**Synthesis and characterization of Eu³⁺ doped CaZrO₃-based perovskite type phosphors. Part II:
PL properties related to the two different dominant Eu³⁺ substitution sites**

Yohei Shimokawa^a, Satoshi Sakaida^a, Shinya Iwata^a, Koji Inoue^b, Sawao Honda^a and Yuji Iwamoto^{a,*}

^a Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya, 466-8555, Japan

^b Department of Electrical Material Science, Mie Prefecture Industrial Research Institute, 5-5-
45, Takachaya, Tsu, Mie, 514-0819, Japan

* Corresponding author: Yuji Iwamoto

Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya, 466-8555, Japan

TEL/FAX: +81 52 735 5276

Email: iwamoto.yuji@nitech.ac.jp

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1. Introduction

Recently, luminescent properties of rare earth cation-doped perovskite-type compounds have received considerable attention. One of their potential advantages is chemically stable and environment-friendly material system, free from hazardous elements such as sulfur and cadmium which composing previously developed red phosphors like $\text{Zn}_{1-x}\text{Cd}_x\text{:Ag}^+$ or $\text{Y}_2\text{O}_2\text{S:Eu}^{3+}$ [1].

Rare earth cations have been playing important roles for the development of modern displays and lighting devices due to their abundant emission colors based on their $4f-4f$ or $5d-4f$ transitions [1]. So proper host material should be chosen to improve the rare earth cation-derived luminescent property.

A great deal of ABO_3 -like perovskite-type compounds have been studied as a host material, and the luminescent properties were reported for $\text{CaTiO}_3\text{:Eu}^{3+}$ [2], $\text{MSnO}_3\text{:Eu}^{3+}$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$) [3], $\text{LaAlO}_3\text{:Eu}^{3+}$, $\text{GdAlO}_3\text{:Eu}^{3+}$ [4], $\text{LaInO}_3\text{:Eu}^{3+}$ [5], $\text{LaGaO}_3\text{:Eu}^{3+}$, Dy^{3+} [6] $\text{CaTiO}_3\text{:Pr}^{3+}$ [7], $\text{SrTiO}_3\text{:Pr}^{3+}$, Al^{3+} [8-12], $\text{MSnO}_3\text{:Tb}^{3+}$, Mg^{2+} ($\text{M} = \text{Ca}, \text{Sr}$) [13-15], $\text{CaSnO}_3\text{:Pr}^{3+}$ [15], and $\text{LaGaO}_3\text{:Sm}^{3+}$, Tb^{3+} [16].

Perovskite-type alkaline earth zirconates (MZrO_3 , $\text{M} = \text{Ca}, \text{Sr}$ and Ba) are also attractive as the host material [17]. Eu^{3+} -doped CaZrO_3 exhibits intense red luminescence under UV excitation [18-20], and the photoluminescence (PL) intensity was improved by Mg^{2+} co-doping, which could be achieved by enhancing the local lattice distortion around the Eu^{3+} ion [21]. The CaZrO_3 has orthorhombic perovskite structure [17], and there are two cation sites; A-site (Ca^{2+}) and B-site (Zr^{4+}). Generally, the Eu^{3+} substitution site was considered as A-site because of the similar ionic radius of Eu^{3+} (0.95 Å) and Ca^{2+} (0.99 Å) [18, 22, 23]. However, in our previous study, the site substituted by Eu^{3+} in the CaZrO_3 -based compounds was intensively studied by the X-ray diffraction (XRD) analysis and the energy-dispersive X-ray analysis based on electron channeling effects in transmission electron microscopy, so called statistical atom location by channeling enhanced microanalysis (ALCHEMI) [24], and the dominant Eu^{3+} substitution site was found as B-site in the CaZrO_3 . It was also clarified that the Eu^{3+} substitution site was strongly influenced by the co-dopant, especially the ionic radius of the co-dopant was found as one of the important factors for determining the dominant Eu^{3+} substitution site [25].

