

# Photoluminescence enhancement of $\text{Eu}^{3+}$ by energy transfer from $\text{Bi}^{2+}$ to $\text{Eu}^{3+}$ in bismuth glass nanocomposites

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## Abstract

$\text{Bi}^{2+}$ -enhanced photoluminescence of  $\text{Eu}^{3+}$  doped  $\text{Bi}^0$ -bismuth glass nanocomposites are demonstrated here. The generation of bismuth nanoparticles (NPs) and its typical surface plasmon resonance at 460 nm are controlled by the oxidative method instead of conventional reduction technique during melt-quench processing. TEM image evidences the presence of spherical  $\text{Bi}^0$  NPs of 10-15 nm sizes and SAED pattern reveals their crystalline rhombohedral phase formation. The enhanced photoluminescence of  $\text{Eu}^{3+}$  is found to occur at 613 and 703 nm due to  $^5D_0 \rightarrow ^7F_2$  and  $^5D_0 \rightarrow ^7F_4$  transitions respectively. We believe that it has happened due to energy transfer from  $\text{Bi}^{2+}$  to  $\text{Eu}^{3+}$ .

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## Introduction

Rare earth doped glasses have attracted much attention world wide for their extensive applications such as in glass lasers, optical fiber amplifiers, optoelectronic and memory devices, flat-panel displays, etc. The luminescent properties of  $\text{Eu}^{3+}$  have fascinated researchers as a dopant since they can emit red fluorescence with high luminescence efficiency under UV light excitation.<sup>1</sup> Many researchers have activated it to enhance the europium emission intensity by co-doping with either another rare earth or transition metal ions in different matrices. Moreover, enhancement of rare earth luminescence in presence of metal nanoparticles is again a very fascinating area for researchers.<sup>2,3</sup> In this context, bismuth ions are one of efficient luminescent activator with applications in lasers and a sensitizer for some rare earth ions, and are nowadays being investigated.<sup>4</sup> However, the luminescence origin from bismuth ions is still unclear and hence is highly debated. Many reports are available for the enhancement of luminescence of  $\text{Eu}^{3+}$  in presence of  $\text{Bi}^{3+}$  as a sensitizer in various matrices.<sup>5</sup> But the enhancement of luminescence of  $\text{Eu}^{3+}$  in presence of other valance state of bismuth ion has not been reported previously.

In view of above, bismuth glasses are considered as one of the most important amongst the heavy metal oxide glasses as a host matrix for rare earths.<sup>6</sup> But the problem associated with these glasses is its dark-brown or black coloration due to formation of metallic bismuth ( $\text{Bi}^0$ ) during melting.<sup>7</sup> These glasses are, therefore, restricted to a great extent for optical and photonic applications. Consequently, synthesis of transparent bismuth glasses by suppressing the formation of  $\text{Bi}^0$  nanoparticles (NPs) in bismuth glasses is very important for both scientific as well as technological points of view.

Recently, we have reported the suppression of metallic bismuth formation in bismuth glasses by the oxidative process using  $\text{KNO}_3$  and  $\text{KClO}_4$ .<sup>8</sup>

In this letter, we demonstrate the enhancement of emission intensity of  $\text{Eu}^{3+}$  ion by the  $\text{Bi}^{2+}$  ions during controlled formation of  $\text{Bi}^0$  using  $\text{K}_2\text{S}_2\text{O}_8$  as oxidizing agent in the  $\text{B}_2\text{O}_3$ - $\text{ZnO}$ - $\text{Bi}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{K}_2\text{O}$  glass system.

