



White light emission from γ -irradiated Ag/Eu co-doped phosphate glass under NUV light excitation

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ABSTRACT

We reported on a new white light emission phosphor from γ -irradiated Ag/Eu co-doped phosphate glass $65\text{NaPO}_3\text{-}30\text{Al}(\text{PO}_3)_3\text{-}5\text{SiO}_2$. Absorption and EPR results confirm the appearance of Eu^{2+} and silver aggregates (Ag_2^+ and Ag_3^{2+}) after γ -irradiation. Ag_2^+ and Ag_3^{2+} show strong absorption in near ultra-violet (NUV) range with a maximum at 320 and 370 nm, respectively. Energy transfers of silver aggregates $\rightarrow \text{Eu}^{2+}$, silver aggregates $\rightarrow \text{Eu}^{3+}$ and $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ greatly enhanced luminescence intensity of Eu^{2+} and Eu^{3+} after γ -irradiation. The white light emission can be tuned simply by changing excitation wavelength. Pure white light emission close to standard white light ($x = 0.333, y = 0.333$) in CIE chromaticity diagram was obtained under 337–385 nm excitation. Pure white emission, broad excitation bands and easy fabrication suggest its potential application in white LEDs.

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1. Introduction

White light emitting diodes (W-LEDs) received lots of interests because of their real application in substituting fluorescence or incandescent lamps for solid state lighting source over the last two decades [1–6]. Compared with the traditional lighting sources, W-LEDs have many advantages such as high efficiency, less energy consumption and longer lifetime [1]. To date many approaches have been acquired successfully to get white light emission [7,8]. One of the most common ways to get white emission is combination of the yellow-emitting phosphor e.g. cerium doped yttrium aluminum garnet (YAG:Ce^{3+}) and blue-emitting GaN chips [1]. However, the difference between the individual degradation rates of the blue LED chip and the phosphors coated on the chip result in chromatic aberration and thus poor white-light performance [7]. This problem can be avoided by rare earth ions co-doped single-phased white-emitting phosphors based on UV LEDs [4,8,9].

It is well known that glasses have many advantages over crystals on higher doping levels of rare earth ions, simpler manufacture procedure and lower production cost [10–12]. Consequently, rare earth ions doped glasses for white light emission are more attractive than conventional crystal phosphors. Since rare earth ions doped

white light luminescence glass was first reported by Zhang et al. in 1991 [13], it has been investigated by many researchers. The most widely used matrices for white light emission were silicate glasses [5,14,15]. On the contrary, rare earth ions doped phosphate glasses, broadly used in high power laser application, has been seldom studied for W-LEDs. Among various dopants, europium in divalent or trivalent oxidation state is playing a dominant role [16–20]. Luminescence from Eu^{3+} in glass is characterized by a series of sharp emission bands at 550–710 nm due to the $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 0, 1, 2, 3, 4$) transitions. For Eu^{2+} , the emission spectrum is a broad band at 400–550 nm as a result of $^4\text{f}_6^5\text{d}_1 \rightarrow ^4\text{f}_7$ transition [21,22]. However, the absorption coefficient of europium ions at UV range is very small leading to low efficiency of emission under UV excitation. As a consequence, many researchers investigated the effect of silver particles on the emission efficiency of Eu^{3+} ions [5,6,23,24]. Malta et al. and Hayakawa et al. investigated the effect of silver nanoparticles on the luminescence properties of Eu^{3+} ions in borofluoride glass and silicate glass, respectively. They attributed the fluorescence enhancement of Eu^{3+} ions to the plasma field enhancement effect of silver nanoparticles. Recently, the energy transfer between silver aggregates and Eu^{3+} ions were studied by Eichelbaum and Rademann [5]. They pointed out X-ray irradiation induced sub-nanometer sized silver particles could absorb effectively UV light and transfer energy to trivalent rare earth ions in silicate glass. This energy transfer mechanism can also improve the excitation efficiency of Eu^{3+} . The effect of gamma rays on different phosphate glasses were systematically investigated by F.H. Elbatal and H.A. Elbatal [25–27]. The reduction of Eu^{3+} in glass can be realized by

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γ -irradiation [16]. However, to the author's knowledge, the effect of silver particles on the emission properties of Eu^{2+} ions has been scarcely reported.

