


 Cite this: *RSC Adv.*, 2023, 13, 6861

Optical band gaps and spectroscopy properties of Bi^{m+}/Euⁿ⁺/Yb³⁺ co-doped (*m* = 0, 2, 3; and *n* = 2, 3) zinc calcium silicate glasses†

 Ho Kim Dan,^{id}*^{ab} Nguyen Dinh Trung,^{cd} Nguyen Minh Tam,^{id}^e L. T. Ha,^f C. V. Ha,^{id}^g Dacheng Zhou^h and Jianbei Qiu^h

In this study, the indirect/direct optical band gaps and spectroscopy properties of Bi^{m+}/Euⁿ⁺/Yb³⁺ co-doped (*m* = 0, 2, 3; and *n* = 2, 3) zinc calcium silicate glasses under different excitation wavelengths were investigated. Zinc calcium silicate glasses with the main compositions of SiO₂–ZnO–CaF₂–LaF₃–TiO₂ were prepared by the conventional melting method. EDS analysis was performed to determine the elemental composition existing in the zinc calcium silicate glasses. Visible (VIS)-, upconversion (UC)-, and near-infrared (NIR)-emission spectra of Bi^{m+}/Euⁿ⁺/Yb³⁺ co-doped glasses were also investigated. Indirect optical band gaps and direct optical band gaps of Bi^{m+}-, Euⁿ⁺- single-doped, and Bi^{m+}–Euⁿ⁺ co-doped SiO₂–ZnO–CaF₂–LaF₃–TiO₂–Bi₂O₃–EuF₃–YbF₃ zinc calcium silicate glasses were calculated and analyzed. CIE 1931(*x*, *y*) color coordinates for VIS and UC emission spectra of Bi^{m+}/Euⁿ⁺/Yb³⁺ co-doped glasses were determined. Besides, the mechanism of VIS-, UC-, NIR-emissions, and energy transfer (ET) processes between Bi^{m+} and Euⁿ⁺ ions were also proposed and discussed.

Received 18th November 2022

Accepted 2nd February 2023

DOI: 10.1039/d2ra07310b

rsc.li/rsc-advances

1. Introduction

During the last several decades, the optical band gaps and spectroscopy properties of host materials single-doped by a rare earth (RE) atom as well as co-doped by rare earth ions (REIs), or doped by REIs together with transition metals (TMs)^{1,2} or pnictogen³ have been extensively studied due to their great potential for applications in many technological fields such as displays, solar cells, and medical diagnosis.^{4–6} Among the REIs, europium ions (Euⁿ⁺) have attracted much research interest, particularly in lighting, light emitting diodes (LED), white LED (WLED), and display applications owing to

the Euⁿ⁺ ions favoring existing in two valence states as the Eu³⁺ trication and Eu²⁺ dication in glass materials with ⁵D₀ → ⁷F_{*J*} (*J* = 0, 1, 2, 3, and 4) and 4f⁶5d¹ → 4f⁷ transitions, respectively.^{7,8} Visible (VIS) emission spectra of Eu³⁺/Eu²⁺ ions can emit blue, green, orange, orange-red, and red color light depending on the different excitation wavelengths and host materials.^{9,10} Bismuth (Bi) element is the post-transition metal belonging to the pnictogen group; Bi exhibits many optoelectronic properties and exists in various valence states such as Bi⁵⁺, Bi³⁺, Bi²⁺, Bi⁺, and Bi⁰ depending on the experimental conditions and the host materials. In the VIS wavelength region, the ¹P₁ → ¹S₀ transition of Bi³⁺ ions can emit blue color light,^{11,12} and the ²S_{1/2}-, ²P_{3/2}(2)-, ²P_{3/2}(1)- → ²P_{1/2} transitions of Bi²⁺ ions can emit orange, orange-red, and red color light, respectively.^{12,13} In the near-infrared (NIR) wavelength region, the ³P₂-, ³P₁- → ³P₀ transitions of Bi⁺ ions and the ²D_{3/2}- → ⁴S_{3/2} transition of Bi⁰ neutral can produce NIR emission bands from ~1.0 to 1.35 μm.^{14,15} In addition, Bi^{m+} (*m* = 0, 2, and 3) ions can combine with the ²F_{5/2} → ²F_{7/2} transition of Yb³⁺ ions to generate NIR emission spectra in the ~950 nm to 1350 nm wavelength region.^{16,17} Therefore, NIR emission spectra of Bi^{m+}–Yb³⁺ have been extensively studied with the aim of improving the efficiency and quantum effect of NIR emission spectra utilized in solar cell applications.^{18,19} In recent years, many investigations focusing on the energy transfer (ET) processes from Bi^{m+} to Eu³⁺ ions that can be color-tuned in the VIS emission to create light bands with different colors have been carried out. The obtained results

^aOptical Materials Research Group, Science and Technology Advanced Institute, Van Lang University, Ho Chi Minh City, Vietnam

^bFaculty of Applied Technology, School of Technology, Van Lang University, Ho Chi Minh City, Vietnam. E-mail: hokimdan@vlu.edu.vn

^cCenter for Analysis and Testing, Dalat University, Lam Dong, Vietnam

^dFaculty of Chemistry and Environment, Dalat University, Lam Dong, Vietnam

^eFaculty of Basic Sciences, University of Phan Thiet, 225 Nguyen Thong, Phan Thiet City, Binh Thuan, Vietnam

^fInstitute of Science and Technology, TNU-University of Sciences, Thai Nguyen, 250000, Vietnam

^gFaculty of Physics, TNU-University of Education, Thai Nguyen, 250000, Vietnam

^hKey Laboratory of Advanced Materials of Yunnan Province, School of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d2ra07310b>



confirmed that the energy was transferred from Bi³⁺ and Bi²⁺ ions to ⁵D₀ → ⁷F_{*J*} (*J*=0, 1, 2, 3, and 4) transitions of Eu³⁺ and thus color-tuned the VIS emission spectra of Eu³⁺/Eu²⁺ ions.^{20–23} Besides, the measurement and calculation of the optical band gap parameters of REIs doped in different host materials have also been performed to determine the optical band gap energy (*E_g*) value of REIs in the host materials²⁴ and thereby directing the relevant optical applications such as color display, LED, WLED, and solar energy. Zinc silicate glasses can be used for optical material applications due to their advantages such as high thermal expansion properties,²⁶ relatively low glass transition temperature (*T_g*), and the value of $\Delta T = T_c - T_g$ greater than 100.²⁵ Based on these advantages as well as the results obtained from a recent study,²⁵ in this work, we chose zinc calcium silicate glass as the host material. In addition, Na₂O was replaced by CaF₂ to enhance the self-reduction process from Eu³⁺ to Eu²⁺ ions through F⁻ ions.⁸ Simultaneously, we investigated and reported the results concerning the direct/indirect optical band gaps, VIS-, UC-, and NIR-emission spectra of Bi^{*m+*}/Eu^{*n+*}/Yb³⁺ co-doped in SiO₂-ZnO-CaF₂-LaF₃-TiO₂ (SZC) zinc calcium silicate glasses. Remarkably, through analyzing the optical properties of Bi^{*m+*}/Eu^{*n+*}/Yb³⁺ co-doped, we have also calculated and determined the direct/indirect optical band gaps values, CIE 1931 (*x*, *y*) color coordinates to develop for LED, WLED, and display applications.