## Experimental

Glasses were prepared by the melt-quench technique with the composition (wt %)  $19\text{B}_2\text{O}_3$ - $23\text{ZnO}$ - $45\text{Bi}_2\text{O}_3$ - $9\text{SiO}_2$ -( $4-x$ ) $\text{K}_2\text{O}$ - $x\text{K}_2\text{S}_2\text{O}_8$  (where  $x$  is 0, 0.2, 1.0 and 3.0, and named as a, b, c, and d respectively). All the glasses were doped with 0.5 wt % of  $\text{Eu}_2\text{O}_3$  and designated as e, f, g and h respectively. The composition of glass has also been provided in Table 1.  $\text{Bi}_2\text{O}_3$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{ZnO}$  and  $\text{K}_2\text{CO}_3$  from Loba Chemie;  $\text{SiO}_2$  (Bremthaler/Quarzitwerk),  $\text{K}_2\text{S}_2\text{O}_8$  (Merck) and  $\text{Eu}_2\text{O}_3$  (Alfa Aesar) were used as raw materials. The batch for 25 g glass was melted in a silica crucible at  $1100^\circ\text{C}$  for 30 min followed by casting and annealing at  $420^\circ\text{C}$  for 2h in air.

The UV-Vis absorption spectra were recorded using Perkin-Elmer (Lambda 20) double beam UV-visible spectrophotometer. The X-ray diffraction patterns of the bulk samples were recorded in an X'pert Pro MPD diffractometer (PANalytical) operating at 40 kV and 30 mA using Ni-filtered  $\text{CuK}\alpha$  radiation with the X'celerator with step size  $0.05^\circ$  ( $2\theta$ ) step time 0.5 s, from  $5^\circ$  to  $90^\circ$ . The TEM and SAED images were taken using a FEI instrument (Tehnai-30, ST G<sup>2</sup>) operating at an accelerating voltage of 300 kV. The fluorescence spectra were measured with a Perkin Elmer Luminescence

Spectrophotometer (Model LS55) exciting at 393 nm using a Xenon lamp as the excitation source.

## Results and discussion

Figure 1 (A) shows the UV-Vis absorption spectra of a, b, c and d samples with increase in concentration of oxidant  $K_2S_2O_8$  (0 to 3 wt %) in the glasses. The base glass is deep black in color, but the transparency increases with addition of  $K_2S_2O_8$ . The glass melted using 3 wt % of  $K_2S_2O_8$  is highly transparent. The base glass reveals a very weak surface plasmon resonance (SPR) band (shown in inset) due to presence of huge amount of  $Bi^0$  NPs. When 0.2 wt %  $K_2S_2O_8$  has added to the base glass, the surface plasmon band has visualized very distinctly. The intensity of SPR band gradually decreases with addition of further amount of  $K_2S_2O_8$  (up to 3.0 wt %). The observed broad absorption band at 460 nm is appeared due to the SPR of  $Bi^0$  NPs.<sup>7-9</sup> The SPR comes up due to collective oscillation of conduction band electrons of metallic nanoparticles embedded in dielectric host in response to optical excitation. Peng *et al.*<sup>7</sup> have found a broad absorption peak around 465 nm for  $Bi_2O_3$  contained glasses and assigned the peak as surface plasmon resonance (SPR) of metallic bismuth. Singh *et al.*<sup>8</sup> and Khonthon *et al.*<sup>9</sup> have also described such absorption band of  $Bi^0$  NPs at 460 nm in the different glass matrices, which correlates well with the present result. The UV-Vis absorption spectra of the glasses containing a constant amount of  $Eu_2O_3$  (0.5 wt %) are also shown in the Fig. 1 (B). They exhibit characteristic absorption bands of  $Eu^{3+}$  at 393 and 464 nm which are attributed to transitions from  $^7F_0$  to  $^5L_6$  and  $^5D_2$  states respectively as well as broad SPR band at 460 nm.<sup>1</sup> The intensity of SPR band gradually decreases with addition of oxidant

$\text{K}_2\text{S}_2\text{O}_8$ , but the characteristic absorption bands of  $\text{Eu}^{3+}$  remain unchanged in all the glasses (e-h).