In the present work, Ag/Eu co-doped phosphate glasses were prepared by melt quenching method. Silver aggregates and Eu^{2+} ions in glass were generated by γ -irradiation. Under NUV excitation, white light emission was realized by silver aggregates as a sensitizer for Eu^{3+} and Eu^{2+} ions. The mechanism for white light emission was proposed.

2. Experimental

2.1. Sample preparation

Phosphate glass $65\text{NaPO}_3\text{-}30\text{Al}(\text{PO}_3)_3\text{-}5\text{SiO}_2$ (in mol%) was prepared by melt-quenching method. 2.25 wt% AgNO_3 and 2.35 wt% Eu_2O_3 were added as dopants. Glass samples singly doped with Eu_2O_3 (2.25 wt%) or AgNO_3 (2.35 wt%) were also prepared as references. All the start materials were analytical reagents. The well-mixed stoichiometric chemicals were put into an alumina crucible and melted at 1250°C for 2 h. The melts were cast into a pre-heated iron mould, and then annealed in a muffle furnace at 450°C for 2 h. The glass samples were cut and polished into size of $25\text{ mm} \times 10\text{ mm} \times 0.5\text{ mm}$ and optically polished for optical absorption, excitation, emission and lifetime measurements. The powder glass samples were also prepared for electron paramagnetic resonance (EPR) tests. All samples were irradiated by γ -rays from ^{60}Co , the dose was 5 KGy, and the dose rate was 20.8 Gy/min. Subsequently, these samples were annealed at 200°C for 40 min to stabilize luminescence centers.

2.2. Sample characterization

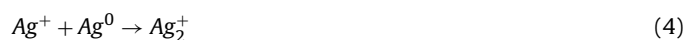
Optical absorption spectra were recorded on a JASCO V-570 spectrophotometer over a spectral range of 200–800 nm. The excitation and emission spectra and luminescence decay curves were conducted on a FLS 920 fluorescence spectrophotometer, using a 450 W Xe lamp, a μs flash lamp and an nF900 nanosecond lamp as excitation sources. Electron Paramagnetic Resonance (EPR) measurements were conducted on a JEOL-FA200 EPR spectrometer operating in X band ($\nu = 9.084\text{ GHz}$). All of the measurements were carried out at room temperature.

3. Results and discussion

3.1. Optical absorption and formation mechanism of silver aggregates

Fig. 1(a) and (b) show optical absorption spectra of Ag and Eu singly and co-doped phosphate glasses before and after γ -irradiation. The absence of the plasma resonance absorption (centered about 450 nm) of silver nanoparticles [28] in both Ag containing glasses suggests that the effect of silver plasmonic filed enhancement on luminescence will not be considered in this study. Before γ -irradiation, the cut-off wavelengths are 240, 255 and 268 nm for Ag singly doped, Eu singly doped and Ag/Eu co-doped phosphate glasses, respectively. The changes of cut-off wavelengths for various glasses are due to the increase of the non-bridging oxygen ions and UV absorption of Ag^+ and Eu^{3+} . For Ag singly doped glass, the absorption band centered at about 227 nm is due to the parity-forbidden transition $d^{10}(^1S_0) \rightarrow d^9s^1(^3D_1)$ of Ag^+ [29]. For Eu doped glasses, the charge-transfer absorption bands peaked at about 250 nm and sharp absorption peaks at 393 and 464 nm are assigned to Eu^{3+} [30]. The weak peak centered at about 320 nm is due to the 4f–5d transition of Eu^{2+} [31], which indicates that a few part of Eu^{3+} ions were reduced to Eu^{2+} during melting. For acidic glasses, redox equilibria exists for ion couples $\text{Eu}^{3+}/\text{Eu}^{2+}$ during glass melting [32–34]. The lower optical basicity of phosphate glass favours the reduction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$. As for Ag/Eu co-doped glass, the Ag^+ related absorption band was overlapped by the charge-transfer absorption band of Eu^{3+} . After γ -irradiation, the absorption spectra for all samples undergo great changes, as shown in Fig. 1(b). Firstly, the cut-off wavelengths of the two Ag containing glasses are greatly red-shifted, while that of Eu singly doped glass is almost unchanged. The cut-off wavelengths of Ag singly doped, Eu singly doped and Ag/Eu co-doped glass samples are 405, 257