In this study, the chemical composition of the Eu^{3+} -doped CaZrO_3 -based compounds were controlled by taking into account of the two different dominant Eu^{3+} substitution site related to the second dopant of Mg^{2+} or Sr^{2+} . The amount of the co-dopant was systematically changed, and their PL emission properties have been evaluated and discussed.

2. Experimental Procedure

2.1 Material synthesis

Reagent of CaCO_3 (99.99%, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan), SrCO_3 (99%, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan), MgCO_3 (99.9%, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan), ZrO_2 (99.9%, Kishida Chemical Co., Ltd., Osaka, Japan), and EuCl_3 (99.9%, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan) were used as starting powders.

The second dopants were selected to change the short range structure around Eu^{3+} in the CaZrO_3 -based compounds: Sr^{2+} having a larger ionic radius ($r(\text{VIII}) = 1.26 \text{ \AA}$) compared to that of Ca^{2+} ($r(\text{VIII}) = 1.12 \text{ \AA}$), and oppositely Mg^{2+} with a smaller one ($r(\text{VIII}) = 0.89 \text{ \AA}$) [26]. Then, the chemical composition of the CaZrO_3 -based compounds were designed based on the dominant Eu^{3+} substitution site as A-site (Ca^{2+}) for $\text{Ca}_{1-x}\text{Sr}_{x-0.05}\text{ZrO}_3:\text{Eu}^{3+}_{0.05}$ ($x = 0.2, 0.4$), and that as B-site (Zr^{4+}) for $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ ($y=0, 0.02, 0.04, 0.06, 0.08, 0.1$) [25]. All the samples were synthesized by the solid state reaction method. According to the nominal composition, the starting powders were mixed using ethanol, and dried. The mixed powders were heated at 1400°C for 6 h in air.

2.2 Characterizations

The crystalline phases of the heat-treated samples were identified by powder XRD measurements with $\text{CuK}\alpha$ radiation using an automated powder diffractometer (X'pert Pro $\alpha 1$, Philips, Netherlands). The morphology of the heat-treated samples was characterized using a scanning electron microscope (SEM, JSM-6360LVS, JEOL Ltd., Tokyo, Japan). The PL excitation and emission spectra were recorded using Hitachi F-7000 spectrophotometer (Hitachi High-Technologies Corp, Tokyo, Japan). The spectrophotometer was equipped with a 150 W Xe lamp as the excitation source. All the measurements were performed at room temperature.

3. Results and discussion

As a typical microstructure observation result, SEM image of the $\text{CaZrO}_3:\text{Eu}^{3+}_{0.05}$ is shown in Fig. 1. All the samples synthesized in this study exhibited aggregated particles composed of partially sintered crystallites having a size range of about 1.0 to 3 μm .

Figure 2(a) shows XRD patterns of $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$, $\text{Ca}_{1-x}\text{Sr}_{x-0.05}\text{ZrO}_3:\text{Eu}^{3+}_{0.05}$ ($x = 0.2, 0.4$) and $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ ($y = 0.02, 0.04, 0.06, 0.08, 0.1$) synthesized in this study. The diffraction peaks of $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ were well consistent with those of the standard powder diffraction file JCPDS No. 35-0645 (orthorhombic CaZrO_3). The Sr^{2+} -doping up to 35 mol % was successfully achieved without secondary phase formation, while the 10 mol % Mg^{2+} -doped sample presented a weak diffraction peak corresponding to $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$ (JCPDS No. 26-0341).

Figure 2(b) shows typical peak shift behaviors detected at the diffraction angles (2θ) ranging from 73 to 76 degrees (The dashed line indicates the diffraction peak position of the $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$).

