Photoluminescence characteristics and energy transfer between Bi^{3+} and Eu^{3+} in Na_2O–CaO–GeO_2–SiO_2 glass*

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(Received 15 May 2014; revised manuscript received 10 July 2014; published online 10 October 2014)

We report the photoluminescence (PL) of Eu^{3+}-doped glass with Bi^{3+} as a sensitizer. The specific glass system with the strong enhancement of the red emission of Eu^{3+} is obtained by adding a small number of Bi^{3+} ions instead of increasing the Eu^{3+} concentration. The emission band of Bi^{3+} overlaps with the excitation band of Eu^{3+} and the lifetime decay curves, resulting in a very efficient energy transfer from Bi^{3+} to Eu^{3+}. The probability of energy transfer is strongly dependent on Bi^{3+} concentration. In addition, the intensity of 4f–4f transition is much stronger than that of a charge-transfer (CT) band in the excitation spectrum, which indicates that the Na_2O–CaO–GeO_2-SiO_2 glass is a suitable red-emitting phosphor with high stability as a candidate for light-emitting diodes (LEDs).

Keywords: germinate glass, energy transfer, thermal quenching

PACS: 78.55.–m **DOI:** 10.1088/1674-1056/23/12/127803

1. Introduction

The spectroscopic properties of Eu^{3+} ion have been extensively investigated in different host materials due to their intense red emissions.[1–3] Many Eu^{3+}-doped materials are of commercial importance in the display devices as efficient red emitting phosphors and light-emitting diodes (LEDs). White light can be produced by using the ultraviolet (UV) LED chip (390 nm–410 nm) and the combination of red/green/blue tricolor phosphors. At present, a white-light LED (W-LED) with a blue InGaN chip (450 nm–470 nm) in combination with a yellow phosphor (YAG:Ce^{3+}) is commercially available.[4] However, such a combination exhibits a poor color rendering index (< 80) because of the lack of a red light component.[5] So the red phosphor plays an important role. Nevertheless, the red light emitting phosphors for a white LED are commercially limited to Eu^{3+} ions activated nitrides and sulfides with the obvious drawbacks such as being thermally unstable and very sensitive to moisture.[6] Some people try to apply commercial red phosphors with better performance to a W-LED field, such as Y_2O_2S:Eu^{3+}, Y_2O_3:Eu^{3+}, and $GdBO_3$:Eu^{3+}. But there are still many issues to be resolved in those commercial red phosphors, such as low luminous efficiency, chemical instability, and easily biodegradable.

Compared with the conventional phosphor, luminescent glass is a promising phosphor candidate for W-LEDs due to its specific advantages such as easy formation of any shape, higher transparency, simpler manufacture procedure, and environment protection. On the other hand, luminescent glass exhibits merits, such as resistance of hydrolysis, UV, and acid. As is well known Bi^{3+} usually acts as a sensitizer for Eu^{3+} in a variety of hosts such as rare earth oxides, phosphates, silicates, tungstates, molybdates, and vanadates.[7–11] In Bi^{3+}/Eu^{3+} co-doped phosphors, strong red emission can be obtained by adding Bi^{3+} instead of increasing the concentration of Eu^{3+}, which is of great value in improving luminescence efficiency of the red phosphor at a much lower cost.

At present, although researches on luminescent glasses primarily focus their efforts on phosphate, silicate, and borate-based glasses, the poor chemical stability as well as the physical properties of phosphate and borate-based glasses restrict their applications. In this work, we consider a red photoluminescence (PL) from a Eu^{3+}, Bi^{3+} co-doped germinate-silicate Na_2O–CaO–GeO_2–SiO_2 (NCGS) glass system to enhance luminous efficiency. We mainly report on its synthesis, the PL properties, and thermal quenching properties as well as its potential application in W-LEDs.