and 370 nm, respectively. The red-shift of the cut-off wavelength for Ag containing glasses is ascribed to γ -irradiation induced UV absorption bands of sub-nanometer sized Ag aggregates [35–38]. The optical absorption bands at 265, 320 and 345 nm are assigned to Ag_2^+ , Ag_2^+ and Ag^0 , respectively [35,36]. The absorption band at 370 nm is ascribed to Ag_3^{2+} [37,38]. In γ -irradiated Ag containing glasses, the following reactions could occur [35,39]:



The Ag_3^+ trimer may also be formed after γ -irradiation. The reaction can be described as follows:



The concentration of irradiation induced color centers was calculated by Smakula's formula [40]. In this study, the concentration of γ -irradiation induced Ag^0 is much lower than that of the residual Ag^+ ions after irradiation. The reaction (5) is dominant in the formation of silver trimers. Therefore, only Ag_3^{2+} is considered as silver trimer. γ -irradiation greatly enhances the intensity of Eu^{2+} related absorption band at 320 nm. Obviously, Eu^{3+} ions are partly reduced to Eu^{2+} ions during γ -irradiation. This can be expressed by the following reaction:



Noteworthy, the co-doping Eu to silver doped phosphate glass suppresses the absorption band of Ag^0 , Ag_3^{2+} and Ag_2^+ as depicted in Fig. 1(b). This can be explained as follows. In Ag/Eu co-doped phosphate glass, Eu^{3+} and Ag^+ ions compete to trap electron centers during γ -irradiation, thus the concentration of Ag^0 , Ag_3^{2+} and Ag_2^+ of γ -irradiated Ag/Eu co-doped phosphate glass is less than that of γ -irradiated Ag singly doped glass.

Furthermore, the absorption band centered at 535 nm due to irradiation induced hole centers was observed in γ -irradiated Eu singly doped phosphate glass [41]. This suggests that the ability of Eu^{2+} trapping holes is much weaker than that of Ag^+ . Nonetheless, the absorption intensity of Ag_2^+ slightly decreases because of the introduction of Eu to Ag doped glass.

3.2. EPR spectra

Ag^+ and Eu^{3+} ions are not paramagnetic sensitive, while Ag^{2+} , silver aggregates and Eu^{2+} ions can be easily identified by EPR spectroscopy at room temperature [21,42]. Therefore, EPR measurements can be used to confirm the formation of Eu^{2+} , silver aggregates and Ag^{2+} after γ -irradiation. Fig. 2(a) and (b) show EPR spectra of glass samples before and after irradiation, respectively. The signal at $g \sim 4.6$ before γ -irradiation in Eu doped sample belongs to Eu^{2+} . The weak intensity confirms that only a few part of Eu^{3+} ions were reduced to Eu^{2+} ions during melting [21]. The EPR signals located at $g \sim 2.3$ are correlated to impurities. The appearance of Eu^{2+} after γ -irradiation was confirmed by so-called characteristic "U" spectra (at $g \sim 2.0$, $g \sim 2.8$ and $g \sim 6.0$) of Eu^{2+} as shown in Fig. 2(b). Similarity, the EPR lines $g_{\perp} \sim 2.05$ and $g_{\parallel} \sim 2.35$ [42], $g \sim 1.994$, and $g \sim 1.980$ after γ -irradiation confirm the appearance of Ag_2^+ , Ag_2^+ , and Ag_3^{2+} respectively [35,43]. Moreover, POHC doublet ($g \sim 2.01$) and PO_3 electron center doublet ($g \sim 2.06$) [44] were observed for the two singly doped glass samples, while for Ag/Eu co-doped glass, only PO_3 electron center doublet was found