With increasing amount of the Sr^{2+} -doping, the diffraction peak shifted toward lower angles, i.e. the lattice constants increased consistently with the amount of the Sr^{2+} -doping (Fig. 3(a)). On the other hand, with increasing amount of the Mg^{2+} -doping up to 6 mol %, the peak shifted toward higher angles. Then, at and above 8 mol %, the degrees of the peak shift turned out to be smaller. As a result, the lattice constants reached the minimum at the 6 mol % Mg^{2+} -doping (Fig. 3(b)). These results indicated that both of the second dopants, Sr^{2+} and Mg^{2+} mainly substituted to Ca^{2+} at the A-site as designed. Excess amount of the Mg^{2+} -doping lead to the secondary phase formation, and $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$ appeared at the 10 mol% Mg^{2+} -doping. Since no additional phase with Mg^{2+} was detected for the samples with the amount of Mg^{2+} -doping above 6 mol%, the excess Mg^{2+} could be existed as amorphous state in the samples. Based on these results, the maximum amount of the Mg^{2+} in the $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ was estimated to be approximately 6 mol %. This value was much lower than that of Sr^{2+} , however, at least three times higher than that determined for the $(\text{Ca}_{1-y}\text{Mg}_y)\text{ZrO}_3:\text{Eu}^{3+}$ synthesized in our previous study without taking into account of the dominant Eu^{3+} substitution site as B-site [25].

PL excitation ($\lambda_{\text{em.}} = 614 \text{ nm}$) spectra of the Eu^{3+} -doped CaZrO_3 -based compounds synthesized in this study are shown in Fig. 4. All the samples exhibited two broad peaks over 200-350 nm wavelength. The most intense broad peak around 240 to 315 nm is charge transfer band (CTB) corresponding to an electron transfer from an oxygen 2p orbital to an empty 4f orbital of Eu^{3+} ion ($\text{O}^{2-} \rightarrow \text{Eu}^{3+}$), while another broad peak at 200-230 nm is host absorption band (HAB) assigned to the charge transfer from oxygen ligands to the central zirconium atom inside the ZrO_3^{2-} group [27]. The several narrow peaks over 350-500 nm are due to the direct excitation of Eu^{3+} ion ground state into higher level of the 4f-manifold [28].

The $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ exhibited the CTB excitation peak centered at 278 nm. The CTB excitation peak intensity decreased with increasing amount of the Sr^{2+} -doping, and the peak center was shifted toward longer wavelength, being centered at 279 nm for 15 mol %, and 282 nm for 35 mol % Sr^{2+} -doped sample. The peak shift was also observed for the Mg^{2+} -doped samples. At 6 to 8 mol % Mg^{2+} -doping, the peak center shifted to 281 nm, but the peak intensity increased with increasing amount of the Mg^{2+} -doping up to 6 mol %, then slightly deceased at the 8 mol % Mg^{2+} -doping.

The PL emission spectrum excited at the appropriate CTB excitation wavelength was recorded for each sample. The spectra were summarized and shown in Fig. 5. $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ presented several emission peaks over 550-700 nm wavelength caused by the $f-f$ transitions from the excited $^5\text{D}_0 - ^7\text{F}_J$ ($J = 0, 1, 2, 3, 4$) [1]. The emission peak centered at 594 nm is due to the magnetic dipole transition $^5\text{D}_0 - ^7\text{F}_1$. The most intensive emission peak centered at 614 nm is attributed to the electric dipole transition $^5\text{D}_0 - ^7\text{F}_2$. Thus, $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ exhibited red color emission.

According to the parity selection rules, the magnetic dipole transition is permitted, but the electric dipole transition is sensitive to local symmetry and allowed exceptionally on the condition that the

Eu^{3+} ion occupies a site without inversion symmetry [1]. $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ exhibited dominant PL emission due to the electric dipole transition $^5\text{D}_0 - ^7\text{F}_2$. The Eu^{3+} ion could mainly occupy the B site (Zr^{4+}) with low symmetry due to the formation of oxygen vacancies related to the Eu^{3+} substitution to Zr^{4+} .

