ with $0\leq y\leq0.03$ (λ_{ex}=291 nm)

For $Ca_9Al(PO_4)_7$:$0.05Ce^{3+}$, $y$$Eu^{2+}$, the energy transfer efficiency (η_T) can be achieved by[13]

$$\eta_T = 1-(I_S / I_{S0}), \tag{1}$$

where I_{S0} and I_S are luminescent intensities of sensitizer Ce^{3+} in the absence and presence of activator Eu^{2+}, respectively. The variation of η_T for $Ca_9Al(PO_4)_7$:$0.05Ce^{3+}$, $y$$Eu^{2+}$ (y=0.001–0.03) with Eu^{2+} content is shown in Fig.4. It can be seen that the emission intensity continuously enhances with the increase of Eu^{2+} content, and the energy transfer efficiency is observed as 80.03%.

On the basis of Dexter's energy transfer formula for exchange and multipolar interactions, the following relation can be obtained[14]

$$\ln(\eta_0 / \eta) \propto C, \tag{2}$$

$$(\eta_0 / \eta) \propto C^{\alpha/3}, \tag{3}$$

where η_0 and η are luminescence quantum efficiencies of Ce^{3+} in the absence and presence of Eu^{2+}, respectively, and C is the total concentration of Ce^{3+} and Eu^{2+}. Eq.(2) corresponds to the exchange interaction, and Eq.(3) with α=6, 8 and 10 belongs to dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively.

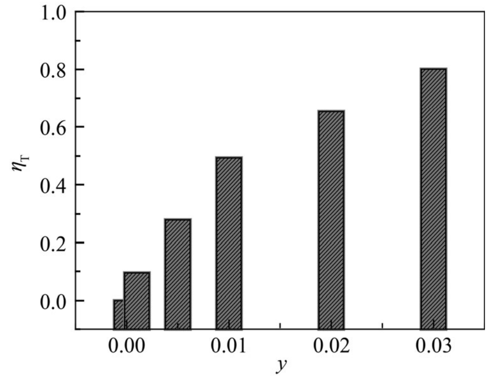


Fig.4 Dependence of energy transfer efficiency η_T on Eu^{2+} content y

In general, the critical distance (R_c) can be calculated by concentration quenching method. The critical distance $R_{Ce\text{-}Eu}$ between Ce^{3+} and Eu^{2+} can be estimated by[15]

$$R_{Ce\text{-}Eu} = 2[3V/(4\pi x_c N)]^{1/3}, \tag{4}$$

where x_c is the total concentration of Ce^{3+} and Eu^{2+}, i.e., x_c=9(0.05+y) for $Ca_9Al(PO_4)_7$:$0.05Ce^{3+}$, $y$$Eu^{2+}$. N is the number of Z ions in the unit cell (for $Ca_9Al(PO_4)_7$, N=6), and V is the volume of unit cell (for $Ca_9Al(PO_4)_7$, V=3.426 6 nm^3).

The estimated distances ($R_{Ce\text{-}Eu}$) for $Ca_9Al(PO_4)_7$: $0.05Ce^{3+}$, $y$$Eu^{2+}$ phosphors with x_c=0.459, 0.495, 0.54, 0.63 and 0.72 are 1.335 nm, 1.301 nm, 1.264 nm, 1.201 nm and 1.149 nm, respectively. The distance between Ce^{3+} and Eu^{2+} becomes shorter with the increase of Eu^{2+} content. x is the critical concentration at which emission intensity of donor (Ce^{3+}) in the presence of acceptor (Eu^{2+}) is half of that in the absence of acceptor (Eu^{2+}). Therefore, R_c of energy transfer is calculated to be about 1.264 nm for $Ca_9Al(PO_4)_7$:$0.05Ce^{3+}$, $y$$Eu^{2+}$. $R_{Ce\text{-}Eu}$ for various Ce^{3+} contents is much larger than the typical critical distance for exchange interaction (0.5 nm)[15]. This means that the exchange interaction plays no role in energy transfer process for $Ca_9Al(PO_4)_7$:$0.05Ce^{3+}$, $y$$Eu^{2+}$. Therefore, the emission intensity of Eu^{2+} is enhanced by efficient energy transfer from Ce^{3+} to Eu^{2+} in $Ca_9Al(PO_4)_7$, which belongs to the multipolar interaction. The relationship of $(I_{S0} / I_S) \propto C^{\alpha/3}$ is illustrated in Fig.5. The linear relationship reaches the optimal one for $(I_{S0} / I_S) \propto C^{\alpha/3}$ by comparing the fitting factor of R value. It can be seen from Fig.5(c) that the energy transfer from Ce^{3+} to Eu^{2+} occurs via the quadrupole-quadrupole interaction.