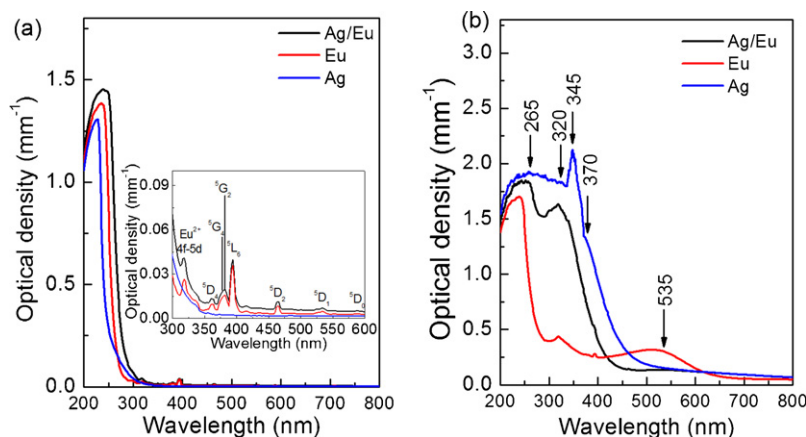


Fig. 1. Optical absorption spectra of Ag singly doped, Eu singly doped and Ag/Eu co-doped phosphate glasses (a) before and (b) after γ -irradiation. Inset of (a): zoom at the spectral region of 300–600 nm.

after γ -irradiation. This indicates that the introduction of Eu is helpful for Ag⁺ to trap holes.

3.3. Luminescence properties

Fig. 3 shows emission spectra of Eu singly doped, Ag singly doped and Ag/Eu co-doped phosphate glasses before and after γ -irradiation excited by 375 nm UV light. Before irradiation, for Eu doped glasses, the emission peaks centered at 590, 612 and 700 nm are ascribed to $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_4$ transitions of Eu³⁺, respectively, as shown in Fig. 3(a), [16,21]. Ag has no clear influence on the emission from Eu³⁺ ions and for Ag singly doped glass, no emission was observed. After irradiation, for Ag singly doped sample, the broad luminescence band centered at 655 nm and a shoulder centered at 470 nm are assigned to silver aggregates as shown in Fig. 3(b). For Eu singly doped sample, the sharp emission lines assigned to Eu³⁺ ions were also observed. The very weak peak centered at about 470 nm is ascribed to Eu²⁺ ions [16,21], as shown in the inset of Fig. 3. According to EPR and absorption results, the co-doping Eu to silver doped glass results in the decrease of silver aggregates, thus both the emission bands at 655 and 470 nm ascribed to silver aggregates should decrease. However, for Ag/Eu co-doped sample, comparing with that of Ag singly doped glass sample, the luminescence band peaked at 655 nm decreases greatly, on the contrary the luminescence band centered at 470 nm increases greatly. The appearance of Eu²⁺ after γ -irradiation, thus corresponding emission from Eu²⁺ at around

470 nm and energy transfer from Ag aggregate to Eu²⁺ mainly contributes to the enhancement of 470 nm emission. An undoped black glass was also prepared as reference and no luminescence in the studied range was found excited by 375 nm, which excludes the emission from γ -irradiated induced glass defects.