The intensity of the PL emission peak at 614 nm increased consistently with Mg^{2+} -doping, and the 6 mol % Mg^{2+} -doped sample exhibited the highest emission peak intensity which was approximately 1.4 times higher than that of the Mg^{2+} -free $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$, then, the intensity slightly decreased at the 8 mol % doping. On the other hand, the peak intensity at 614 nm monotonously decreased with the increase amount of the Sr^{2+} -doping (Fig. 5).

The emission peak intensities of the Eu^{3+} -doped CaZrO_3 -based compounds investigated in this study were found to be well correlated with their lattice constants as shown in Fig. 6. Among the measured lattice parameters shown in Fig. 2, the parameter c was selected as a typical one, and their relationship was plotted. The relative PL emission peak intensity was found to be enhanced consistently with decreasing the lattice parameter. Especially, the PL emission intensity of the $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}$ was found to be remarkably increased with the lattice shrinkage.

According to the previous report on the bond lengths in CaZrO_3 , there are five different Ca - O bond lengths including Ca - O (1) 2.341, Ca - O (2) 2.461, Ca - O (3) 2.680, Ca - O (4) 2.362 and Ca - O (5) 2.844, and three different Zr - O bond lengths having Zr - O (2) 2.097, Zr - O (3) 2.091 and Zr - O (5) 2.101, the average bond length of Ca - O (2.572 Å) is apparently longer than that of Zr - O (2.096 Å) [17]. As shown in Fig. 4, the CTB excitation peak of $\text{Ca}_{1-x}\text{Sr}_x\text{O}_3:\text{Eu}^{3+}_{0.05}$ shifted toward longer wavelength and its intensity decreased consistently with the lattice expansion. Due to the elongation of the distance between oxygen and the europium at the A-site, the efficiency of the electron transfer from O^{2-} to the Eu^{3+} could be deteriorated, which leading to the observed decrease in the PL emission intensity.

On the other hand, the peak intensities of both the CTB excitation and the PL red emission due to the $^5\text{D}_0 - ^7\text{F}_2$ transition of $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}$ remarkably increased consistently with the amount of Mg^{2+} -doping up to the estimated solubility limit of 6 mol %. The efficiency of the electron transfer from O^{2-} to the Eu^{3+} at the B-site seemed to be improved by the lattice shrinkage. Essentially in CaZrO_3 , the average bond length of Zr - O was shorter than that of Ca - O, and the distance between oxygen and europium at the B-site was thought to be further reduced due to the lattice shrinkage. However, as shown in Fig. 4, the CTB excitation peak of the $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}$ shifted toward longer wavelength consistently with the lattice shrinkage. Thus, it was difficult to recognize the reduced distance of the Eu - O as a dominant reason for the enhanced red emission intensity. Then, the local environment around the Eu^{3+} in the CaZrO_3 -based compounds synthesized in this study was further examined.

It is well known that the relative intensity of the $^5\text{D}_0 - ^7\text{F}_1$ and $^5\text{D}_0 - ^7\text{F}_2$ emission depends strongly

on the local symmetry of the Eu^{3+} , and the ${}^5\text{D}_0 - {}^7\text{F}_2 / {}^5\text{D}_0 - {}^7\text{F}_1$ emission intensity ratio (which is so called asymmetry ratio) gives a measure of degree of distortion from inversion symmetry of the local environment around the Eu^{3+} ion in the host lattice [29]. Figure 7 shows the relationships between the amount of co-dopant, the asymmetry ratio, and the relative PL emission peak intensity at 614 nm under the CTB excitation of the Eu^{3+} -doped CaZrO_3 -based compounds. The asymmetry ratio of the $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ was 3.06 and increased with increasing Sr^{2+} -doping to reach 3.55 at the 35 mol % Sr^{2+} -doping, however, the relative intensity of the PL emission peak contrarily decreased (Fig. 7(a)). On the other hand, both the asymmetric ratio and the relative peak intensity increased consistently with the amount of the Mg^{2+} -doping, and reached the maximum at the 6 mol % Mg^{2+} -doping (Fig. 7(b)).