The significant effects of strong oxidizing agent  $\text{K}_2\text{S}_2\text{O}_8$  are, therefore, the controlled generation of  $\text{Bi}^0$  NPs and its SPR which results in the elimination of blackening color of bismuth glasses. By comparing the standard reduction potentials,<sup>10</sup> it is clear that the standard reduction potential of  $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$  (2.01 V) is much higher than that of  $\text{Bi}^+/\text{Bi}^0$  (0.50 V),  $\text{Bi}^{3+}/\text{Bi}^0$  (0.31 V),  $\text{Bi}^{3+}/\text{Bi}^+$  (0.20 V) and  $\text{Bi}^{3+}/\text{Bi}^{2+}$  (<0.20 V) species. Consequently, it easily favors the suppression of the formation of  $\text{Bi}^0$  NPs and the glasses gradually become more transparent with increasing  $\text{K}_2\text{S}_2\text{O}_8$  content.

Figure 2 shows the XRD pattern of the glass obtained by using 0.2 wt. % of  $\text{K}_2\text{S}_2\text{O}_8$  (Glass b) as a representative. Although the glasses have not shown very distinct XRD patterns, the unresolved peaks depict around 27.63 and 28.78 degree  $2\theta$  indicate the existence of  $d_{116}$  and  $d_{122}$  Miller planes of rhombohedral metallic bismuth (JCPDS file no. 01-0699). However, TEM image (Fig. 3) of the same glass (Glass b) confirms the clear existence of bismuth nanoparticles. The TEM image shows 10-15 nm size of bismuth nanoparticles. The selected area electron diffraction (SAED) patterns inserted in the inset of Fig. 3, show  $d_{104}$  and  $d_{012}$  planes of bismuth nanoparticles correspond to rhombohedral crystal system (JCPDS file no. 85-1330). These results of TEM and SAED pattern again support that the glass contained  $\text{Bi}^0$  NPs and correlated well with the SPR of  $\text{Bi}^0$  NPs.

In Fig. 4 (A), emission spectra were obtained at 587, 613, 652 and 703 nm due to  $^5D_0 \rightarrow ^7F_1$ ,  $^5D_0 \rightarrow ^7F_2$ ,  $^5D_0 \rightarrow ^7F_3$ , and  $^5D_0 \rightarrow ^7F_4$  transitions respectively of  $\text{Eu}^{3+}$  when excited by 393 nm at a fixed concentration of  $\text{Eu}^{3+}$  for all samples (e, f, g and h). These emission spectra compared with the base glass, it is observed that a peak has appeared at 703 nm in

the base glass. This peak is also present in the glasses containing  $\text{Eu}^{3+}$  ion. To examine the origin of this peak, the emission spectra of all the glasses without containing  $\text{Eu}^{3+}$  has been analyzed. In Fig. 4 (B), the emission spectra at 703 nm of the glasses a, b, c and d has been recorded by excitation at 393 nm. This emission intensity at 703 nm increases with decrease in the intensity of SPR band of bismuth nanoparticles. The excitation spectra at 393 nm for the glasses a, and d have been shown in Fig. 5 to examine the origin of the emission center at 703 nm. The composition and emission centers have also been listed in Table 1. Here, the emission intensity significantly increases with the concentration of  $\text{K}_2\text{S}_2\text{O}_8$ . Therefore, it is reasonable to believe that some emission center of bismuth gradually formed due to oxidation process during suppression of  $\text{Bi}^0$  formation. Various researchers have reported about the different emission centers for the different valence state of bismuth such as  $\text{Bi}^{3+}$ ,  $\text{Bi}^{2+}$  and  $\text{Bi}^+$ .<sup>11-18</sup> However, it is difficult to predict the exact valence state of Bi ion formed during melting process as their reduction potentials are very close to each other as indicated earlier.