Fig. 4(a) and (b) show the luminescence decay curves of two Ag containing glass samples under excitation of 375 nm monitoring at 470 nm. Microsecond and nanosecond lamps are used as excitation sources. For microsecond excitation lamp, decay curves show a double exponential decay characteristic as shown in Fig. 4(a). Silver aggregates are responsible for these decay components [29,45]. The obtained effective lifetimes ($1/e$ of initial intensity) are $\tau \approx 1170 \mu\text{s}$, and $\tau \approx 665 \mu\text{s}$ for γ -irradiated Ag/Eu co-doped and Ag singly doped phosphate glasses, respectively. For nanosecond excitation lamp, the decay curve of irradiated Ag/Eu co-doped phosphate glass follows a single exponential decay with a lifetime about 5 ns. This decay component belongs to Eu²⁺ ions and the lifetime is in the same range as those reported elsewhere [46–48]. For Eu singly doped glass, the luminescence decay curve could not be obtained because of the too weak emission intensity. This shows that Eu²⁺ emission intensity of Ag/Eu co-doped sample is much stronger than that of Eu singly doped sample, which proves our conclusion that the co-doping Ag to Eu doped glass enhances the emission intensity of Eu²⁺, and the emission of Eu²⁺ is responsible for the enhancement of the emission band centered at 470 nm.

Fig. 5 shows excitation spectra of γ -irradiated Ag/Eu co-doped, Eu doped and Ag doped phosphate glass samples monitoring at

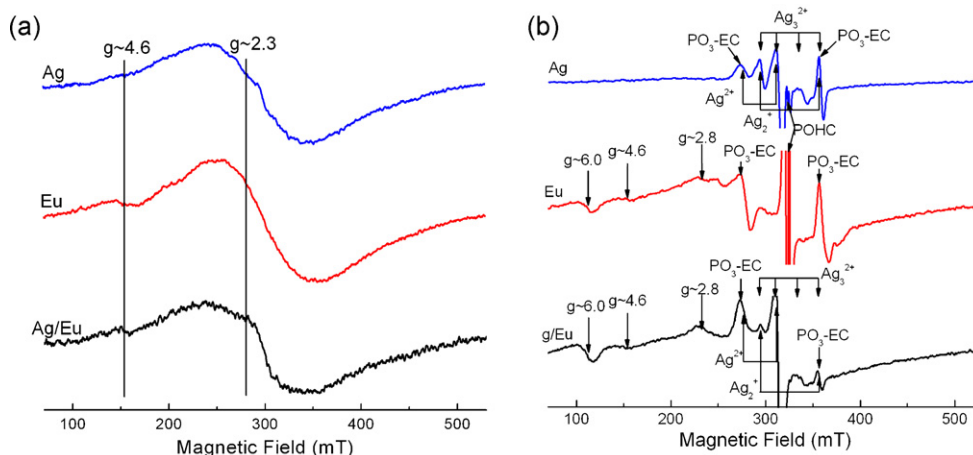


Fig. 2. EPR spectra of Ag singly doped, Eu singly doped and Ag/Eu co-doped phosphate glasses (a) before and (b) after γ -irradiation.

