Synthesis and characterization of Eu³⁺-doped CaZrO₃-based perovskite-type phosphors. Part I: Determination of the Eu³⁺ occupied site using the ALCHEMI technique

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Abstract

Eu³⁺-doped CaZrO₃, SrZrO₃, and Mg²⁺- or Sr²⁺-co-doped CaZrO₃ were synthesized by conventional solid state reaction and their photoluminescence (PL) properties were characterized. The Eu³⁺-doped CaZrO₃-based compounds exhibited characteristic emissions of Eu³⁺ (*f-f* transition). The intensity of the main PL emission peak at 614 nm increased with Mg²⁺ co-doping, while it decreased with the amount of co-doped Sr²⁺. The site substituted by Eu³⁺ cations in the CaZrO₃-based compounds was investigated by X-ray diffraction analysis and energy-dispersive X-ray analysis based on the electron channeling effects in transmission electron microscopy. The Eu³⁺ cations were determined to occupy mainly the B site (Zr⁴⁺) in CaZrO₃. The dominant Eu³⁺ substitution site was also strongly influenced by the co-dopant, and the ionic radius of the co-dopant was identified as an important factor that determines the dominant Eu³⁺ substitution site.

Keywords: A. ceramics, A. oxides, C. electron microscopy, D. luminescence, D. optical properties

1. Introduction

ABO₃-like oxides with the perovskite-type structure, such as calcium zirconate (CaZrO₃), are attractive as host materials for red phosphors. These oxides are stable and environmentally benign because they are free from hazardous elements such as sulfur and cadmium that have comprised previously developed red phosphors such as Zn_{1-x}Cd_xS:Ag⁺ or Y₂O₂S:Eu³⁺ [1].

CaZrO₃ belongs to the orthorhombically distorted perovskite-type structure with space group *Pnma* [2]. The crystal structure consists of a three dimensional sublattice of corner-connected ZrO₆ octahedra, where the Ca²⁺ cation is in eightfold coordination with oxide ions, and offers potential application as a host material for phosphors. All the octahedra are corner-sharing and are slightly tilted with respect to their position in the ideal cubic perovskite structure due to the mismatch in the fit of the alkaline earth ions to the dodecahedral cavity of the crystal structure [3].

The trivalent europium ion (Eu³⁺) is a good activator with red or red-orange emission due to its ⁵D₀–⁷F_{*J*} (*J* = 0, 1, 2, 3, 4, usually ranging from 578 nm for *J* = 0 to 700 nm for *J* = 4) transition. The emission in the vicinity of 600 nm is due to the magnetic dipole transition ⁵D₀–⁷F₁, which is insensitive to the site symmetry. The emission around 610-630 nm is derived from the electric dipole transition ⁵D₀–⁷F₂,

induced by the lack of inversion symmetry at the Eu^{3+} site [1]. Therefore, the site symmetry around Eu^{3+} is very important with respect to improvement of the emission properties.

Eu^{3+} -doped CaZrO_3 has previously been reported to exhibit intense red luminescence under UV excitation [4-6]. The strong red emission due to the $^5\text{D}_0$ - $^7\text{F}_2$ transition is achieved by the asymmetric environment around the Eu^{3+} site in the distorted structure of CaZrO_3 [4]. Moreover, magnesium (Mg) co-doping with rare earth metal ions increased the photoluminescence (PL) intensity due to an increase of the local lattice distortion around the Eu^{3+} ion by the substitution of Ca for Mg [7].

Perovskite-type ABO_3 oxides offer two different cation sites; A- and B-sites. In CaZrO_3 , the coordination numbers of the A- and B-sites are 8 and 6, respectively [2]; therefore, the degree of symmetry is dependent on the site that Eu^{3+} occupies. However, there are few reports regarding the effect of the site that the Eu^{3+} cation occupies in CaZrO_3 -type compounds.