2. Experimental materials and methods

2.1. Materials

Raw materials of SiO₂, ZnO, CaF₂, LaF₃, TiO₂, Bi₂O₃, EuF₃, and YbF₃ used in the experiments of this study are high-purity laboratory-grade materials (99.99%). Chemical compositions and ratios for each glass sample are listed in detail in Table 1.

2.2. Experimental methods

The raw material mixtures weighing 12 g for each experimental glass sample were crushed with an onyx mortar and pestle.^{8,27} These mixtures were compacted into platinum crucibles with lids.⁸ The platinum crucibles with lids were then placed in an electric furnace to melt at 1600 °C for 1 hour using the conventional melting method.^{8,27} After melting, the mixture was quenched on the surface of the polished stainless steel plate to form the glass.⁸ Glass samples were heat treated at 520 °C for 6 hours^{8,25} to increase mechanical strength and reduce the possibility of breakage when cut. For the convenience and accuracy of optical measurements, glass samples were cut to the size of 10 mm × 10 mm × 2 mm with polished surfaces and edges.⁸ Details for EDS analysis, absorption spectra, VIS-, UC-, and NIR-emission spectra measuring and analyzing devices have been described in detail in our recent studies.^{8,27–29}

3. Results and discussion

3.1. EDS analysis

Fig. 1 shows the results of the EDS spectrum analysis of the SZC-1.0Bi0.6Eu2Yb zinc calcium silicate glass sample. Energy levels at ~0.45 and 4.51 keV were determined for titanium (Ti) element,³⁰ energy levels at ~2.42 and 10.84 keV were determined for the Bi element, energy levels at ~0.83 and 4.65 keV were attributed to lanthanum (La) element.³⁰ Energy levels of the Eu element were defined at ~1.13 and 5.85 keV.³⁰ Energy levels of the ytterbium (Yb) element were also defined at ~1.52 and 7.41 keV. Energy levels at ~0.53, 0.68, 1.74, 3.69, and 8.63 keV were determined for oxygen (O), fluorine (F), silicon (Si), calcium (Ca), and zinc (Zn) elements, respectively.^{30,31} The element composition table including weight and atomic percentages of the SZC-1Bi0.6Eu2Yb zinc calcium silicate glass sample inserted in Fig. 1 also described in detail the

Table 1 Chemical compositions and ratios of SiO₂-ZnO-CaF₂-LaF₃-TiO₂-Bi₂O₃-EuF₃-YbF₃ glasses

| Notation of glass samples | Chemical compositions and ratios of glasses (in mol%) | | | | | | | |
|---------------------------|---|-----|------------------|------------------|------------------|--------------------------------|------------------|------------------|
| | SiO ₂ | ZnO | CaF ₂ | LaF ₃ | TiO ₂ | Bi ₂ O ₃ | EuF ₃ | YbF ₃ |
| SZC-1Bi | 45 | 25 | 15 | 10 | 4 | 1.0 | 0 | 0 |
| SZC-0.6Eu | 45 | 25 | 15 | 9.4 | 5 | 0 | 0.6 | 0 |
| SZC-1Bi0.6Eu | 45 | 25 | 15 | 9.4 | 4 | 1.0 | 0.6 | 0 |
| SZC-1.8Bi0.6Eu | 45 | 25 | 15 | 9.4 | 3.2 | 1.8 | 0.6 | 0 |
| SZC-1.0Bi0.6Eu2Yb | 45 | 25 | 15 | 7.4 | 4 | 1.0 | 0.6 | 2.0 |
| SZC-1.2Bi0.6Eu2Yb | 45 | 25 | 15 | 7.4 | 3.8 | 1.2 | 0.6 | 2.0 |
| SZC-1.4Bi0.6Eu2Yb | 45 | 25 | 15 | 7.4 | 3.6 | 1.4 | 0.6 | 2.0 |
| SZC-1.6Bi0.6Eu2Yb | 45 | 25 | 15 | 7.4 | 3.4 | 1.6 | 0.6 | 2.0 |
| SZC-1.8Bi0.6Eu2Yb | 45 | 25 | 15 | 7.4 | 3.2 | 1.8 | 0.6 | 2.0 |
| SZC-1.8Bi0.7Eu2Yb | 45 | 25 | 15 | 7.3 | 3.2 | 1.8 | 0.7 | 2.0 |
| SZC-1.8Bi0.8Eu2Yb | 45 | 25 | 15 | 7.2 | 3.2 | 1.8 | 0.8 | 2.0 |
| SZC-1.8Bi0.9Eu2Yb | 45 | 25 | 15 | 7.1 | 3.2 | 1.8 | 0.9 | 2.0 |
| SZC-1.8Bi1.0Eu2Yb | 45 | 25 | 15 | 7 | 3.2 | 1.8 | 1.0 | 2.0 |
| SZC-1.8Bi0.6Eu2.2Yb | 45 | 25 | 15 | 6.8 | 3.2 | 1.8 | 0.6 | 2.2 |
| SZC-1.8Bi0.6Eu2.4Yb | 45 | 25 | 15 | 6.6 | 3.2 | 1.8 | 0.6 | 2.4 |
| SZC-1.8Bi0.6Eu2.6Yb | 45 | 25 | 15 | 6.4 | 3.2 | 1.8 | 0.6 | 2.6 |
| SZC-1.8Bi0.6Eu2.8Yb | 45 | 25 | 15 | 6.2 | 3.2 | 1.8 | 0.6 | 2.8 |

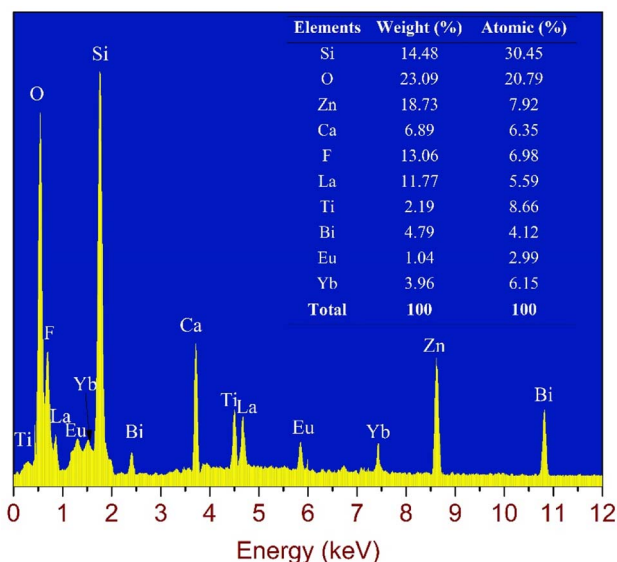


Fig. 1 EDS spectrum of SZC-1.0Bi0.6Eu2Yb zinc calcium silicate glass sample.

proportions of elements present in the host glass. From the results of the EDS analysis, it can be seen that all elements Si, O, Zn, Ca, F, La, Ti, Bi, Eu, and Yb presenting in $\text{SiO}_2\text{-ZnO-CaF}_2\text{-LaF}_3\text{-TiO}_2\text{-Bi}_2\text{O}_3\text{-EuF}_3\text{-YbF}_3$ raw materials were distributed and existed in zinc calcium silicate glass matrix.