The typical luminescence spectra of  $\text{Bi}^{3+}$  centered in the blue to green region when excited in the UV region has been reported by some researchers.<sup>11, 12</sup> The emission due to  $\text{Bi}^+$  has been reported in NIR region.<sup>12-14</sup> Zhou *et al.*<sup>12</sup> have found emission due to  $\text{Bi}^+$  ion in the NIR region centered at 1100 and 1400 nm when excited at 532 and 800 nm respectively. Peng *et al.*<sup>13</sup> have demonstrated NIR emission centered at 1250 nm in the BBSPS glasses, upon optical excitation at 785 nm and this emission center ascribed to  $\text{Bi}^+$  species. The energy levels of  $\text{Bi}^0$  was explained by Peng *et al.*<sup>15</sup> and they assigned red and NIR emission bands due to  $\text{Bi}^0$  at 630 nm and 843 nm to electron transition  $^2D_{5/2} \rightarrow ^4S_{3/2}$  and  $^2D_{3/2} \rightarrow ^4S_{3/2}$  respectively. But, in this study, the luminescence due to  $\text{Eu}^{3+}$

increases instead of decrease with the decrease in  $\text{Bi}^0$  concentration. Therefore, here the possibility of the emission band at 703 nm could not be assigned to  $\text{Bi}^{3+}$ ,  $\text{Bi}^+$  or  $\text{Bi}^0$  species.

Hamstra *et al.*<sup>16</sup> have suggested the red luminescence due to  $\text{Bi}^{2+}$  ion, varying in the range of  $17100\text{-}16000\text{ cm}^{-1}$  (585-625 nm) in the alkaline earth metal sulfates. Ren *et al.*<sup>17</sup> have exposed the visible luminescence spectra excited in the range 400-650 nm. The observed luminescence, when excited within this range, consists of two bands centered between 650 and 760 nm respectively. They assigned this red luminescence as characteristic spectra of  $\text{Bi}^{2+}$ . Such red luminescence bands arise from the electron transition between the first excited level  $^2P_{3/2}(1)$  and ground level  $^2P_{1/2}$  of  $\text{Bi}^{2+}$ . Because the absorption band observed by them is about 500 nm and the red luminescence from the glass are almost the same with the absorption and luminescence from  $\text{Bi}^{2+}$  activated crystals. They have ascribed this peak to the electron transition  $^2P_{1/2} \rightarrow ^2P_{3/2}$  and  $^2P_{3/2} \rightarrow ^2P_{1/2}$ , respectively. Zhou *et al.*<sup>12</sup> have also reported the red emission due to  $\text{Bi}^{2+}$  ion. Taking into account all the above arguments, it is reasonable to assign the observed emission band at 703 nm to the emission of  $\text{Bi}^{2+}$  ions.

Emission intensity of  $\text{Eu}^{3+}$  ions in Fig. 4 (A) increased monotonically with the concentration of  $\text{K}_2\text{S}_2\text{O}_8$  as shown in the inset, evidencing the energy transfer (ET) mechanism from  $\text{Bi}^{2+}$  to  $\text{Eu}^{3+}$  ions. Such energy transfer mechanism can also be well understood from the excitation spectra of the glass a, and d as shown in Fig. 5. The glasses a, and d revealed the excitation center at 393 nm for the emission at 703 nm which also matched well with the excitation wavelength of  $\text{Eu}^{3+}$ . Hence, upon excitation at 393 nm, both  $\text{Bi}^{2+}$  and  $\text{Eu}^{3+}$  ions are simultaneously excited from their ground levels to