2. Experiment

For the present study, the glass-forming system of Na_2O–CaO–GeO_2–SiO_2 was chosen to be host for Eu^{3+} and Bi^{3+} due to the generally high rare earth solubility which occurs in silicates. Precursor glasses with nominal compositions of $14Na_2O$–$(7-x-y)$CaO–$57GeO_2$–$22SiO_2$–xEu_2O_3–yBi_2O_3 (mol%, NCGS-x Eu^{3+}, $y$$Bi^{3+}$; $x = 0.03$, 0.06, 0.12, 0.2, 0.25. 0.32. 0.45. 0.65, and 0.8, $y = 0.0006$, 0.0012, 0.0018, 0.0024, 0.0030, and 0.0036) were melted conventionally from batches of Na_2CO_3 (99.99%), $CaCO_3$ (99.99%), GeO_2 (99.99%), SiO_2 (99.99%) in alumina crucibles at 1500 °C for 1 h in

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11204113 and 61308091) and the Specialized Research Fund for the Doctoral Program of Higher Education of China (Grant No. 20115314120001).

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air. Melts were poured into a preheated graphite mold and annealed at 550 °C for 4 h to obtain stress-free glass slabs. These were cut into disks of ∼ 15 mm×13 mm×3 mm and polished on both sides.

The PL and photoluminescence excitation (PLE) spectra of the samples were measured by using an FLS-920T fluorescence spectrophotometer equipped with a 450-W Xe light source and double excitation monochromator. The PL decay curves were measured by an FLS-920T fluorescence spectrophotometer equipped with an nF900 nanosecond flash lamp as a light source. The thermal quenching was tested using a heating apparatus (TAP-02) in combination with PL equipment.

3. Results and discussion

The PL and PLE spectra of NCGS:Eu^{3+} glasses are shown in Fig. 1. The excitation spectrum by monitoring the $^5D \rightarrow {}^7F_2$ emission (612 nm) of Eu^{3+} ions consists of a broad band and a sharp line from the characteristic intra-configurational 4f–4f transition: 393 nm ($^7F \rightarrow {}^5L_6$). The broad excitation band centered at 300 nm can be ascribed to the charge-transfer (CT) transition band of Eu^{3+}–O^{2-}. Upon the excitation of 393 nm, Eu^{3+} ions emit intense red light beams with main peaks at 591, 612, 659, and 705 nm, which are assigned to $^5D \rightarrow {}^7F_J$ ($J = 1$, 2, 3, and 4) transition respectively. The emission spectra of NCGS:Eu^{3+} glass show that the most intense peak is located at 612 nm, which corresponds to the electric-dipole $^5D \rightarrow {}^7F_2$ transition of Eu^{3+}in this glass without inversion symmetry. A suitable phosphor with emitting UV-LED should exhibit absorption around 400-nm (LED excitation wavelength). Obviously, the excitation spectra indicate that NCGS:Eu^{3+}-glasses can be efficiently excited by the radiation of UV-emitting InGaN-based LED chips. Compared with the other reported Eu^{3+}-doped red-emitting materials, Eu^{3+}-doped NCGS glasses have some different characteristics as stated below.

The NCGS:Eu^{3+} glass exhibits efficient absorption around 400 nm (4f–4f transition of Eu^{3+} ions), which is much stronger than the absorption in the CT region. Usually, the 4f–4f transition of Eu^{3+}ions is a forbidden transition with a low oscillator strength ($< 10^{-6}$), so the absorption of InGaN LED radiation by Eu^{3+} ions will be weak. In other words, in each of the Eu^{3+}-doped phosphors such as Y_2O_2S:Eu^{3+}, Y_2O_3:Eu^{3+},[12] and RBO_3:Eu^{3+} ($R = Y^{3+}$, La^{3+}, Gd^{3+}).[13] the intensity of the CT band is much stronger than that of the 4f–4f transition in the excitation spectrum. Nevertheless, the excitation intensities of the 4f–4f transition in NCGS: Eu^{3+} glasses are different from those in commercial phosphors. This is due to the nature of the host structures of NCGS: Eu^{3+} glasses. Van der Voort and Blasse have investigated the influence of an effective charge at the Eu^{3+} ion on the quantum efficiency under the CT excitation (q_{CT}) in the calcium compound. The Eu^{3+} ion is subject to a high rate of a radiationless process in its excited CT state if it is incorporated into a calcium compound. Van der Voort and Blasse have suggested that in some calcium compounds the ions with intra-ionic transitions seem to show efficient luminescences if they have a positive effective charge. Whereas ions with an interionic transition (CT between Eu^{3+} and O^{2-}) show the weak luminescences. A positive effective charge gave rise to a large relaxation in the CT state and a low q_{CT} value.[14] For a negative effective charge the relaxation was predicted to be low and q_{CT} was high.[15] In an NCGS:Eu^{3+} glass, the low intensity of the CT band of Eu^{3+} ions could follow this model. This can match the emission of UV-emitting InGaN-based LED chips.