3.2. Absorption spectra

Absorption spectra of SZC-1.0Bi, SZC-0.6Eu, and SZC-1.0Bi0.6Eu zinc calcium silicate glass samples in the wavelength range from 300 to 1200 nm are shown in Fig. 2. Curve (a) (black curve) in Fig. 2 is the absorption spectrum of Bi^{m+} ions which has three main bands, generated by the transitions of Bi^{m+} ions, with the peaks at ~ 458 , 653, and 700 nm, corresponding to $^1\text{S}_0 \rightarrow ^3\text{P}_1$ transition of Bi^{3+} ions,^{11,18,29} $^4\text{S}_{3/2} \rightarrow ^2\text{P}_{1/2}$ transition of Bi^0

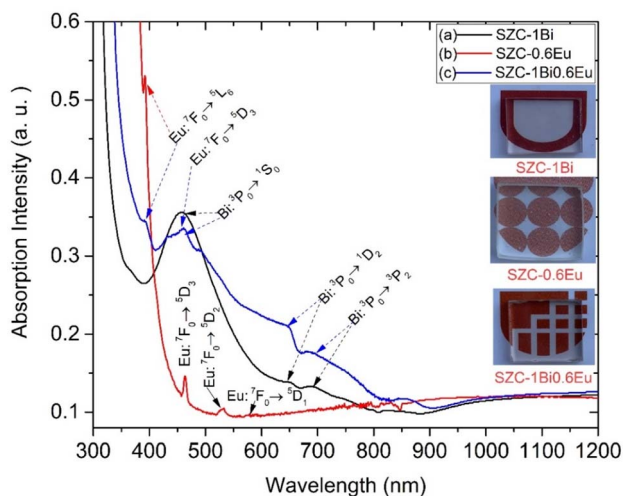


Fig. 2 Absorption spectra of SZC-1.0Bi, SZC-0.6Eu, and SZC-1.0Bi0.6Eu zinc calcium silicate glass samples.

ions,^{14,15} and $^2\text{P}_{1/2} \rightarrow ^2\text{P}_{3/2}(1)$ transition of Bi^{2+} ions.¹³ We did not analyze and discuss the absorption spectrum of Bi^{m+} ($m = 0, 2,$ and 3) ions in detail in this study. The absorption spectrum of the SZC-0.6Eu zinc calcium silicate glass sample is shown by curve (b) (red curve) in Fig. 2. It can be observed that the absorption spectrum of this curve includes four main absorption peaks at ~ 394 , 434, 465, and 536 nm corresponding to transitions from $^7\text{F}_0$ ground-state to $^5\text{L}_6$, $^5\text{D}_3$, $^5\text{D}_2$, and $^5\text{D}_1$ excited states of Eu^{3+} ions.^{7,8,32} The absorption spectrum of the SZC-1.0Bi0.6Eu zinc calcium silicate glass sample is shown by curve (c) (blue curve) of Fig. 2. This absorption spectrum includes all the absorption peaks of Bi^{m+} and Eu^{n+} ions present in curves (a) and (b) due to overlapping and combining absorption spectra of Bi^{m+} and Eu^{n+} ions.^{7,8,11,13,32} The images inserted in Fig. 2 are photographs of SZC-1Bi, SZC-0.6Eu, and SZC-1Bi0.6Eu zinc calcium silicate glass samples.

3.3. Optical band gaps

Fig. 3 shows the direct optical band gaps (DOBG) (Fig. 3a) and indirect optical band gaps (IOBG) (Fig. 3b) of SZC-1.0Bi, SZC-0.6Eu, and SZC-1.0Bi0.6Eu zinc calcium silicate glass samples. DOBG and IOBG values for SZC-1.0Bi, SZC-0.6Eu, and SZC-1.0Bi0.6Eu zinc calcium silicate glass samples can be calculated based on the absorption spectra of these glass samples, and T_{auc} following formula:⁸

$$\alpha(\lambda) = A \cdot \frac{(h\nu - E_g)^\gamma}{h\nu} \quad (1)$$

In there, $\gamma = 1/2$ for the DOBG, and $\gamma = 2$ for the IOBG; E_g is the energy gap of SZC-1.0Bi, SZC-0.6Eu, and SZC-1.0Bi0.6Eu zinc calcium silicate glass samples; (λ) is the absorption coefficient; A is a proportionality constant; ν is the frequency; h is Planck's constant; λ is the wavelength. The relation between $\alpha(\lambda)$ and $h\nu$ is given by the Davis and Mott theory.³³ For each glass sample, (λ) is determined based on the expression:^{8,33}

$$\alpha(\lambda) = \frac{2.303}{d} \cdot E_{\text{opt}}(\lambda) \quad (2)$$

In there, $E_{\text{opt}}(\lambda)$ is the absorbance; d is the thickness of SZC zinc calcium silicate glass samples.³³

Thus, the DOBG values for SZC-1.0Bi, SZC-0.6Eu, and SZC-1.0Bi0.6Eu zinc calcium silicate glass samples were determined to be ~ 4.01 , 3.47, and 3.96 eV, respectively. Compared with the DOBG value of the SZC-0.6Eu zinc calcium silicate glass sample, the DOBG value of SZC-1.0Bi0.6Eu zinc calcium silicate glass sample was significantly greater with the energy difference $\Delta E_{g(\text{DOBG})} = 3.96 \text{ eV} - 3.47 \text{ eV} = 0.49 \text{ eV}$. The IOBG values for SZC-1.0Bi, SZC-0.6Eu, and SZC-1.0Bi0.6Eu zinc calcium silicate glass samples were determined to be ~ 3.78 , 2.83, and 3.65 eV, respectively. Compared with the IOBG value of the SZC-0.6Eu zinc calcium silicate glass sample, the IOBG value of the SZC-1.0Bi0.6Eu zinc calcium silicate glass sample was also increased significantly with the energy difference $\Delta E_{g(\text{IOBG})} = 3.65 \text{ eV} - 2.83 \text{ eV} = 0.82 \text{ eV}$. This result thus confirmed that both DOBG and IOBG values were significantly increased with the presence of Bi^{m+} ions in the SZC-1.0Bi0.6Eu zinc calcium silicate glass sample. On the contrary, when comparing the

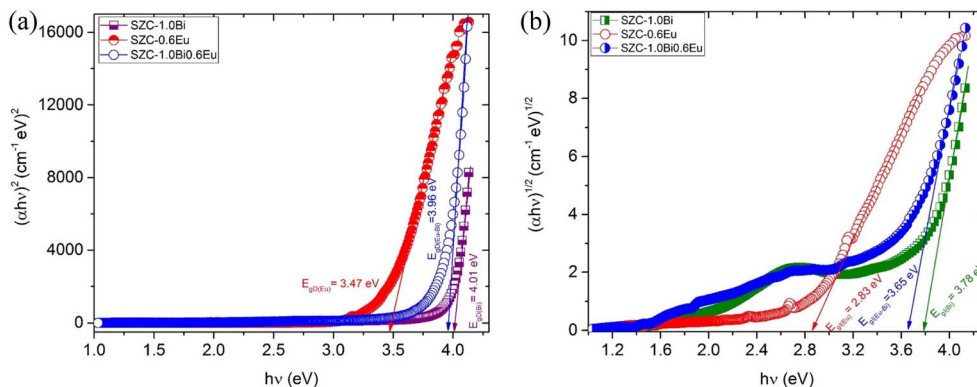


Fig. 3 (a) Direct optical band gaps of SZC-1.0Bi, SZC-0.6Eu, and SZC-1.0Bi0.6Eu zinc calcium silicate glass samples. (b) Indirect optical band gaps of SZC-1.0Bi, SZC-0.6Eu, and SZC-1.0Bi0.6Eu zinc calcium silicate glass samples.