The relation between the degree of the crystal structural distortion and the PL emission intensity has been often discussed for the perovskite-type phosphors [3, 18, 21], and the dominant PL red emission peak intensity of the Mg^{2+} -doped samples, $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}$ synthesized in this study showed a good correlation with the asymmetry ratio, suggesting that the observed enhancement in the PL red emission intensity could be achieved by increasing the crystal structural distortion. The room temperature crystal structures of the three kinds of perovskite-type alkaline earth zirconates have been reported in the literature: BaZrO_3 crystallizes with an ideal cubic $Pm\bar{3}m$ perovskite structure [30], while SrZrO_3 [31] and CaZrO_3 [17] exhibit orthorhombic $Pbnm$ symmetry determined by rotation of the oxygen octahedron. Tolerance factors t of the CaZrO_3 , SrZrO_3 , and BaZrO_3 are 0.914 [17], 0.965 [32] and 1.011 [33], respectively. The distortion of the crystal structure given by the deviation from the ideal t value (1.0) increases with decreasing the ionic radius of the A-site cation M^{2+} in the MZrO_3 ($\text{M}^{2+} = \text{Ca}^{2+}$ (1.12 Å), Sr^{2+} (1.26 Å), and Ba^{2+} (1.42 Å)). The distortion in the $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}$ was thought to be further increased by the partial replacement of Ca^{2+} at the A-site with Mg^{2+} having a smaller ionic radius, which leading to increasing the local distortion around the Eu^{3+} at the B-site in the CaZrO_3 -based compounds, and thereby enhancing the efficiency of the electron transfer from O^{2-} to the Eu^{3+} for the red color emission by the ${}^5\text{D}_0 - {}^7\text{F}_2$ transition.

4. Conclusions

Eu^{3+} -doped perovskite type CaZrO_3 -based compounds, $\text{Ca}_{1-x}\text{Sr}_{x-0.05}\text{ZrO}_3:\text{Eu}^{3+}_{0.05}$ ($x = 0.2, 0.4$), and $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ ($y = 0, 0.02, 0.04, 0.06, 0.08, 0.1$) were synthesized by the solid state reaction at 1400 °C for 6 h in air. According to the results obtained by our previous study on the Eu^{3+} substitution site, the chemical composition of these compounds was controlled based on the dominant Eu^{3+} substitution site as A-site (Ca^{2+}) for $\text{Ca}_{1-x}\text{Sr}_{x-0.05}\text{ZrO}_3:\text{Eu}^{3+}_{0.05}$, and that as B-site (Zr^{4+}) for $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$. The results of the X-ray diffraction analysis revealed that both Sr^{2+} and Mg^{2+} mainly occupied the A-site as designed. The Sr^{2+} -doping was successfully achieved up to 35 mol % without secondary phase formation, while the solubility of Mg^{2+} in the $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ was

found to be low, approximately 6 mol %.

The Eu^{3+} -doped CaZrO_3 -based compounds synthesized in this study exhibited PL red emission by the CTB excitation. The peak intensities of both the CTB excitation and the dominant PL emission peak at 614 nm ($^5\text{D}_0 - ^7\text{F}_2$ transition) of $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ remarkably increased consistently with the amount of Mg^{2+} -doping up to the estimated solubility limit of 6 mol %. On the other hand, both the CTB excitation peak intensity and the PL red emission peak intensity decreased with increasing amount of the Sr^{2+} -doping.

Sr^{2+} substitution to Ca^{2+} at the A-site in the $\text{Ca}_{1-x}\text{Sr}_x\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ was found to be effective to increase the local distortion around Eu^{3+} at the A-site, which allowed the PL red emission due to the $^5\text{D}_0 - ^7\text{F}_2$ transition. As one possible reason for the observed decrease in the PL emission intensity, the efficiency of electron transfer from O^{2-} to the Eu^{3+} was thought to be reduced by the lattice expansion due to the Sr^{2+} substitution.