the respective higher energy levels  ${}^2P_{3/2}(2)$  and  ${}^5L_6$ . The energy level diagram of  $\text{Bi}^{2+}$  and  $\text{Eu}^{3+}$  ions and possible energy transfer process are schematically presented in Fig. 6. An excited  $\text{Bi}^{2+}$  ion relaxes from  ${}^2P_{3/2}(2)$  to  ${}^2P_{3/2}(1)$  state nonradiatively and transfers the energy to a neighboring  ${}^5D_0$  level of  $\text{Eu}^{3+}$  ions, which is energetically close to each other. Thus, it ( $\text{Bi}^{2+}$ ) enhances the emission intensities of  ${}^5D_0 \rightarrow {}^7F_2$  and  ${}^5D_0 \rightarrow {}^7F_4$  transitions of  $\text{Eu}^{3+}$  ions at 613 and 703 nm respectively. Similar study has been carried out by Guo *et al.*<sup>19</sup>. They have systematically investigated the energy transfer mechanism between luminescent centers of molecule-like, non-plasmonic Ag particles (ML-Ag-particles) and  $\text{Eu}^{3+}$ . They have demonstrated that upon 347 nm excitation, ML-Ag-particles are excited from the ground state to the excited state. Because the excited state of ML-Ag particles and the  ${}^5L_6$  level of  $\text{Eu}^{3+}$  ions are energetically close to each other, energy transfer from ML-Ag-particles to  $\text{Eu}^{3+}$  ions can easily proceed.

## Conclusions

$\text{Eu}^{3+}$  doped  $\text{Bi}^{2+}$ -bismuth glasses nanocomposites containing  $\text{Bi}^{2+}$  were prepared. Luminescence investigations revealed the enhancement of emission intensity of  $\text{Eu}^{3+}$  ion. This enhancement in the emission intensity supposed to be due to energy transfer from  $\text{Bi}^{2+}$  to  $\text{Eu}^{3+}$  ion. This is the first demonstration of energy transfer from  $\text{Bi}^{2+}$  to  $\text{Eu}^{3+}$  ions in bismuth glass. We believe that these findings would certainly facilitate more study on luminescence property of bismuth active centers and its application in photonics.



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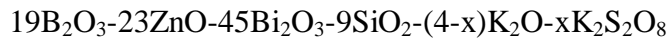
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**Table 1** Chemical composition of the glass and emission centers in the system (wt. %):



Glass identity	Oxidant, $\text{K}_2\text{S}_2\text{O}_8$ content, x, wt. %	Concentration of $\text{Eu}_2\text{O}_3$ in excess, wt. %	Emission center, nm
a	0.0	-	703
b	0.2	-	703
c	1.0	-	703
d	3.0	-	703
e	0.0	0.5	587, 613, 652, 703
f	0.2	0.5	587, 613, 652, 703
g	1.0	0.5	587, 613, 652, 703
h	3.0	0.5	587, 613, 652, 703

## Figure captions

**Fig. 1** (Color online) Absorption spectra of glasses (A) without and (B) with  $\text{Eu}_2\text{O}_3$  contained glasses. For composition, see Table1.

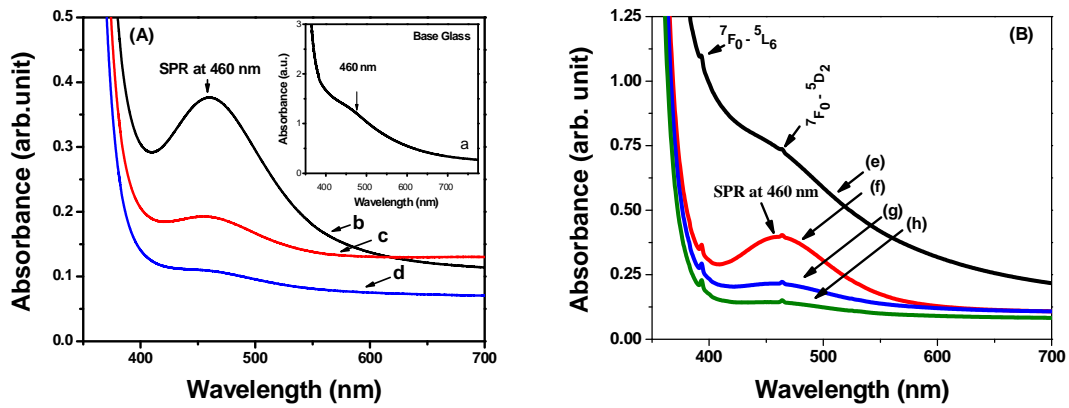
**Fig. 2** X-ray diffraction pattern of the glass obtained by using 0.2 wt. % of  $\text{K}_2\text{S}_2\text{O}_8$ .