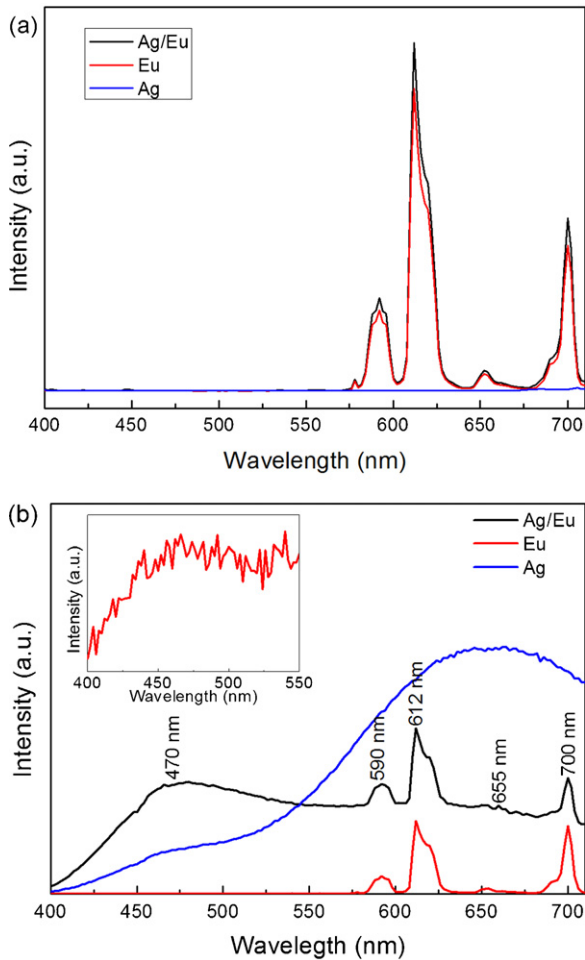


Fig. 3. Emission spectra ($\lambda_{\text{ex}} = 375 \text{ nm}$) of Ag singly doped, Eu singly doped and Ag/Eu co-doped phosphate glass samples (a) before and (b) after γ -irradiation. Inset of (b): zoom at the spectral region of 400–550 nm of Eu singly doped sample.

470 nm. For Ag singly doped and Ag/Eu co-doped glasses, the excitation bands centered at 270 nm and 365 nm are assigned to silver aggregates [49]. Although the silver doping concentration is identical in the two glasses, the excitation of Ag/Eu co-doped glass is

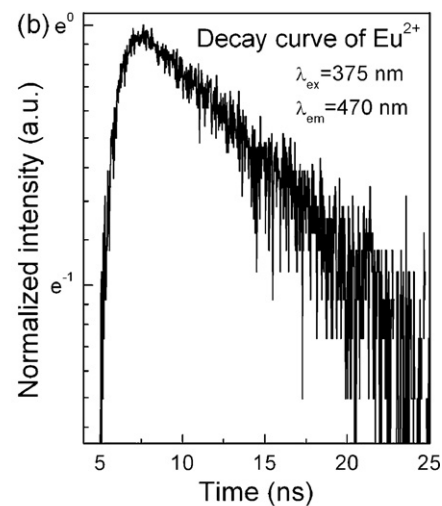
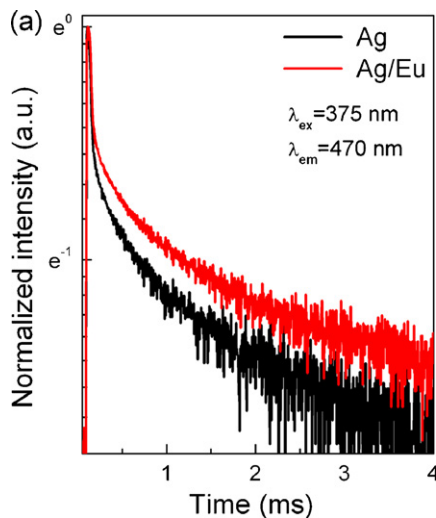


Fig. 4. Luminescence decay curves of 470 nm emission for Ag singly doped and Ag/Eu co-doped phosphate glass under 375 nm excitation by using different excitation sources (a) microsecond and (b) nanosecond lamp.

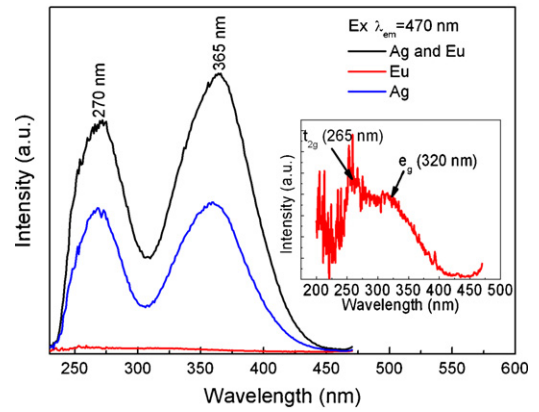


Fig. 5. Excitation ($\lambda_{\text{em}} = 470 \text{ nm}$) spectra of Eu singly doped, Ag singly doped and Ag/Eu co-doped phosphate glasses. Inset: amplified excitation spectra of Eu singly doped sample.

more efficient than that of Ag singly doped glass. This indicates that Eu^{2+} ions play an important role in the increase of the excitation efficiency of silver aggregates. The increase of the excitation efficiency of silver aggregates and the enhancement of Eu^{2+} fluorescence are caused by the energy transfer from silver aggregates to Eu^{2+} . On the other hand, for Eu singly doped glass, only weak excitation bands due to $^8\text{S}_{2/7} \rightarrow ^5\text{d}$ transition of Eu^{2+} were observed, as shown in the inset of Fig. 5. These bands consist of two components t_{2g} (265 nm) and e_g (320 nm) splitted by the crystal field around Eu^{2+} ions [50]. Since the excitation efficiency of Eu^{2+} is very weak, the energy transfer from Eu^{2+} to silver aggregates can be ignored.