As shown in Fig.3, for $Ca_9Al(PO_4)_7$:$0.05Ce^{3+}$, $y$$Eu^{2+}$, the indigo emission intensity of Ce^{3+} decreases, and the blue emission intensity of Eu^{2+} gradually increases with the increase of Eu^{2+} content. As shown in Fig.6, the emission color of $Ca_9Al(PO_4)_7$:$0.01Eu^{2+}$ locates in the blue region.

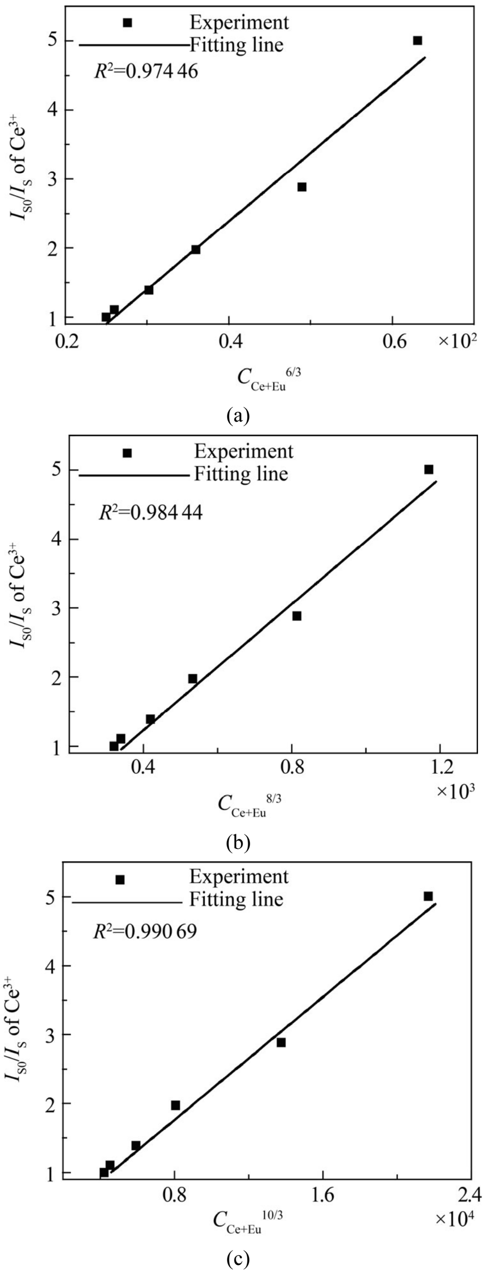


Fig.5 Dependence of I_{S0}/I_S on $C^{\alpha/3}$ with (a) α=6 for dipole-dipole interaction, (b) α=8 for dipole-quadrupole interaction and (c) α=10 for quadrupole-quadrupole interaction