**Fig. 3** TEM image of the glass containing 0.2 wt % of  $\text{K}_2\text{S}_2\text{O}_8$ . Its SAED pattern (inset) shows  $\langle 104 \rangle$  and  $\langle 012 \rangle$   $\langle hkl \rangle$  planes of rhombohedral bismuth (JCPDS file 85-1330).

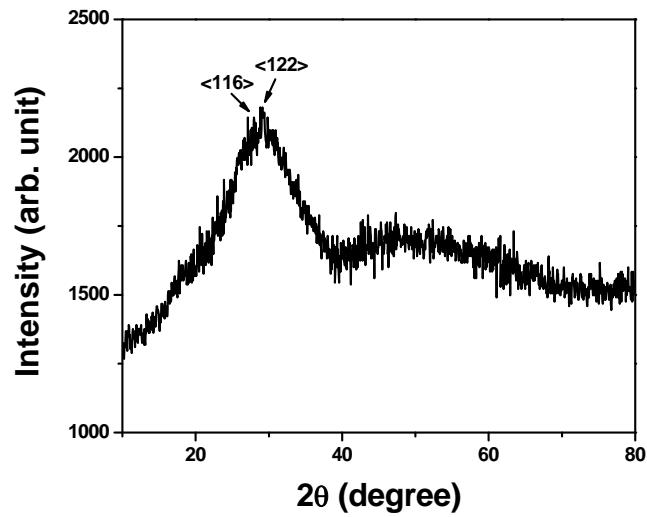
**Fig. 4** (Color online) Photoluminescence (PL) spectra for excitation at 393 nm of (A) with and (B) without  $\text{Eu}_2\text{O}_3$  contained glasses. In insets of (A) and (B), the PL intensities have shown as a function of concentration of  $\text{K}_2\text{S}_2\text{O}_8$ . For composition, see Table1.

**Fig. 5** Photoluminescence excitation (PLE) spectra for emission at 703 nm. For composition, see Table1.

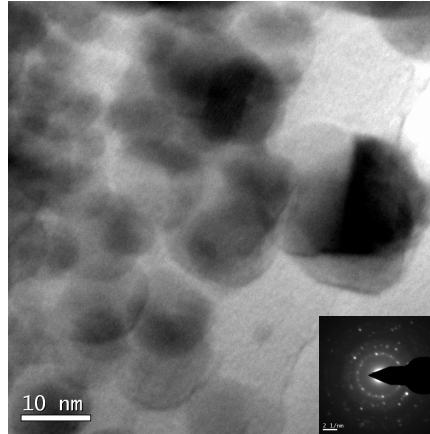
**Fig. 6** Schematic representation of energy transfer from  $\text{Bi}^{2+}$  to  $\text{Eu}^{3+}$  in bismuth glass.