In this study, Eu^{3+} -doped CaZrO_3 , SrZrO_3 , and Mg^{2+} - or Sr^{2+} -doped CaZrO_3 were synthesized and their PL excitation/emission properties were characterized. The Eu^{3+} cation substitution site in the host CaZrO_3 , SrZrO_3 , and Mg^{2+} - or

Sr²⁺-doped CaZrO₃ was examined using X-ray diffraction (XRD) analysis and energy-dispersive X-ray spectroscopy (EDS) analysis based on the electron channeling effects in transmission electron microscopy (TEM), i.e., statistical atom location by channeling enhanced microanalysis (ALCHEMI) [8].

2. Experimental Procedure

2. 1. Material synthesis

The reagents CaCO₃ (99.99%, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan), SrCO₃ (99%, Kojundo Chemical Laboratory Co., Ltd.), MgCO₃ (99.9%, Kojundo Chemical Laboratory Co., Ltd.), ZrO₂ (99.9%, Kishida Chemical Co., Ltd., Osaka, Japan), and EuCl₃ (99.9%, Kojundo Chemical Laboratory Co., Ltd.) were used as starting materials. All samples were synthesized by conventional solid state reaction. The starting powders were mixed using EtOH according to the nominal chemical composition of the target host materials: CaZrO₃, SrZrO₃, (Ca_{0.6}Sr_{0.4})ZrO₃, and (Ca_{1-x}Mg_x)ZrO₃ (x = 0.02, 0.06). The mixed powders were then dried and heated at 1400 °C for 6 h in air. The 5 mol% Eu³⁺-doped compounds were synthesized in the same manner.

2. 2. Characterization

Powder XRD measurements of the synthesized samples were performed at room temperature using Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) with an automated powder diffractometer (X'pert Pro $\alpha 1$, Philips, Amsterdam, The Netherlands).

The morphology of the synthesized samples was observed using scanning electron microscopy (SEM, JSM-6360LVS, JEOL Ltd., Tokyo, Japan) and TEM (JEM-2100F, JEOL Ltd.). EDS spectra were measured using the TEM operated at an accelerating voltage of 200 kV. TEM observations and EDS measurements were conducted with ground samples adhered onto copper (Cu) grids.

The fraction of the site substitution with Eu^{3+} cations was evaluated using the statistical ALCHEMI technique. The basic concept of this technique was first introduced by Taftø and Spence to determine the location of minor species on atomic sites in a crystal structure [9]. Electron channeling for an orientation under or near a strong diffraction condition results in a standing wave with a peak that is dependent on the site in the crystal unit cell and changes by variation of the incident electron beam for a crystal orientation. The ALCHEMI technique is thus used to determine the substituted site by comparison of the appropriate EDS spectra. The

statistical ALCHEMI method, which successfully overcomes difficulties such as sensitivity against several significant sources of error, was originally proposed by Rossouw *et al.* for a single impurity element that occupies a site in a compound with multiple nonequivalent host sites [10]. The method was extended by Fujimichi *et al.* for a material system that contains multiple impurities [8].

In the present study, 20-30 datasets of EDS spectra for one crystal grain were measured by tilting the sample slightly and consecutively around the low-index zone axes within a few degrees. The fraction of dopant-occupied sites was then evaluated according to the established procedures [8], as follows.

The X-ray count N_x , for impurity x , can be written in the following form as a function of the X-ray count N_i , of host element i , where i is an A- or B-site cation and a_i is a coefficient.

$$N_x = \sum_i a_{ix} N_i = a_{Ax} N_A + a_{Bx} N_B \quad (1)$$

The impurity atom concentration c_x , and the fractional partition f_{ix} , at each site i are respectively given by the following equations, where k_i is the k factor of element i :

$$c_x = \sum_i \frac{a_{ix} n_i}{\left(\sum_x a_{ix} + k_i / k_x \right)} \quad (2)$$

$$f_{ix} = \frac{a_{ix}n_i}{c_x \left(\sum_x a_{ix} + k_i/k_x \right)} \quad (3)$$

The results obtained by this technique are discussed with respect to the results of the XRD analysis.

PL emission and excitation spectra were measured at room temperature with a spectrophotometer (Hitachi F-7000, Hitachi High-Technologies Corp, Tokyo, Japan) equipped with a Xe lamp (150 W) as the excitation source.