Eu^{3+} in the $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ could mainly occupy the B-site (Zr^{4+}) with low symmetry due to the formation of oxygen vacancies related to the Eu^{3+} substitution to Zr^{4+} . The local distortion around the Eu^{3+} was found to be further enhanced consistently with the amount of the Mg^{2+} -doping. The distortion of the host crystal structure of orthorhombic $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}$ was thought to be increased by the partial replacement of Ca^{2+} at the A-site with Mg^{2+} with a smaller ionic radius, which leading to enhancing the local distortion around the Eu^{3+} at the B-site in the CaZrO_3 -based compounds. As a result, the 6 mol % Mg^{2+} -doped sample ($\text{Ca}_{0.94}\text{Mg}_{0.06}\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$) exhibited the highest PL red emission peak intensity which was approximately 1.4 times higher than that of the Mg^{2+} -free $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$.

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Figure captions

Fig. 1. SEM image of $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ showing a typical morphology of the Eu^{3+} -doped CaZrO_3 -based compounds synthesized in this study.

Fig. 2. XRD patterns of (a) $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$, $\text{Ca}_{1-x}\text{Sr}_{x-0.05}\text{ZrO}_3:\text{Eu}^{3+}_{0.05}$ ($x = 0.2, 0.4$) and $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ ($y = 0.02, 0.04, 0.06, 0.08, 0.1$) after heat treatment at 1400°C for 6 h in air, and (b) magnified XRD patterns showing typical peak shift behaviors detected at the diffraction angles (2θ) ranging from 73 to 76 degrees (The dashed line indicates the position of the XRD line in $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ without second dopant).

Fig. 3. Lattice parameters determined by XRD analysis. (a) $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ and $\text{Ca}_{1-x}\text{Sr}_{x-0.05}\text{ZrO}_3:\text{Eu}^{3+}_{0.05}$ ($x = 0.2, 0.4$), and (b) $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ ($y = 0, 0.02, 0.04, 0.06, 0.08$) synthesized by heat treatment at 1400°C for 6 h in air.

Fig. 4. PL excitation spectra of $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$, $\text{Ca}_{1-x}\text{Sr}_{x-0.05}\text{ZrO}_3:\text{Eu}^{3+}_{0.05}$ ($x = 0.2, 0.4$) and $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ ($y = 0.02, 0.04, 0.06, 0.08$).

Fig. 5. PL emission spectra of $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$, $\text{Ca}_{1-x}\text{Sr}_{x-0.05}\text{ZrO}_3:\text{Eu}^{3+}_{0.05}$ ($x = 0.2, 0.4$) and $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ ($y = 0.02, 0.04, 0.06, 0.08$).

Fig. 6. Relative intensity of PL emission peak at 614 nm under CTB excitation as a function of lattice parameter c of $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$, $\text{Ca}_{1-x}\text{Sr}_{x-0.05}\text{ZrO}_3:\text{Eu}^{3+}_{0.05}$ ($x = 0.2, 0.4$) and $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ ($y = 0.02, 0.04, 0.06, 0.08$).

Fig. 7. Relationships between amount of co-dopant, asymmetry ratio, and relative PL emission peak intensity at 614 nm under the CTB excitation of Eu^{3+} -doped CaZrO_3 -based compounds. (a) $\text{CaZr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ and $\text{Ca}_{1-x}\text{Sr}_{x-0.05}\text{ZrO}_3:\text{Eu}^{3+}_{0.05}$ ($x = 0.2, 0.4$) and (b) $\text{Ca}_{1-y}\text{Mg}_y\text{Zr}_{0.95}\text{O}_3:\text{Eu}^{3+}_{0.05}$ ($y = 0, 0.02, 0.04, 0.06, 0.08$).

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7