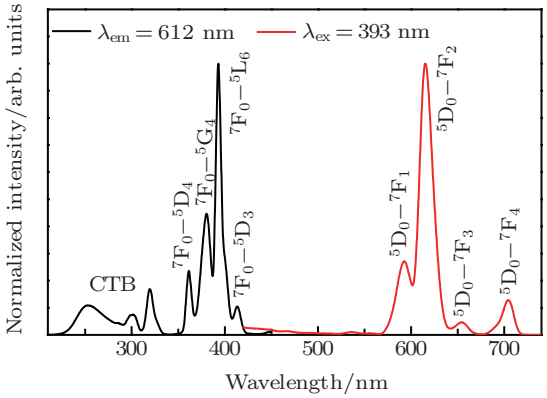


Fig. 1. (color online) PL and PLE spectra of NCGS:0.2-mol%Eu^{3+} glass excited at 393 nm and monitored at 612 nm.

In order to study the influence on this kind of red-emitting glass after the co-dopant of Bi^{3+} ions, the excitation spectra of NCGS:0.2-mol%Eu^{3+} and NCGS:0.2-mol%Eu^{3+}, 0.003-mol%Bi^{3+} at 612 nm ($^5D \rightarrow {}^7F_2$) are shown in Fig. 2(a). It is easy to conclude that for the Bi^{3+}/Eu^{3+} co-doped NCGS glass, the 300-nm excitation band is greatly enhanced compared with NCGS: Eu^{3+} glass. The inset shows the excitation spectrum for NCGS:Bi^{3+} at 403 nm. It is assigned to the $^1S_0 \rightarrow {}^3P_1$ transition of Bi^{3+}, and this phenomenon could be due to Bi^{3+} doping. In order to further study the PL properties of Bi^{3+}/Eu^{3+} co-doped NCGS glass under 300-nm excitation, the PL spectrum of NCGS:0.32-mol%Eu^{3+} glass, and that of NCGS:0.32-mol%Eu^{3+} plus 0.0030-mol%Bi^{3+} glass both under 300-nm excitation are presented in Fig. 2(b). This figure shows that the PL spectrum of Bi^{3+}/Eu^{3+} co-doped NCGS glass exhibits strong emission peaks from the $^5D \rightarrow {}^7F_J$ ($J = 1$, 2, 3, and 4) transitions of Eu^{3+}. When compared with NCGS:Eu^{3+} glasses, the Bi^{3+}/Eu^{3+} co-doped NCGS glass exhibits a characteristic emission peak of Bi^{3+}. The overlap between the PL spectrum of Bi^{3+} ions and PLE spectrum of Eu^{3+} ions can be observed in Fig. 2(c), so Eu^{3+} ions may be sensitized by Bi^{3+} ions through the ET process.

