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Luminescent characteristics of Dy^{3+}-doped polymethyl methacrylates for white light-emitting diode

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ABSTRACT

To explore white-light-emitting materials, a series of Dy^{3+}-doped polymethyl methacrylate (PMMA) samples are prepared by polymerization method. Excitation spectra and emission spectra are experimentally investigated. It is found that the luminous color of the PMMA sample doped with 0.1 mol% Dy^{3+} ion is white to the naked eye under 326 nm excitation. The CIE chromaticity coordinates (X = 0.321, Y = 0.336) of the emission are close to the standard white-light illumination (0.333, 0.333). The results are helpful in developing luminescent materials aimed for white light-emitting diodes.

Introduction

Conventional illuminations (incandescent and fluorescent lamps) have some disadvantages, such as low emission efficiency, short using lifetime, and big volume, and so forth. To replace conventional incandescent and fluorescent lamps, white light-emitting diodes have attracted much attention [1–6]. In the beginning, white light-emitting diode was realized by using a blue LED chip and a yellow phosphor. However, its color rendering index is very low [7,8]. To obtain high quality white light, three-primary-colors phosphors have been widely explored. In the previous work, transition-element and rare-earth ions doped glasses, glass ceramics and nanopowders were studied [9–16]. The host composition of phosphor is very important. On the one hand, it can affect the optical characters of the luminous ions. On the other hand, it is related to the assembling of the phosphor and the chip. Compared with the above host materials, the PMMAs have good tenacity and plasticity, which is favorable to subsequent processing. And co-doping of polymers including PMMA is well known as a technique to enhance the emission band of the rare earth ions [17–20]. In this work, we will investigate the photoluminescence of PMMAs doped with different Dy^{3+} concentration.

Experimental

PMMAs doped with x mol% Dy^{3+} (x = 0, 0.1, 0.6), 4 mol%Al^{3+} were prepared and marked as Dy0, Dy0.1, and Dy0.6, respectively. The thick and diameter of the sample are 1 mm and 5 mm. The detailed preparation procedure can be found in Ref. [21]. The excitation light is from a Xe-lamp. The luminescence spectra were recorded with a HORIBA Fluorolog-3 luminescence spectrometer (Horiba Jobin Yvon, Edison, USA). The excitation spectra of the different samples are measured under the same conditions. The spectral resolution of all spectra is 0.5 nm. The spectral resolution of spectrometer is 0.1 nm.

Results and discussion

Fig. 1 shows the excitation spectra of PMMA samples with different Dy^{3+} doping concentrations. Dy0 is for the undoped sample. Dy0.1 and Dy0.6 denotes the samples doped with 0.1 mol% and 0.6 mol% Dy^{3+} ion, respectively. The excitation spectra of sample Dy0 is monitored at the emission wavelength (λ_{em}) of 450 nm but the excitation spectra of samples Dy0.1, and Dy0.6 are monitored at the emission wavelength (λ_{em}) of 574 nm. The reason that different monitoring wavelengths are chosen is due to their different emission peaks. The strong emission peak for sample Dy0 is at 450 nm. However, for the samples Dy0.1 and Dy0.6 the strong emission peak is at 574 nm. The corresponding monitored wavelengths are indicated in Fig. 1. It is seen For sample Dy0, shown by blue curve, the wavelength of excitation peak is about 323 nm. This excitation results from the transition of the ligand of PMMA. For sample Dy0.1, the excitation peak of 323 nm is still observable, which is a result of the transition of the ligand of PMMA. Besides, there are other excitation peaks, which are located at 326 nm, 352 nm, 372 nm, 386 nm, 428 nm, 455 nm, and 476 nm. These new peaks are ascribed to the transitions of Dy^{3+} ion: $^6H_{15/2} \rightarrow {}^4M_{17/2}$, $^6H_{15/2} \rightarrow {}^6P_{7/2}$, $^6H_{15/2} \rightarrow {}^6P_{5/2}$, $^6H_{15/2} \rightarrow {}^4I_{13/2}$, $^6H_{15/2} \rightarrow {}^4G_{11/2}$, $^6H_{15/2} \rightarrow {}^4I_{15/2}$, and $^6H_{15/2} \rightarrow {}^4F_{9/2}$. In comparison with sample Dy0.1, the spectral shapes and peak positions of sample Dy0.6 are roughly the same. Nevertheless, the excitation intensities are increased.