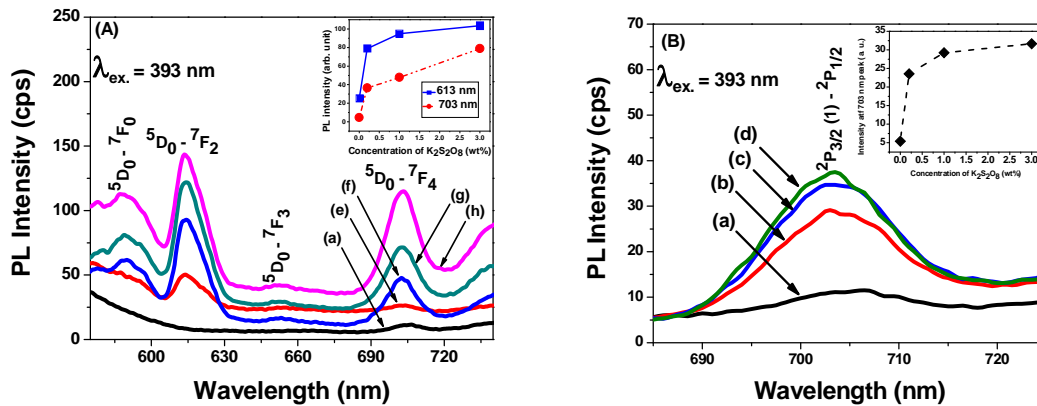
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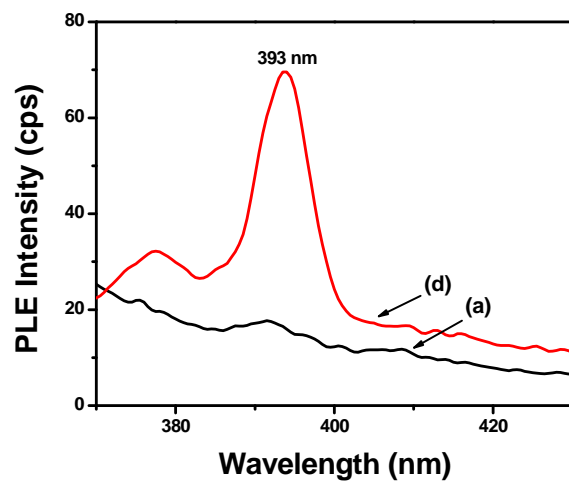
**Fig. 2** X-ray diffraction pattern of the glass obtained by using 0.2 wt. % of  $\text{K}_2\text{S}_2\text{O}_8$ .



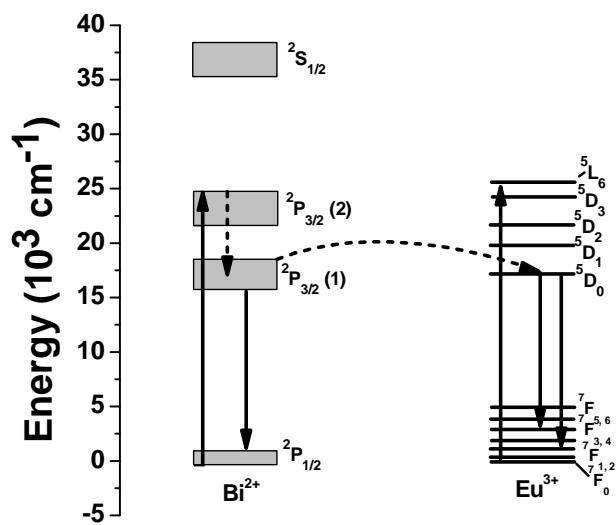
**Fig. 3** TEM image of the glass containing 0.2 wt % of  $K_2S_2O_8$ . Its SAED pattern (inset) shows  $\langle 104 \rangle$  and  $\langle 012 \rangle$   $\langle hkl \rangle$  planes of rhombohedral bismuth (JCPDS file 85-1330).



**Fig. 4** (Color online) Photoluminescence (PL) spectra for excitation at 393 nm of (A) with and (B) without  $Eu_2O_3$  contained glasses. In insets of (A) and (B), the PL intensities have shown as a function of concentration of  $K_2S_2O_8$ . For composition, see Table 1.



**Fig. 5** Photoluminescence excitation (PLE) spectra for emission at 703 nm. For composition, see Table1.



**Fig. 6** Schematic representation of energy transfer from  $\text{Bi}^{2+}$  to  $\text{Eu}^{3+}$  in bismuth glass.