DOBG and IOBG values of the SZC-1Bi sample with the corresponding DOBG and IOBG values of the SZC-1Bi0.6Eu sample, both DOBG and IOBG values of the SZC-1Bi0.6Eu sample are all significantly decreased. These results can be rationalized by the following reasons: (i) the absorption spectrum of the SZC-0.6Eu sample does not appear in the surface plasmon resonance (SPR),³⁴ whereas for the SZC-1Bi0.6Eu, sample, the absorption spectrum appears in the SPR at the peak of ~ 458 nm of Bi^{m+} ions. Therefore, the $E_{\text{opt}}(\lambda)$ value of the SZC-1Bi0.6Eu sample increases more than the $E_{\text{opt}}(\lambda)$ value of the SZC-0.6Eu sample³⁴ leading to the values of both DOBG and IOBG of the sample SZC-1Bi0.6Eu increase according to formula (1); (ii) compared with the SZC-1Bi sample, the $E_{\text{opt}}(\lambda)$ value of the SZC-1Bi0.6Eu

sample decreases linearly in the presence of Eu^{n+} ions due to Eu^{n+} ions combining with Bi^{m+} ions to increase the non-bridging oxygen (NBO) bonds³⁵ leading to the band edge shift to higher energies.³⁵ The calculated results for DOBG and IOBG values in this work are also completely consistent with the results of previous studies^{36–39} and are compared in detail in Table 2. The IOBG value of SZC-1.0Bi, SZC-0.6Eu, and SZC-1.0Bi0.6Eu zinc calcium silicate glass samples showed that the green and blue curves exhibited shallow collisions centered about 2.71 eV. This result is due to both absorption spectra of SZC-1Bi and SZC-1Bi0.6Eu samples, the peak was at about 458 nm, corresponding to the $h\nu = 2.71$ eV, and thus it appeared the SPR attributed to Bi^{m+} ions.

Table 2 The comparison of direct and indirect optical band gaps in this work with previous related studies^{36–39}

| Host materials | Doped/co-doped | DOBG (eV) | IOBG (eV) | Ref. |
|-------------------------------|--|-----------|-----------|--|
| Germanium-borate glasses | 1.0Bi ³⁺ | — | 3.43 | X. Y. Liu <i>et al.</i> ³⁶ |
| Germanium-borate glasses | 1.0Bi ³⁺ / 3.5Eu ³⁺ | — | 3.35 | X. Y. Liu <i>et al.</i> ³⁶ |
| Boron glasses | 1Eu ³⁺ | 3.529 | 3.306 | K. Maheshvaran <i>et al.</i> ³⁷ |
| Boro-tellurite glasses | 1Eu ³⁺ | 3.161 | 3.011 | K. Maheshvaran <i>et al.</i> ³⁷ |
| Zinc soda lime silica glasses | 4.7Eu ³⁺ | 3.20 | — | N. A. S. Omar <i>et al.</i> ³⁸ |
| Borosilicate glasses | 10Bi ³⁺ / 0.6Eu ³⁺ | 3.430 | 3.419 | D. V. K. Reddy <i>et al.</i> ³⁹ |
| Borosilicate glasses | 10Bi ³⁺ / 1Eu ³⁺ | 3.456 | 3.449 | D. V. K. Reddy <i>et al.</i> ³⁹ |
| Zinc calcium silicate glasses | 0.6Eu ³⁺ | 3.47 | 2.83 | This study |
| Zinc calcium silicate glasses | 1Bi ³⁺ | 4.01 | 3.78 | This study |
| Zinc calcium silicate glasses | 1Bi ³⁺ / 0.6Eu ³⁺ | 3.96 | 3.65 | This study |

3.4. Visible (VIS) emission

Visible (VIS) emission spectra of SZC-1.0Bi, SZC-0.6Eu, SZC-1.0Bi0.6Eu2Yb, and SZC-1.8Bi0.6Eu2Yb zinc calcium silicate glass samples under 320 nm excitation are shown in Fig. 4. For

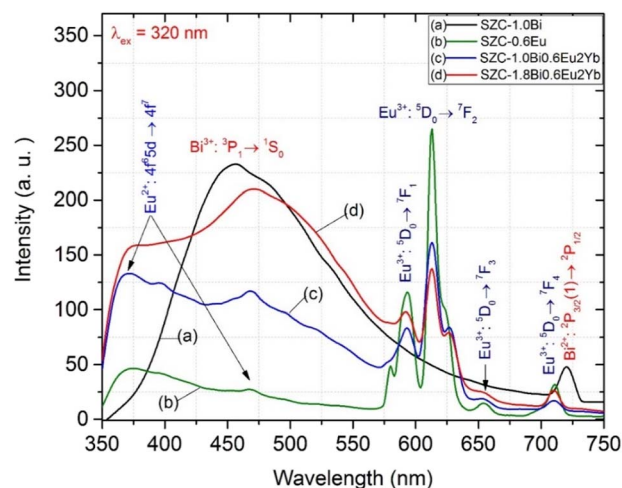


Fig. 4 VIS emission spectra of SZC-1.0Bi, SZC-0.6Eu, SZC-1.0Bi0.6Eu2Yb and SZC-1.8Bi0.6Eu2Yb zinc calcium silicate glass samples under 320 nm excitation.

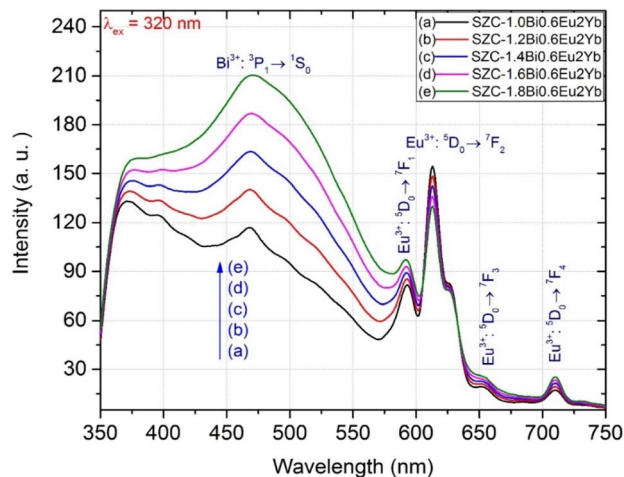


Fig. 5 VIS emission spectra of SZC- x Bi $_{0.6}$ Eu $_{2}$ Yb ($x = 1.0, 1.2, 1.4, 1.6,$ and 1.8 mol%) zinc calcium silicate glass samples under 320 nm excitation.