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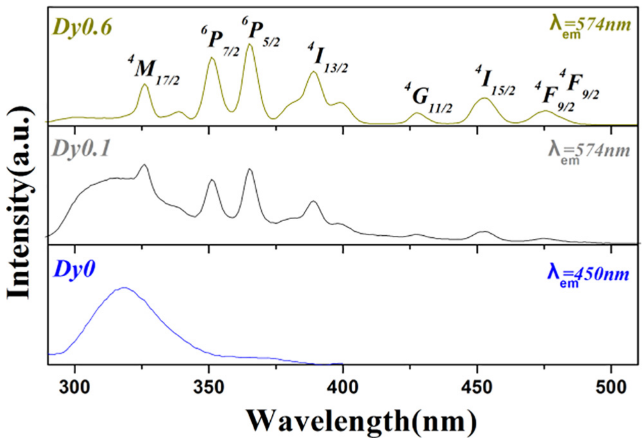

Fig. 1. Excitation spectra of the PMMAs doped with Dy^{3+} ion.

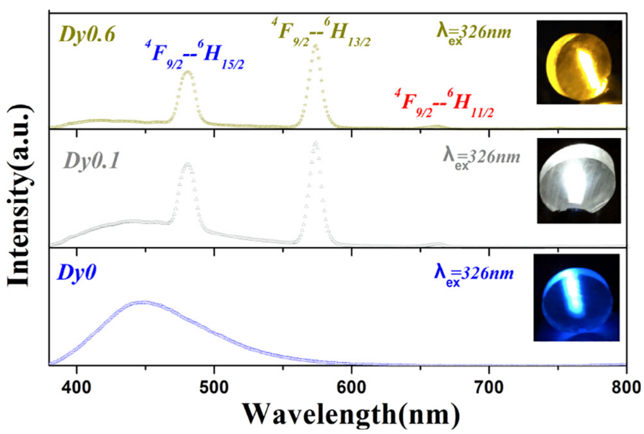

Fig. 2. Emission spectra of the PMMAs doped with Dy^{3+} ion with excitation wavelength λ_{ex} = 326 nm; the insets are the luminous photos of the samples.

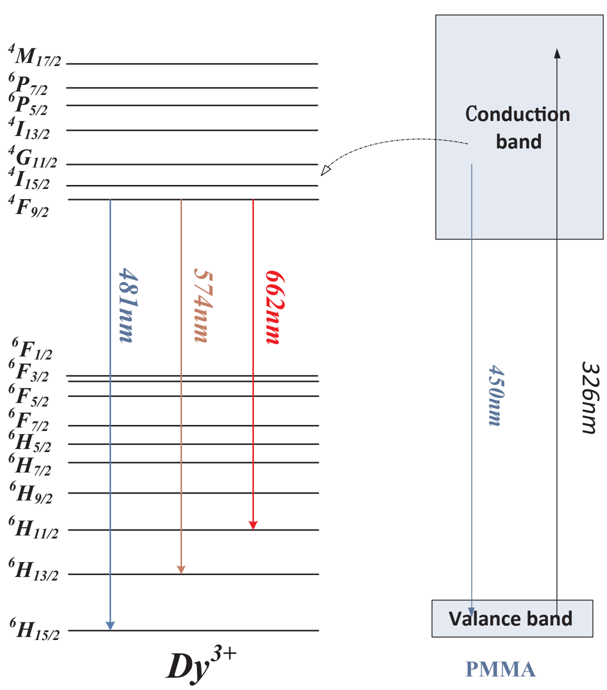

Fig. 3. Energy level diagrams of PMMA and Dy^{3+} ion.