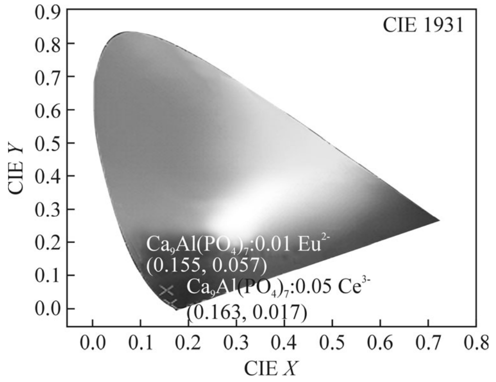


Fig.6 CIE chromaticity coordinates (X, Y) of Ca$_9$Al(PO$_4$)$_7$: 0.01Eu^{2+} and Ca$_9$Al(PO$_4$)$_7$:0.05Ce^{3+}

In summary, Ca$_9$Al(PO$_4$)$_7$:Ce^{3+}, Eu^{2+} phosphors are synthesized by the conventional solid-state method. Ca$_9$Al(PO$_4$)$_7$:Ce^{3+}, Eu^{2+} can produce two emission bands, which correspond to 4f^{0}5d^1→4f^1 transition of Ce^{3+} and 4f^{6}5d^1→4f^7 transition of Eu^{2+}, respectively. The energy transfer from Ce^{3+} to Eu^{2+} in Ca$_9$Al(PO$_4$)$_7$ is validated and proved to be a resonant type via a quadrupole-quadrupole interaction. The energy transfer efficiency gradually increases with the increase of Eu^{2+} content. Moreover, the critical distance (R_c) of Ce^{3+} to Eu^{2+} in Ca$_9$Al(PO$_4$)$_7$ is calculated to be 1.264 nm. Furthermore, the emission intensity and emission color of Ca$_9$Al(PO$_4$)$_7$:Ce^{3+}, Eu^{2+} can be tuned by properly adjusting the relative doping composition of Ce^{3+}/Eu^{2+}.

References

[1] Li Jian, Deng Jia-chun, Lu Qi-fei and Wang Da-jian, Optoelectronics Letters **9**, 293 (2013).

[2] Wang Q., Ci Z., Zhu G., Que M., Xin S., Wen Y. and Wang Y., ECS Journal of Solid State Science and Technology **1**, R92 (2012).

[3] Dai Xiu-hong, Li Hong-lian, Pang Li-bin and Gao Shao-jie, Optoelectronics Letters **9**, 194 (2013).

[4] Sun J., Sun Y., Zeng J. and Du H., Optical Materials **35**, 1276 (2013).

[5] Wang Z., Lou S. and Li P., Journal of Alloys and Compounds **586**, 536 (2014).

[6] Hou J., Jiang W., Fang Y., Wang Y., Yin X. and Huang F., ECS Journal of Solid State Science and Technology **1**, R57 (2012).

[7] Wang Q., Deng D., Hua Y., Huang L., Wang H., Zhao S., Jia G., Li C. and Xu S., Journal of Luminescence **132**, 434 (2012).

[8] Fang Y., Li L., Chen Y., Wang H. and Zeng R., Journal of Luminescence **144**, 13 (2013).

[9] Song X., Fu R., Agathopoulos S., He H., Zhao X. and Li R., Journal of the Electrochemical Society **157**, J34 (2010).

[10] Fu R., Agathopoulos S., Song X., Zhao X., He H. and Yu X., Optical Materials **33**, 99 (2010).

[11] Sun J., Zeng J., Sun Y. and Du H., Journal of Alloys and Compounds **540**, 81 (2012).

[12] Huang C.-H., Luo L. and Chen T.-M., Journal of the Electrochemical Society **158**, J341 (2011).

[13] Paulose P. I., Jose G., Thomas V., Unnikrishnan N. V. and Warrier M. K. R., Journal of Physics and Chemistry of Solids **64**, 841 (2003).

[14] Dexter D. L. and Schulman J. H., The Journal of Chemical Physics **22**, 1063 (1954).

[15] Blass G., Philips Res. Rep. **24**, 131 (1969).