The PL spectra of NCGS:xEu^{3+}, 0.003-mol%Bi^{3+} glasses (0.03 mol% $\leq x \leq$ 0.80 mol%) are presented in

Fig. 2(d). Among all the emission spectra, the electric-dipole $^5D \rightarrow {}^7F_2$ transition of Eu^{3+} has the strongest intensity, which is a consequence of Eu^{3+} without an inversion symmetry in NCGS glass. The PL intensity of $^5D \rightarrow {}^7F_2$ transition grows as Eu^{3+} concentration x increases. Under the excitation of 300 nm, the emission spectra NCGS:0.003-mol%Bi^{3+} x-mol%Eu^{3+} present not only a strong blue band of the Bi^{3+} ions but also a strong red band of the Eu^{3+} ions. By increasing the Eu^{3+} content, the distance between Eu^{3+} and Bi^{3+} ions becomes smaller, and the probability of energy transfer increases. The emission intensity of the Eu^{3+} ions increases systematically and reaches saturation as x is about 0.80, whereas the intensity of Bi^{3+} sensitizer is found to decrease remarkably from $x = 0.03$ to 0.80. The result affirmed that there is an energy transfer from the Bi^{3+} to Eu^{3+} ions in the NCGS:Bi^{3+} Eu^{3+} glass.

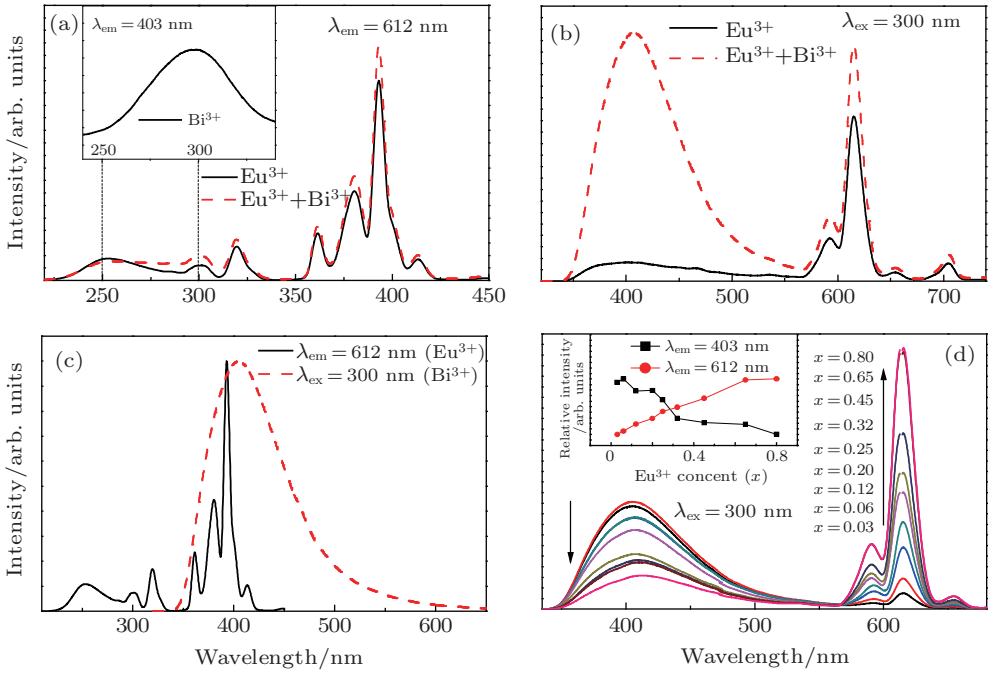


Fig. 2. (color online) (a) Excitation spectra for NCGS: 0.2-mol%Eu^{3+} and NCGS:0.2-mol% Eu^{3+}, 0.003-mol%Bi^{3+} monitored at 612 nm. The inset shows the excitation spectrum for NCGS:0.003-mol%Bi^{3+}. (b) PL spectra of NCGS:0.32-mol%Eu^{3+} glass and NCGS: 0.32-mol%Eu^{3+} plus 0.003-mol%Bi^{3+} glass ($\lambda_{ex} = 300$ nm). (c) Spectrum overlap between the PL spectra of NCGS:0.003-mol%Bi^{3+} glass (dashed line) and PLE spectrum of NCGS:0.32-mol%Eu^{3+} glass (solid line). (d) PL spectra of NCGS:x-mol%Eu^{3+}, 0.003-mol%Bi^{3+} glasses ($\lambda_{ex} = 300$ nm). The insert shows the relative excitation intensities at 403 nm and 612 nm each as a function of Eu^{3+} content.