Fig. 2 presents the emission spectra of the PMMA samples Dy0, Dy0.1, and Dy0.6 when the excitation wavelength λ_{ex} is 326 nm. Strong blue luminescence at 450 nm is observed in the Dy0 sample, which originates from the transition of the ligand of PMMA. Strong emissions at 481 nm, 574 nm, and 662 nm are found in sample Dy0.6, which should result from transitions of Dy^{3+} ion: ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$, ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$, and ${}^4F_{9/2} \rightarrow {}^6H_{11/2}$, respectively. Under the excitation of λ_{ex} = 326 nm, the luminous color of sample Dy0.1 is white to the naked eye, whose CIE chromaticity coordinates (X = 0.321, Y = 0.336) are close to the standard white-light illumination (0.333, 0.333).

The Energy level diagrams of PMMA and Dy^{3+} ion are shown in Fig. 3. The luminous population processes can be described as follows. Under 326 nm excitation, the electrons in the valance band of PMMA can be excited to the conduction band (CB). Then, the electrons relax to the bottom of the conduction band by non-radiative transition. Finally, the electrons go back to the valance band (VB) and emit the 450 nm luminescence. The electrons in the conduction band can also go back to the valance band by non-radiative transition, and transfer the energy to Dy^{3+} ion. The electrons in the ground state ${}^6H_{15/2}$ (Dy^{3+}) can be pumped to the higher excited states by energy transition. Then, the electrons non-radiatively relax to the lowest excited state ${}^4F_{9/2}$ (Dy^{3+}), from where the 481 nm, 574 nm, and 662 nm emissions arise. The luminescence peaks of Dy0 sample undoped with Dy^{3+} ion is at 450 nm and the luminescence color is blue by naked eyes. The sample doped high concentration Dy^{3+} ion has strong emission at 574 nm which is yellow color by naked eyes. Consequently, the luminescence color can vary with the concentration change of Dy^{3+}.

Conclusions

PMMAs doped with Dy^{3+} ion are prepared by polymerization method. PMMA undoped with Dy^{3+} can emit strong 450 nm blue emission. PMMA doped with 0.6 mol% Dy^{3+} can emit strong yellow emission. The luminous color of PMMA doped with 0.1 mol% Dy^{3+} is white to the naked eye, whose CIE chromaticity coordinates (X = 0.321, Y = 0.336) are close to the standard white-light illumination (0.333, 0.333). This study provides a useful guidance for developing luminescent materials aimed for white light-emitting diodes.

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References

[1] Singh SK, Giri NK, Rai DK, et al. Enhanced upconversion emission in Er^{3+}-doped tellurite glass containing silver nanoparticles. Solid State Sci 2010;12(8):1480.
[2] Lin CC, Tang YS, Hu SF, Liu RS. $KbaPO_4$: Ln (Ln = Eu, Tb, Sm) phosphors for UV excitable white light-emitting diodes. J Lumin 2009;129:1682.
[3] Chen L, Yu C, Hu L, et al. Preparation and spectroscopic properties of nanostructured glass-ceramics containing Yb^{3+}, Er^{3+} ions and Co^{2+}-doped spinel nanocrystals. Solid State Sci 2012;14(2):287.
[4] Ming CG, Song F, Li CR, Yu Y, Zhang G, Yu H, et al. High efficient down-conversion white light in $Tm^{3+}/Tb^{3+}/Mn^{2+}$ tri-doped P_2O_5-Li_2O-Sb_2O_3 glass. Opt Lett 2011;36:2242.
[5] Guo H, Wei RF, Liu XY. Tunable white luminescence and energy transfer in $(Cu+)_2$, $E^{u3}+$ codoped sodium silicate glasses. Opt Lett 2012;37(10):1670.
[6] Yang WJ, Luo LY, Chen TM, Wang NS. Luminescence and energy transfer of Eu- and Mn-coactivated $CaAl_2Si_2O_8$ as a potential phosphor for white-light UVLED. Chem Mater 2005;17:3883.
[7] Jüstel T, Nikol H, Ronda C. New developments in the field of luminescent materials for lighting and displays. Angew Chem Int Ed 1998;37:3084.
[8] Park JH, Steckl AJ. laser action in Eu-doped GaN thin-film cavity at room temperature. Appl Phys Lett 2004;85(20):4588.
[9] Sundarakannan B, Kottaisamy M. Sol-gel derived flux assisted synthesis of fine particles YAG: Ce^{3+} phosphor for remote phosphor converted white light emitting diodes. Mater Res Bull 2016;74:485.
[10] Zheng JH, Cheng QJ, Wu JY, Cui X, Chen R, Chen WZ, Chen C. A novel single-phase white phosphor $NaBaBO_3$:Dy^{3+}, ${}^K+$ novel single-phase for near-UV white light-emitting diodes. Mater Res Bull 2016;73:38.