3. Results and Discussion

3. 1. Morphology and PL properties

Figure 1 shows typical SEM images of the Eu^{3+} -doped CaZrO_3 -based compounds synthesized at 1400 °C for 6 h. All the samples were homogeneous and were composed of aggregated particles with a size range of approximately 1 to 2 μm .

Figure 2 shows PL excitation spectra ($\lambda_{\text{em}} = 614 \text{ nm}$) for the $\text{CaZrO}_3:\text{Eu}^{3+}$, $\text{SrZrO}_3:\text{Eu}^{3+}$ and Mg^{2+} - or Sr^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}$ samples. $\text{CaZrO}_3:\text{Eu}^{3+}$ exhibits two broad peaks centered at 219 nm and 277 nm, which were assigned to the host absorption band (HAB) caused by charge transfer from the oxygen ligands

to the central zirconium atom inside the ZrO_3^{2-} group [11] and the charge transfer band (CTB) caused by electron transfer from an oxygen $2p$ orbital to an empty $4f$ orbital of Eu^{3+} cation ($\text{O}^{2-} \rightarrow \text{Eu}^{3+}$), respectively. Two broad analogous peaks centered at 233 and 300 nm observed for the $\text{SrZrO}_3:\text{Eu}^{3+}$ sample were assigned to the HAB and CTB, respectively. The sharp lines detected for all the four samples at 350-500 nm are due to the intraconfigurational $4f-4f$ transitions of Eu^{3+} in the host lattice. The peak position of the CTB was shifted by co-doping and those for Mg^{2+} - and Sr^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}$ were detected at 281 and 278 nm, respectively. Figure 3 shows PL emission spectra measured at appropriate excitation wavelengths for $\text{CaZrO}_3:\text{Eu}^{3+}$ ($\lambda_{\text{ex}} = 277$ nm), $\text{SrZrO}_3:\text{Eu}^{3+}$ ($\lambda_{\text{ex}} = 300$ nm) Mg^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}$ ($\lambda_{\text{ex}} = 281$ nm) and Sr^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}$ ($\lambda_{\text{ex}} = 278$ nm).

$\text{CaZrO}_3:\text{Eu}^{3+}$ showed characteristic emissions of Eu^{3+} due to $f-f$ transitions. The two distinct peaks at 591 and 614 nm were assigned to the $^5\text{D}_0-^7\text{F}_1$ and $^5\text{D}_0-^7\text{F}_2$ transitions, respectively. The intensity of the main PL emission peak at 614 nm for $\text{CaZrO}_3:\text{Eu}^{3+}$ was increased by Mg^{2+} -co-doping, while it decreased with the amount of co-doped Sr^{2+} . These changes in intensity were consistent with those previously reported for perovskite compounds [4, 7, 12].

The emission for the ${}^5D_0-{}^7F_2$ transition at 614 nm is due to an electric dipole transition that is only allowed by the lack of inversion symmetry at the Eu^{3+} site [1], while that due to the ${}^5D_0-{}^7F_1$ transition at 591 nm is due to a magnetic dipole transition, which is not affected by the inverse site symmetry. The ${}^5D_0-{}^7F_2/{}^5D_0-{}^7F_1$ luminescence intensity ratio (asymmetry ratio) gives a measure of the degree of distortion from the inversion symmetry of the local environment around the Eu^{3+} cations in the host matrix [13]. The relation between the degree of structural distortion and the PL emission intensity has often been discussed for the perovskite-type phosphors [4, 7, 12]. However, the asymmetry ratios evaluated for the Eu^{3+} -doped CaZrO_3 , $(\text{Ca}_{0.98}\text{Mg}_{0.02})\text{ZrO}_3$, $(\text{Ca}_{0.60}\text{Sr}_{0.40})\text{ZrO}_3$ and SrZrO_3 synthesized in this study were 3.06, 3.39, 3.55 and 3.92, respectively, and the red emission intensity at 614 nm for these compounds did not show the asymmetry ratio dependency.