Fig. 6 shows the excitation spectrum monitored at 612 nm and emission spectrum under 375 nm excitation of γ -irradiated Ag/Eu co-doped glass. The overlap between the broad emission band centered at 470 nm of Eu^{2+} and silver aggregates and the excitation bands of Eu^{3+} ions indicating the energy transfer from Eu^{2+} or silver aggregates to Eu^{3+} ions. As a result, comparing with Eu singly doped glass, the red emission of Eu^{3+} ions is enhanced in Ag/Eu co-doped glass, as shown in Fig. 3, due to the energy transfer from silver particles or Eu^{2+} ions to Eu^{3+} ions.

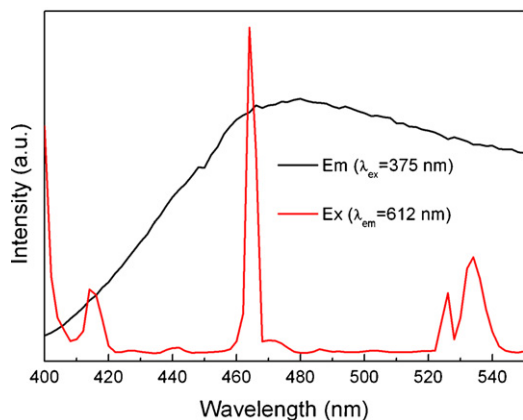


Fig. 6. Emission and excitation spectra of Ag/Eu co-doped phosphate glass after γ -irradiation.

3.4. Energy transfer mechanism

Possible energy transfer processes are proposed based on energy levels of Eu^{2+} , Eu^{3+} and silver aggregates as shown in Fig. 7. The mechanism for energy transfer is generally believed to be resonant multi-polar coupling [51]. Detailed theoretical investigations were carried out by Dexter [52] and Förster [53]. Small mismatch of the upper level of Eu^{2+} , Eu^{3+} and silver aggregates suggests possible energy transfer from excited level of Ag aggregates to upper level Eu^{2+} and Eu^{3+} and from upper level of Eu^{2+} to upper level of Eu^{3+} through cross relaxation resulting in enhanced 470 nm emission from Eu^{2+} and red emission from Eu^{3+} as depicted in Fig. 7. The high absorption efficiency of Ag aggregates in NUV range hints the efficient energy transfer from Ag aggregates to Eu^{2+} and Eu^{3+} .

3.5. CIE chromaticity diagram

Fig. 8(a) shows the emission spectra of Ag/Eu co-doped phosphate glass after γ -irradiation excited with different NUV wavelengths. The corresponding emission spectra were converted to the CIE 1931 chromaticity diagram as shown in Fig. 8(b). The corresponding photographs under UV excitation were also shown in Fig. 8(b). Surprisingly, under 337–385 nm excitation, the emission of Eu^{2+} , Eu^{3+} and silver aggregates can be tuned continuously. Under 360 nm excitation, the CIE coordinate ($x=0.339$, $y=0.338$) close to standard white light ($x=0.333$, $y=0.333$) was obtained. While under 320 and 394 nm excitation, yellow–white light emission was observed. The corresponding CIE coordinate is ($x=0.446$, $y=0.39$) and ($x=0.461$, $y=0.375$), respectively. The