As shown in Fig. 3, the decay curves for the $^3P_1 \rightarrow {}^1S_0$ transition of Bi^{3+} in both samples exhibit double-exponential behaviors. The decay curves for Bi^{3+} emission can be well fitted to a double exponential function as

$$I(t) = I_0 + A_1 \exp(-t/t_1) + A_2 \exp(-t/t_2),$$

where I and I are the luminescence intensities at times t and 0, A_1 and A_2 are constants, t is time, and t_1 and t_2 are decay times for the exponential components, respectively. Further, the average decay lifetimes (t) can be calculated as

$$t = \left(A_1 t_1^2 + A_2 t_2^2\right) / \left(A_1 t_1 + A_2 t_2\right).$$

Thus the average lifetimes of Bi^{3+} in NCGS:0.003-mol% Bi^{3+} and NCGS:0.20-mol%Eu^{3+} plus 0.003-mol%Bi^{3+} can be determined as 0.84 ms and 0.66 ms, respectively. This can be explained as the introduction of the extra decay pathways due to the energy transfer from Bi^{3+} to Eu^{3+}.

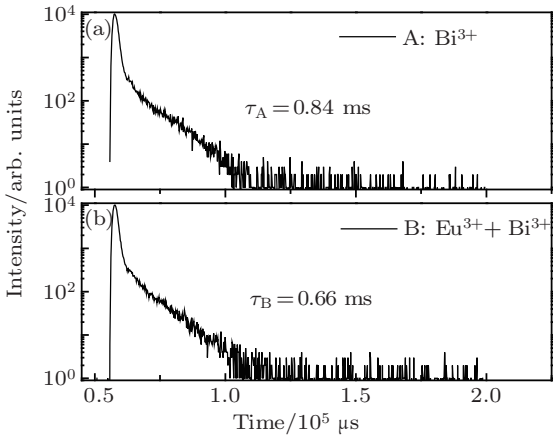


Fig. 3. (color online) Decay curves for the luminescence of Bi^{3+} ions in (a) NCGS:0.003-mol%Bi^{3+} glass and (b) NCGS:0.003-mol%Bi^{3+}, 0.64-mol%Eu^{3+} glass, both excited at 300 nm and monitored at 403 nm.

According to the energy transfer from Bi^{3+} to Eu^{3+}, the emission spectra of different concentration Bi^{3+}-doped glasses are presented in Fig. 4. With the increase of Bi^{3+}

concentration, the emission intensities of Bi^{3+} and Eu^{3+} are greatly enhanced, and reach their highest values when $y = 0.0024$ and $y = 0.0030$, respectively. The concentration quenching of Bi^{3+} happens when Bi^{3+} ion concentration is over 0.0030. In conclusion, the Eu^{3+} ions could be sensitized by Bi^{3+} ions through the ET process based on the above analysis. Through the inset, it is easy to find that the Bi^{3+}/Eu^{3+} co-doped NCGS glass emission band is greatly strengthened compared with NCGS:Eu^{3+} glass excited at 393 nm. Owing to the above experiment, red PL glasses of this kind can be efficiently excited by the emission of UV-emitting InGaN-based LED chips.