the SZC-1.0Bi zinc calcium silicate glass sample, VIS emission spectra of Bi $^{m+}$ ions were observed consisting of two peaks at ~ 457 and 720 nm, which are attributed to VIS emissions from $^3P_1 \rightarrow ^1S_0$ transition of Bi $^{3+}$ and $^2P_{3/2}(1) \rightarrow ^2P_{1/2}$ transition of Bi $^{2+}$,^{12,13} respectively. For the SZC-0.6Eu zinc calcium silicate glass sample, VIS emission spectra of Eu $^{3+}$ /Eu $^{2+}$ ions were observed in a band from ~ 373 to 468 nm, attributed to VIS emission from $4f^65d^1 \rightarrow 4f^7$ transition of Eu $^{2+}$ ions,^{7,8} and four VIS emission peaks at $\sim 593, 613, 654,$ and 710 nm attributed to $^5D_0 \rightarrow ^7F_J$ ($J=1, 2, 3,$ and 4) transitions of Eu $^{3+}$ ions.^{20,21} For the SZC-1.0Bi $_{0.6}$ Eu $_{2}$ Yb and SZC-1.8Bi $_{0.6}$ Eu $_{2}$ Yb zinc calcium silicate glass samples, VIS emission intensity of Eu $^{3+}$ /Eu $^{2+}$ ions in the band of 373 – 468 nm was significantly increased due to ET process from Bi $^{3+}$ to Eu $^{2+}$ ions. The remaining VIS emission spectra of Eu $^{3+}$ ions peaks at $\sim 593, 613, 654,$ and 710 nm were also observed.^{21,22} However, the VIS emission spectra of Bi $^{2+}$ ions peak at ~ 720 nm have ceased to exist and can not be observed. This result also means that the energy from the $^2P_{3/2}(1) \rightarrow ^2P_{1/2}$ transition of Bi $^{2+}$ ions is transferred to $^5D_0 \rightarrow ^7F_4$ neighboring transition of Eu $^{3+}$ ions.^{20–22}

VIS emission spectra of SZC- x Bi $_{0.6}$ Eu $_{2}$ Yb ($x = 1.0, 1.2, 1.4, 1.6,$ and 1.8 mol%) zinc calcium silicate glass samples under 320 nm excitation are shown in Fig. 5. With the increasing of Bi $^{m+}$ concentrations from 1.0 up to 1.8 mol%, the VIS emission intensity of the peak at ~ 468 nm was strongly increased. At the same time, the VIS emission intensity of the peaks at $\sim 593, 613, 654,$ and 710 nm of Eu $^{3+}$ were also increased. This proves that the energy from $^3P_1 \rightarrow ^1S_0$ transition of Bi $^{3+}$ ions^{11,12} and $^2P_{3/2}(1) \rightarrow ^2P_{1/2}$ transition of Bi $^{2+}$ ions^{17,18} is transferred to $^5D_0 \rightarrow ^7F_J$ ($J=1, 2, 3,$ and 4) transitions of Eu $^{3+}$ ions.^{7,8,32}

For the Eu $^{3+}$ /Eu $^{2+}$ -doped and Bi $^{m+}$ /Eu $^{3+}$ /Eu $^{2+}$ co-doped in the glass materials, the determination of color coordinates is significant for LED, WLED, and color display applications. Therefore, we calculated and determined CIE 1931 (x, y) color coordinates for these samples using the CIE chromaticity coordinates calculation software. CIE 1931 (x, y) color

coordinates for the VIS emission spectra of SZC-0.6Eu and SZC- x Bi $_{0.6}$ Eu $_{2}$ Yb ($x = 1.0, 1.2, 1.4, 1.6,$ and 1.8 mol%) zinc calcium silicate glass samples under 320 nm excitation are described in detail in Fig. 6. For the Eu $^{3+}$ /Eu $^{2+}$ -doped in SZC-0.6Eu zinc calcium silicate glass sample, CIE 1931 (x, y) color coordinates for VIS emission were determined at P0 point in the pink region. For the Bi $^{m+}$ /Eu $^{n+}$ co-doped in SZC- x Bi $_{0.6}$ Eu $_{2}$ Yb ($x = 1.0, 1.2, 1.4, 1.6,$ and 1.8 mol%) zinc calcium silicate glass samples, CIE 1931 (x, y) color coordinates were determined at P1, P2, P3, P4, and P5 points in the white pink region, which is the neighborhood around black body curve. CIE 1931 (x, y) color coordinates of P0, P1, P2, P3, P4, and P5 points are listed in detail in Table 3.

3.5. Upconversion (UC) emission

Fig. 7 shows the UC emission spectra of SZC-1.8Bi $_{0.6}$ Eu $_{2}$ Yb ($y = 0.6, 0.7, 0.8, 0.9,$ and 1.0 mol%) zinc calcium silicate glass samples under 980 nm LD excitation. From the results presented in Fig. 7, we can determine that the UC emission peaks at $\sim 580, 593, 613, 654,$ and 706 nm, which are attributed to $^5D_0 \rightarrow ^7F_J$ ($J=0, 1, 2, 3,$ and 4) transitions of Eu $^{3+}$ ions.⁴⁰ Under 980 nm LD excitation, UC emission of Bi $^{m+}$ ions was hardly observed at any peaks. At the same time, when increasing the Eu $^{3+}$ /Eu $^{2+}$ concentrations from 0.6 up to 1.0 mol%, UC emission intensity of Eu $^{3+}$ peaks at $\sim 580, 593, 613, 654,$ and 706 nm was significantly increased.^{41,42} The mechanism of the UC process of Bi $^{m+}$ /Eu $^{n+}$ /Yb $^{3+}$ co-doped is depicted in Fig. 10. When excited at the wavelength of 980 nm, two Yb $^{3+}$ ions are formed Yb $^{3+}$ –Yb $^{3+}$ pairs. Through the CET 1 process, the photons are transferred to the 5D_2 level of Eu $^{3+}$. Then the photons rapidly transfer to the 5D_0 level *via* the non-radiative transition. The $^5D_0 \rightarrow ^7F_J$ ($J = 4, 3,$

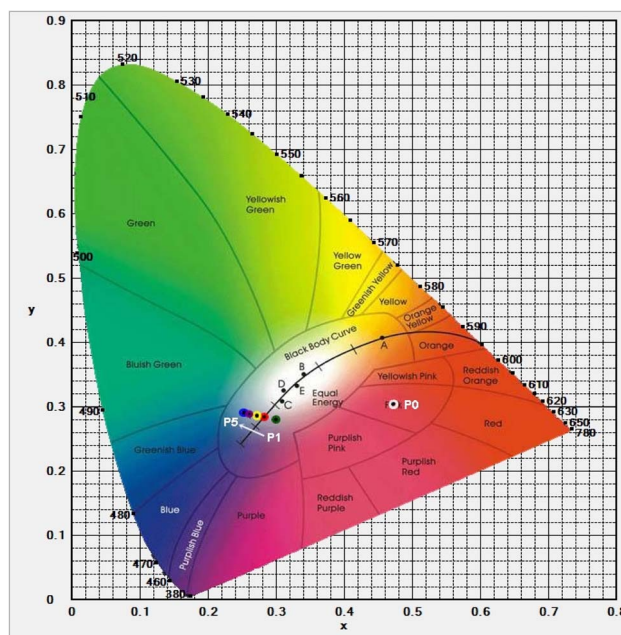


Fig. 6 CIE 1931 (x, y) color coordinates for VIS emission of SZC-0.6Eu and SZC- x Bi $_{0.6}$ Eu $_{2}$ Yb ($x = 1.0, 1.2, 1.4, 1.6,$ and 1.8 mol%) zinc calcium silicate glass samples under 320 nm excitation.