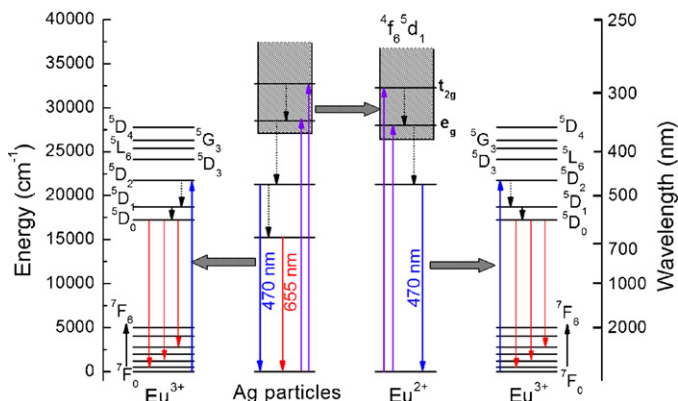


Fig. 7. Schematic energy levels of Eu^{2+} , Eu^{3+} ions and silver aggregates, and possible energy transfer processes.

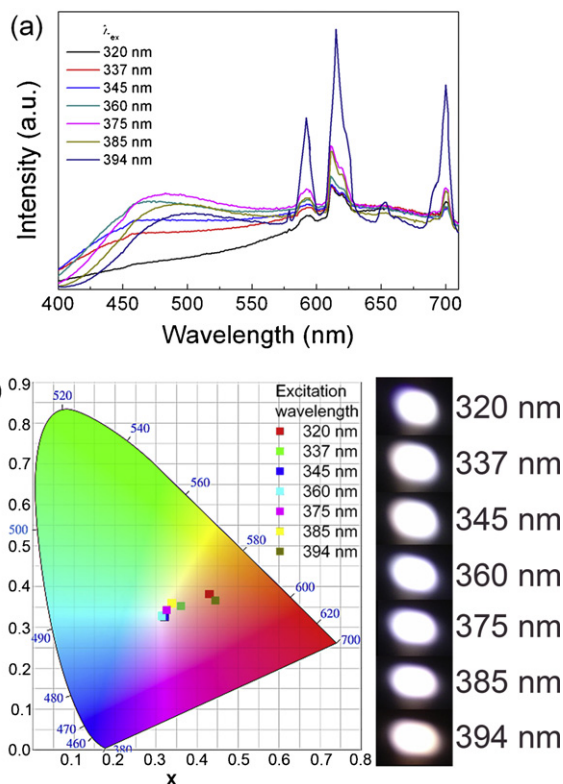


Fig. 8. (a): Emission spectra of Ag/Eu co-doped phosphate glass after γ -irradiation under excitation of various NUV wavelengths. (b): Corresponding CIE 1931 chromaticity diagram (labels: excitation wavelength) and photographs under excitation by using a FLS 920 spectrofluorometer.

excitation efficiency is comparably low under 320 nm excitation as shown in Fig. 4. This results in weak blue light emission and thus yellow–white light emission. Similarity, under 394 nm excitation, because 394 nm is one of the resonant excitation bands of Eu^{3+} , the characteristic red emission of Eu^{3+} is dominant in the emission spectra leading to yellow–white light emission. Therefore, tunable luminescence was obtained by simply control the excitation wavelength suggesting its potential application in W-LEDs.

4. Conclusions

In summary, we present a new white light emission phosphor from γ -irradiated Ag/Eu co-doped phosphate glasses. Silver aggregates (Ag_2^{2+} and Ag_3^{2+}) and Eu^{2+} ions were generated during γ -irradiation. The efficient energy transfers of silver aggregates $\rightarrow \text{Eu}^{2+}$, silver aggregates $\rightarrow \text{Eu}^{3+}$ and $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ resulted in great enhancement of the Eu^{2+} and Eu^{3+} emission intensity. Tunable white light emission was obtained in γ -irradiated Ag/Eu co-doped phosphate glass under 320–394 nm excitation. High pure white light with chromaticity coordinate close to standard white light ($x=0.333$, $y=0.333$) in CIE chromaticity diagram is obtained under 337–385 nm excitation. The results suggest its possible application in white LEDs. Further study will focus on the improvement of luminescence stability and chemical stability of γ -irradiated Ag/Eu co-doped phosphate glass.

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