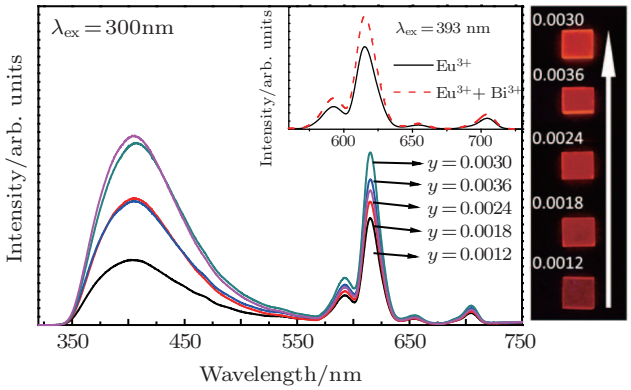


Fig. 4. (color online) PL spectra of NCGS:0.65-mol% Eu^{3+}, y mol%Bi^{3+} glasses (λ_{ex} = 300 nm). The insert shows PL spectra of NCGS:0.65-mol%Eu^{3+} glass and NCGS:0.65-mol%Eu^{3+} plus 0.0024-mol%Bi^{3+} glass (λ_{ex} = 393 nm). The images show the samples under UV box.

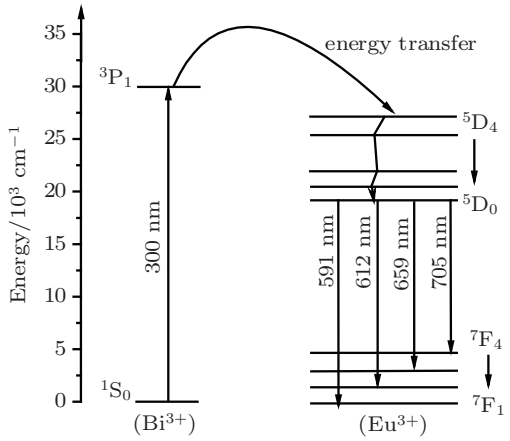


Fig. 5. Energy level model for the ET process of $Bi^{3+} \rightarrow Eu^{3+}$ in NCGS glass.

Figure 5 illustrates the energy level model for the ET process of $Bi^{3+} \rightarrow Eu^{3+}$ in NCGS glass. The probability of ET between Bi^{3+} and Eu^{3+} increases as the concentration of Bi^{3+}/Eu^{3+} increases due to more neighboring Bi^{3+} ions around Eu^{3+} ions. Eu^{3+} ions can strongly absorb near UV light from the ground state ($^1S_0$) to the excited states, and then efficiently transfer the energy to the $^5D_4$ level of Eu^{3+} ions. Subsequently, the $^5D_4$ level gives its characteristic transitions or continues to transfer the energy to the $^5D_3 \rightarrow {}^5D_0$ level via cross relaxation.[16–19] Then a set of characteristic optical transitions $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 3, 4) situated at about 591, 612, 659, and 705 nm are exhibited.

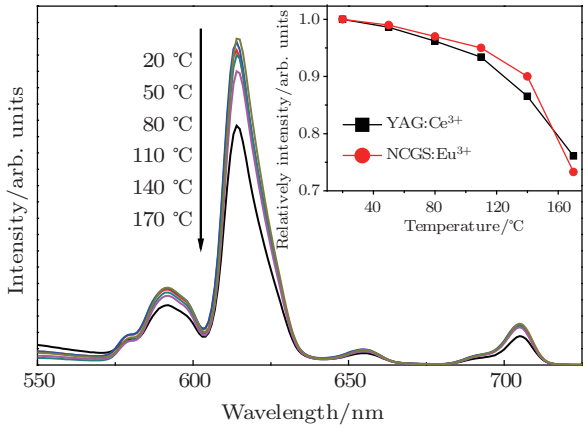


Fig. 6. (color online) Temperature-dependent emission intensities of the optimized NCGS:0.65-mol%Eu^{3+}, 0.0030-mol%Bi^{3+} glass. Inset shows temperature-dependent relative emission intensities of this sample glass and commercial YAG:Ce^{3+}.