Table 3 CIE 1931 (*x*, *y*) color coordinates of SZC-0.6Eu and SZC-*x*Bi0.6Eu2Yb (*x* = 1.0, 1.2, 1.4, 1.6, and 1.8 mol%) zinc calcium silicate glass samples under 320 nm excitation

| Glass samples | Position on CIE 1931 chromaticity diagram | CIE 1931 (<i>x</i>) | CIE 1931 (<i>y</i>) |
|-------------------|---|-----------------------|-----------------------|
| SZC-0.6Eu | P0 | 0.2534 | 0.2902 |
| SZC-1.0Bi0.6Eu2Yb | P1 | 0.2992 | 0.2801 |
| SZC-1.2Bi0.6Eu2Yb | P2 | 0.2832 | 0.2837 |
| SZC-1.4Bi0.6Eu2Yb | P3 | 0.2710 | 0.2865 |
| SZC-1.6Bi0.6Eu2Yb | P4 | 0.2614 | 0.2886 |
| SZC-1.8Bi0.6Eu2Yb | P5 | 0.2537 | 0.2904 |

2, 1 and 0) transitions of Eu^{3+} produce the UC emissions peaks at ~580, 593, 613, 654, and 706 nm, respectively.

CIE 1931 (*x*, *y*) coordinates for the UC emission spectra of SZC-1.8Bi y Eu2Yb (*y* = 0.6, 0.7, 0.8, 0.9, and 1.0 mol%) zinc calcium silicate glass samples under 980 nm LD excitation is also described in detail in Fig. 8. Based on the results in Fig. 8, it can be seen that the CIE 1931 (*x*, *y*) color coordinates for UC emission spectra of SZC-1.8Bi y Eu2Yb (*y* = 0.6, 0.7, 0.8, 0.9 and 1.0 mol%) zinc calcium silicate glass samples were determined at M1, M2, M3, M4, and M5 points in the reddish-orange region. For the SZC-1.8Bi0.8Eu2Yb, SZC-1.8Bi0.9Eu2Yb, and SZC-1.8Bi1.0Eu2Yb zinc calcium silicate glass samples, although the UC emission intensity at ~580, 593, 613, 654, and 706 nm was significantly increased, but CIE 1931 (*x*, *y*) color coordinates changed very little, the M3, M4, and M5 points almost coincide. CIE 1931 (*x*, *y*) color coordinates of M1, M2, M3, M4, and M5 points are listed in detail in Table 4. Moreover, the comparison of the CIE 1931 (*x*, *y*) color coordinates in this study with those in a few previous related studies^{4,36,43–47} is presented in Table 5. From the results revealed in Table 5, we can confirm that with the difference of the host materials, the ratio of $\text{Bi}^{3+}/\text{Eu}^{3+}$ concentrations, and the excitation wavelength, the CIE 1931 (*x*, *y*) color coordinates also changes differently.

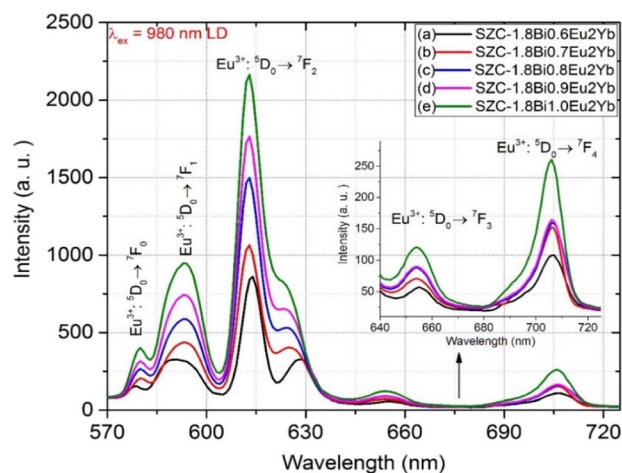


Fig. 7 UC emission spectra of SZC-1.8Bi y Eu2Yb (*y* = 0.6, 0.7, 0.8, 0.9, and 1.0 mol%) zinc calcium silicate glass samples.

3.6. NIR emission

NIR emission spectra of SZC-1Bi0.6Eu z Yb (*z* = 2.0, 2.2, 2.4, 2.6, and 2.8 mol%) zinc calcium silicate glass samples under excitation of 330 nm are shown in Fig. 9. It can be observed that the NIR emission spectra of $\text{Bi}^{m+}/\text{Eu}^{n+}/\text{Yb}^{3+}$ co-doped (*m* = 0, 2, 3 and *n* = 2, 3) consist of two emission peaks at ~986 and 1062 nm, which the NIR emission of $\text{Bi}^{m+}/\text{Eu}^{n+}/\text{Yb}^{3+}$ co-doped peak at ~986 nm due to ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transition of Yb^{3+} ions,⁴⁸ while the NIR emission peak at ~1062 nm can be attributed to ${}^2\text{D}_{3/2} \rightarrow {}^4\text{S}_{3/2}$ transition of Bi^0 ions.^{48–50} In the NIR range of ~960–1040 nm, NIR emission spectra of $\text{Bi}^{m+}/\text{Eu}^{n+}/\text{Yb}^{3+}$ co-doped produced a bandwidth of ~40 nm. However, according to many previous reports, it has been attributed the NIR emission at ~1062 nm to Bi^0 ions because Bi-dopant exists at three states including Bi^{3+} , Bi^+ , and Bi^0 ions that can emit in NIR range from ~950 to 1500 nm.^{12,15–17} It thus has been confirmed that (i) NIR emission of Bi-doped peak around

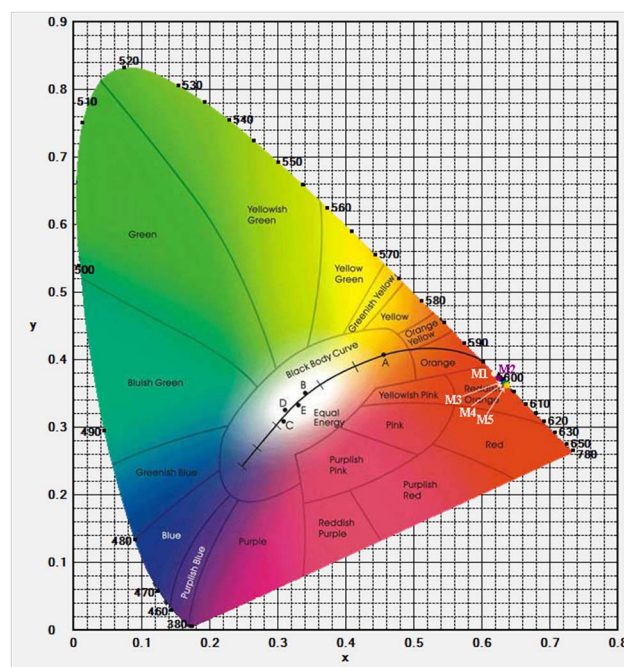


Fig. 8 CIE 1931 (*x*, *y*) for UC emission spectra of SZC-1.8Bi y Eu2Yb (*y* = 0.6, 0.7, 0.8, 0.9, and 1.0 mol%) zinc calcium silicate glass samples under 980 nm LD excitation.