[11] Zhang WH, Zhang YP, Ouyang SY, Zhang ZX, Xia HP. Enhanced luminescent properties of Sm^{3+} doped glass ceramics as potential red-orange phosphor for white light-emitting diodes. Mater Lett 2015;160:459.
[12] Zhong HJ, Chen GH, Yao LQ, Wang JX, Yang Y, Zhang R. The white light emission properties of $Tm^{3+}/Tb^{3+}/Sm^{3+}$ triply doped SrO-ZnO- P_2O_5 glass. J Non-Cryst Solids 2015;427:10.
[13] Zhang PP, Pu YP, Zhu XJ, Zheng HY, Zhao JJ, Wu YR, Luo YJ, Liu YW. Luminescence properties of Dy^{3+} doped and Dy^{3+}/Ce^{3+} co-doped CaO-Al_2O_3-SiO_2-B_2O_3 glass for LED applications. Ceram Int 2015;41:S729.
[14] Yang WJ, Chen TM. White-light generation and energy transfer in $SrZn_2(PO_4)_2$: Eu, Mn phosphor for ultraviolet light-emitting diodes. Appl Phys Lett 2006;88(10):101903.
[15] Liang XL, Yang YX, Zhu CF, Yuan SG, Chen GR, Pring A. Luminescence properties of Tb^{3+}-Sm^{3+} codoped glasses for white light emitting diodes. Appl Phys Lett 2007;91(9):91104.
[16] Chen DQ, Yu YL, Lin H, Huang P, Weng FY, Shan ZF, Wang YS. CeF_3-based glass ceramic: a potential luminescent host for white-light-emitting diode. Opt Lett 2009;34(19):2882.
[17] Zhang AQ, Yang YM, Zhai GM, Jia HS, Xu BS. Tuning the chromaticity of the emission color of the copolymers containing Eu (III), Tb (III), Be (II) ions based on colorimetric principle. Opt Mater 2016;52:92.
[18] Lin MJ, Wang W, Zhang WG. Preparation and Fluorescence Property of $Eu(OPr^i)_3$/ Tb $(OPr^i)_3$ co-doped P (MMA-co-St). Chin J Appl Chem 2004;12:008.
[19] Prajzler V, Jeřábek V, Lyutakov O, Hüttel I, Špirková J, Machovič V, et al. Optical properties of erbium and erbium/ytterbium doped polymethylmethacrylate. Acta Polytech 2008;48:14.
[20] Zelazowska E, Rysiakiewicz-Pasek E, Borczuch-Laczka M. Organic– inorganic hybrid materials doped with Eu^{3+}, Tb^{3+}, La^{3+} and lithium ions. Solid State Phenomena Trans Tech Publ 2013;200:38.
[21] Cai YX, Ming CG, Song F. Eu^{3+}/Tb^{3+} co-doped polymethyl methacrylate for white light-emitting applications. Mater Res Exp 2017;4(2):026201.