The thermal quenching property is one of the important technological parameters for phosphors used in solid-state lighting for it has considerable influences on the light output and color rendering index. The temperature-dependent emission spectra for NCGS:0.65-mol%Eu^{3+}, 0.0030-mol%Bi^{3+} glass under excitation at 393nm are measured and illustrated in Fig. 6. The inset displays a comparison of the thermal luminescence quenching between our glass and the commercial yellow phosphor YAG:Ce^{3+} (Mitsubishi Chemical Corporation, Japan). As can be seen in Fig. 7, the thermal stability of NCGS:0.65-mol%Eu^{3+}, 0.0030-mol%Bi^{3+} glass is inferior to that of YAG:Ce^{3+} when the temperature is above 160 °C, though the intensities of both of them drop down to about 75% of its initial value at a temperature of 170 °C. The observation can be rationalized by the fact that increasing the temperature enhances the population of higher vibration levels, the density of phonons and the probability of non-radiative transfer (energy migration to defects).[20] For use in high power LEDs, the temperature is no more than 150 °C generally, so this kind of glass has a better application prospect in power LEDs. Much attention has been focused on the thermal quenching mechanism of the $^5D \rightarrow {}^7F_2$ emission of Eu^{3+} ions, which demonstrates that the crossover process is responsible for the temperature quenching of the ^5D emission.[21–24] The crossover quenching is a thermal activation process in which the population at the $^5D_0$ level can overcome the energy barrier and migrate to the low-lying $Eu^{3+} \rightarrow O^{2-}$ CTB and finally relax to ^7F_J levels. The crossover process can be described by the Arrhenius-type activation model as[24,25]

$$I(T) = I_0 [1 + A \exp(-\Delta E/kT)]^{-1},$$

where I is the intensity at a given temperature, I_0 is the initial intensity, k is the Boltzmann constant, T is the temperature, and ΔE is the activation energy from the $^5D_0$ state to the CTB and can be regarded as a constant because the shape of the emission curve does not change significantly. As displayed in Fig. 7, the experimental data can be well fitted to a straight line, indicating that the temperature quenching process complies well with the Arrhenius-type activation model. The activation energy of the NCGS:0.65-mol%Eu^{3+} plus 0.0030-mol%Bi^{3+} glass is calculated as 0.31 eV.

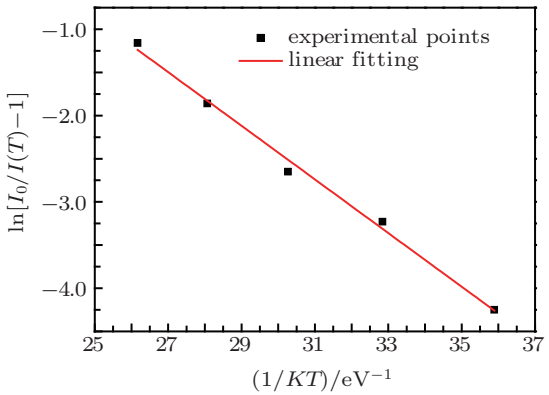


Fig. 7. (color online) The calculated activation energy for thermal quenching of the NCGS:0.65-mol%Eu^{3+} plus 0.0030-mol%Bi^{3+} glass.

4. Conclusion

In this paper, we prepare Eu^{3+}/Bi^{3+} co-doped NCGS glasses and investigate their luminescence properties. The most intense red emission at 612 nm originating from the electric dipole $^5D \rightarrow {}^7F_2$ transition of Eu^{3+} indicates that Eu^{3+} has no inversion symmetry in NCGS glass. The NCGS glass exhibits efficient absorption around 400 nm (4f–4f transition of Eu^{3+} ions), which is much stronger than the absorption in the CT region. This performance signifies that Bi^{3+}/Eu^{3+} co-doped glass can be efficiently excited by the emission of UV-emitting InGaN-based LED chips. According to ET between Bi^{3+} and Eu^{3+} ions, we find that the Bi^{3+}/Eu^{3+} co-doped NCGS glass emission band is greatly strengthened under 393-nm excitation compared with NCGS:Eu^{3+} glass emission band. The thermal quenching properties of NCGS glasses are better than those of YAG:Ce^{3+} phosphors when the temperature is under 160 °C. The Bi^{3+}/Eu^{3+} co-doped glasses can be efficiently excited by the emission of UV-emitting InGaN-based LED chips.

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