Table 4 CIE 1931 (*x*, *y*) color coordinates of SZC-1.8Bi⁰Eu₂Yb (*y* = 0.6, 0.7, 0.8, 0.9, and 1.0 mol%) zinc calcium silicate glass samples under 980 nm LD excitation

| Glass samples | Position on CIE 1931 chromaticity diagram | CIE 1931 (<i>x</i>) | CIE 1931 (<i>y</i>) |
|---|---|-----------------------|-----------------------|
| SZC-1.8Bi ⁰ .6Eu ₂ Yb | M1 | 0.6239 | 0.3756 |
| SZC-1.8Bi ⁰ .7Eu ₂ Yb | M2 | 0.6293 | 0.3703 |
| SZC-1.8Bi ⁰ .8Eu ₂ Yb | M3 | 0.6317 | 0.3679 |
| SZC-1.8Bi ⁰ .9Eu ₂ Yb | M4 | 0.6321 | 0.3675 |
| SZC-1.8Bi ⁰ .1Eu ₂ Yb | M5 | 0.6322 | 0.3674 |

Table 5 The CIE 1931 (*x*, *y*) color coordinates in this work in comparison with those in previous related studies.^{4,36,43–47}

| Host materials | Doped/co-doped | λ_{ex} (nm) | CIE 1931(<i>x</i> , <i>y</i>) | Color region | Ref. |
|---|---|----------------------------|---------------------------------|-------------------------------------|---|
| Germanium-borate glasses | 1.0Bi ³⁺ /0.5Eu ³⁺ | 345 | (0.356, 0.325) | White | X. Y. Liu <i>et al.</i> ³⁶ |
| Germanium-borate glasses | 1.0Bi ³⁺ /3.5Eu ³⁺ | 345 | (0.562, 0.371) | Reddish orange | X. Y. Liu <i>et al.</i> ³⁶ |
| Ba ₂ Y ₅ B ₅ O ₁₇ phosphors | 0.0005Bi ³⁺ /0.4Eu ³⁺ | 365 | (0.415, 0.359) | Orange pink | G. Annadurai <i>et al.</i> ⁴³ |
| Lu ₂ Ge ₂ O ₇ phosphors | 0.06Bi ³⁺ /0.2Eu ³⁺ | 290 | (0.558, 0.232) | Purplish red | Q. F. Li <i>et al.</i> ⁴ |
| (Ba, Sr) ₃ Sc ₄ O ₉ solid solution compounds | 0.03Bi ³⁺ /0.3Eu ³⁺ | 330 | (0.575, 0.340) | Reddish orange | P. P. Dang <i>et al.</i> ⁴⁴ |
| Silicate glasses | 2Bi ³⁺ /0.3Eu ³⁺ | 333 | (0.595, 0.352) | Reddish orange | O. G. Giraldo <i>et al.</i> ⁴⁵ |
| KY ₃ F ₁₀ oxyfluoride glass-ceramics | 0.3Bi ³⁺ /0.4Eu ³⁺ | 280 | (0.2969, 0.2275) | Reddish purple | B. C. Yu <i>et al.</i> ⁴⁶ |
| LaNbO ₄ phosphor | 0.12Eu ³⁺ /0.05Yb ³⁺ | 980 | (0.560, 0.390) | Orange | A. Dwivedi <i>et al.</i> ⁴⁷ |
| Zinc calcium silicate glasses | 0.6Eu ³⁺ | 320 | (0.2534, 0.2902) | Pink | This study |
| Zinc calcium silicate glasses | 1Bi ³⁺ /0.6Eu ³⁺ /2Yb ³⁺ | 320 | (0.2992, 0.2801) | Purplish blue (near the white area) | This study |
| Zinc calcium silicate glasses | 1.8Bi ³⁺ /0.6Eu ³⁺ /2Yb ³⁺ | 980 | (0.6239, 0.3756) | Reddish orange | This study |

1100 nm was attributed to Bi⁰ ions;³⁸ (ii) the NIR emission spectrum of Bi³⁺ ions was unobserved in the NIR wavelength range^{15–17} and that NIR emission of Bi³⁺ under different excitation wavelengths is usually emitted from ~1250 to 1500 nm.^{11,39} With the increase of Yb³⁺ concentrations from 2.0 up to

2.8 mol% and Bi^{m+} concentrations remained unchanged, NIR emission intensity of Bi⁰ ions peak at ~1062 nm was decreased. This result has confirmed that ET from ²D_{3/2} → ⁴S_{3/2} transition of Bi⁰ ions to ²F_{5/2} → ²F_{7/2} transition of Yb³⁺ ions has occurred. At the same time, the NIR emission intensity of Bi^{m+}/Euⁿ⁺/Yb³⁺ co-doped peak at ~986 nm was strongly increased due to the energy contribution of cooperative ET (CET)₄ and CET₅ processes from Eu³⁺ and Eu²⁺ ions to Yb³⁺ ions.^{40,41}

Mechanism of CET_{*I*} (*I* from 1 to 5) and ET_{*J*} (*J* from 1 to 4) processes among Euⁿ⁺, Bi^{m+}, and Yb³⁺ ions in SZC zinc calcium silicate glasses are described and defined in detail in Fig. 10. CET_{*I*} (*I* from 1 to 5) and ET_{*J*} (*J* from 1 to 4) processes were described as follows:^{50–52}

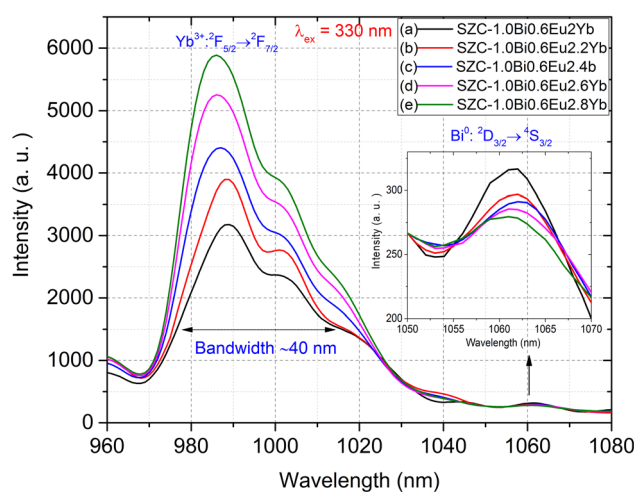
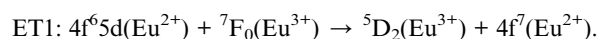
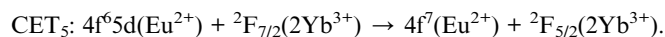
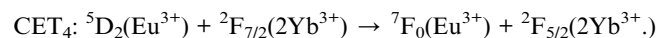
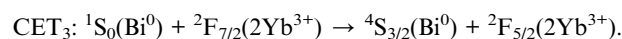
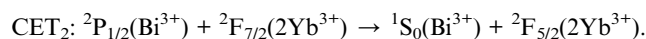
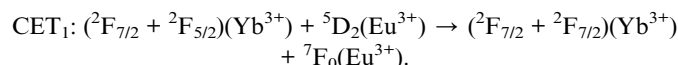


Fig. 9 NIR emission spectra of SZC-1Bi⁰.6Eu₂Yb (*z* = 2.0, 2.2, 2.4, 2.6, and 2.8 mol%) zinc calcium silicate glass samples.

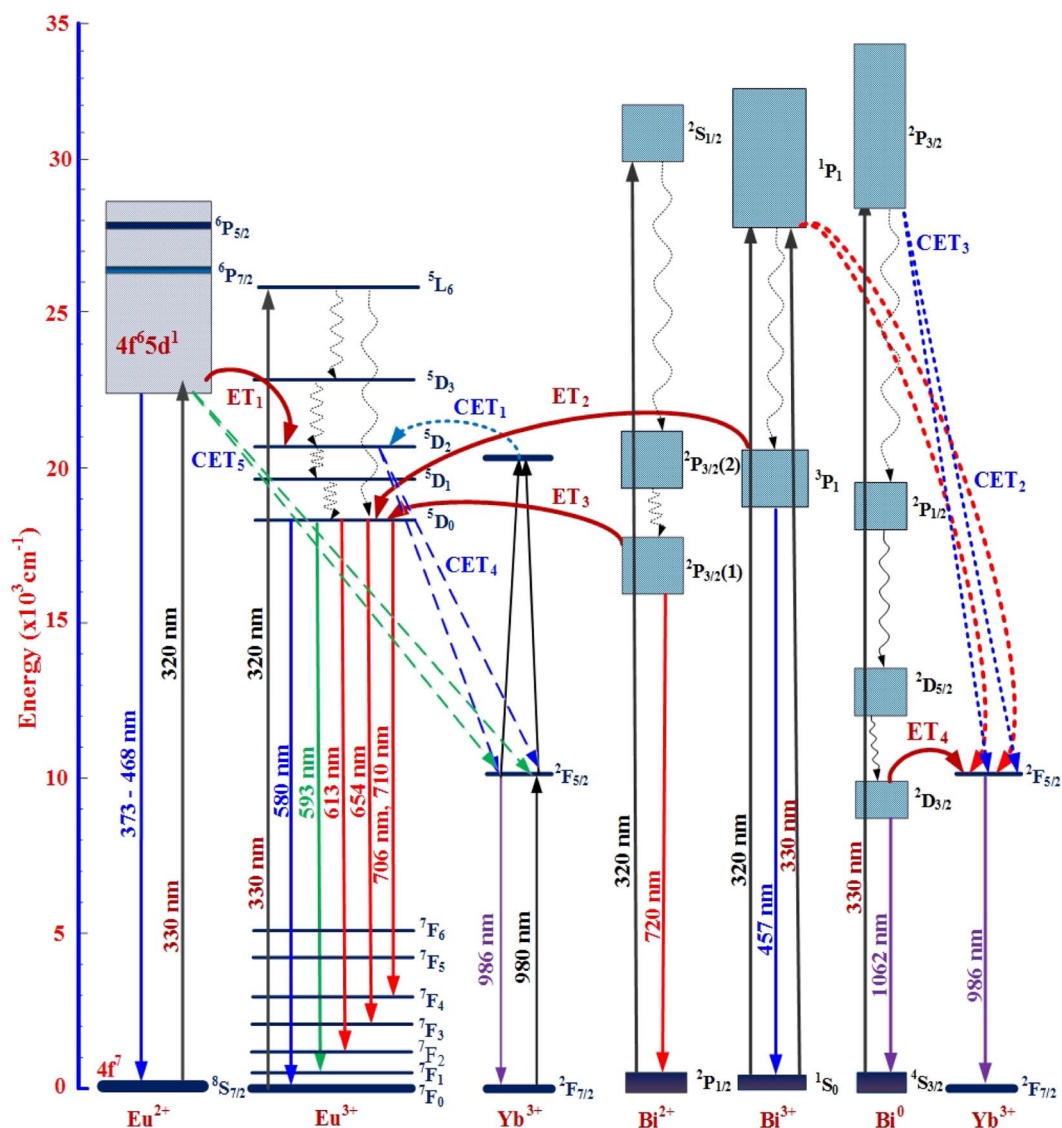
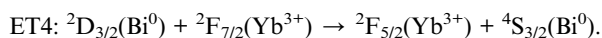
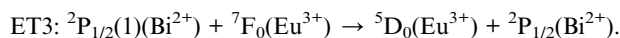
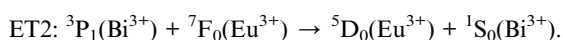


Fig. 10 Energy levels, VIS-, UC-, NIR-emissions and mechanism of CET_l (l from 1 to 5), and ET_j (J from 1 to 4) processes between Bi^{m+} , Eu^{n+} , and Yb^{3+} in SZC zinc calcium silicate glasses.



4. Conclusions

In this work, we have successfully synthesized zinc calcium silicate glass with the main compositions of SiO_2 - ZnO - CaF_2 - LaF_3 - TiO_2 - Bi_2O_3 - EuF_3 - YbF_3 . The DOBG and IOBG values for Bi^{m+}/Eu^{n+} co-doped in SZC-1.0Bi0.6Eu zinc calcium silicate glass samples were determined at ~ 3.65 and 3.96 eV, respectively. Both of these values were increased in the presence of

Bi^{m+} ions in SZC-1.0Bi0.6Eu zinc calcium silicate glass samples. Under the excitation of 320 nm, VIS emission spectra of $Bi^{m+}/Eu^{n+}/Yb^{3+}$ co-doped were observed in the peaks at ~ 468 , 593, 613, 654, and 710 nm attributed to Bi^{3+} , Bi^{2+} , Eu^{3+} , and Eu^{2+} ions. CIE 1931 (x, y) color coordinates for VIS emission spectra of $Bi^{m+}/Eu^{n+}/Yb^{3+}$ co-doped zinc calcium silicate glass samples were determined in the white-pink region neighborhood around the black body curve. UC emission spectra of $Bi^{m+}/Eu^{n+}/Yb^{3+}$ co-doped were observed in the peaks at ~ 580 , 593, 613, 654, and 706 nm attributed to Eu^{2+} ions. CIE 1931 (x, y) color coordinates for UC emission spectra of $Bi^{m+}/Eu^{n+}/Yb^{3+}$ co-doped zinc calcium silicate glass samples were determined in the reddish-orange region. NIR emission spectra of $Bi^{m+}/Eu^{n+}/Yb^{3+}$ co-doped have two emission peaks at ~ 986 and 1062 nm, attributed to Yb^{3+} and Bi^0 ions, respectively. NIR emission

spectra of Bi^{m+}/Euⁿ⁺/Yb³⁺ co-doped produced a bandwidth of ~40 nm in the wavelength range of ~960 to 1040 nm. The energy from ³P₁ → ¹S₀ transition of Bi³⁺ ions and ²P_{3/2}(1) → ²P_{1/2} transition of Bi²⁺ ions transferred to ⁵D₀ → ⁷F_J (J=1, 2, 3, and 4) transitions of Eu³⁺ ions and ET process from ²D_{3/2} → ⁴S_{3/2} transition of Bi⁰ ions to ²F_{5/2} → ²F_{7/2} transition of Yb³⁺ ions also occurred. The Bi^{m+}/Euⁿ⁺/Yb³⁺ co-doped zinc calcium silicate glasses in this study can be further developed for LED, WLED, display, and solar cell applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research is funded by Projects B2022-TNA-37 of the Vietnam Ministry of Education and Training. The author Ho Kim Dan would like to express his gratitude to Van Lang University.

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