3. 2. XRD and ALCHEMI analyses for the Eu^{3+} -occupied site

Figure 4(a) shows XRD patterns for CaZrO_3 and $\text{CaZrO}_3:\text{Eu}^{3+}_{0.05}$. The position and intensity of the diffraction peaks for CaZrO_3 are identical to those of the standard powder diffraction file JCPDS Card No. 35-0645 (CaZrO_3), whereas the

peaks for $\text{CaZrO}_3:\text{Eu}^{3+}_{0.05}$ were shifted toward lower angle. Typical peak shifts observed at diffraction angles (2θ) ranging from 74 to 75° are shown in Fig. 4(b). Figure 5(a) shows that the XRD pattern for SrZrO_3 synthesized at 1400°C is identical to that of JCPDS Card No. 44-0161 (SrZrO_3), whereas the pattern for $\text{SrZrO}_3:\text{Eu}^{3+}_{0.05}$ are shifted in the opposite direction, toward higher angle (Fig. 5(b)).

XRD patterns of Sr^{2+} -doped CaZrO_3 (nominal composition of $(\text{Ca}_{0.60}\text{Sr}_{0.40})\text{ZrO}_3$) and Sr^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}_{0.05}$ are shown in Fig. 6(a). The diffraction patterns of these samples correspond to that of the perovskite-type CaZrO_3 . Compared with Sr^{2+} -doped CaZrO_3 , the diffraction peaks of Sr^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}$ are shifted toward higher angle (Fig. 6(b)).

In the case of Mg^{2+} -doping, the limitation of the amount of Mg^{2+} soluble in CaZrO_3 was quite low, and doping with 2 mol% Mg^{2+} resulted in the formation of a secondary phase assigned to ZrO_2 (JCPDS Card No. 49-1642) (Fig. 6(a)). No difference in the diffraction peak positions between Mg^{2+} -doped CaZrO_3 (nominal composition of $(\text{Ca}_{0.98}\text{Mg}_{0.02})\text{ZrO}_3$) and the Mg^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}_{0.05}$ (nominal composition of $(\text{Ca}_{0.98}\text{Mg}_{0.02})\text{ZrO}_3:\text{Eu}^{3+}$) was detected (Fig. 6(b)), due to the small amount of Mg^{2+} -doping.

Table 1 shows the relation between the coordination number and the ionic radius of the cations investigated in this study [14]. Eu^{3+} -doping to the host CaZrO_3 resulted in lattice expansion, as shown in Fig. 4. Taking into account the size difference of the Ca^{2+} (0.112 nm) and Eu^{3+} (0.107 nm) ions with 8-coordination (A sites), and the Zr^{4+} (0.072 nm) and Eu^{3+} (0.095 nm) ions with 6-coordination (B sites), the Eu^{3+} cations are considered to occupy mainly the B sites (Zr^{4+}) in CaZrO_3 .

However, Eu^{3+} -doping to SrZrO_3 resulted in lattice shrinkage (Fig. 5); therefore, the dominant Eu^{3+} substitution site can be analogously determined as the A site (Sr^{2+}) in SrZrO_3 .

Compared with CaZrO_3 , the XRD peaks for 40 mol% Sr-doped CaZrO_3 synthesized with a nominal composition of $(\text{Ca}_{0.60}\text{Sr}_{0.40})\text{ZrO}_3$ were shifted toward lower angles, i.e., lattice expansion, and $(\text{Ca}_{0.60}\text{Sr}_{0.40})\text{ZrO}_3$ single phase without the formation of SrZrO_3 (Fig. 6(a)). The Sr^{2+} cations are considered to be located mainly at the A sites, as expected. However, Sr^{2+} -co-doped $\text{CaZrO}_3\text{:Eu}^{3+}$ exhibited a lattice shrinkage compared to $(\text{Ca}_{0.60}\text{Sr}_{0.40})\text{ZrO}_3$. These results strongly suggest that the Eu^{3+} substitution site was influenced by the presence of the larger co-dopant of Sr^{2+} at the A sites, and Eu^{3+} cations occupy mainly A sites (Ca^{2+} , Sr^{2+}).

To clarify the effect of the co-dopant on the Eu^{3+} substitution site in CaZrO_3 , further analysis was performed using the ALCHEMI technique. Figures 7(a) to (c) show bright field and dark field TEM images, and a selected area electron diffraction (SAED) pattern for $\text{CaZrO}_3:\text{Eu}^{3+}$, respectively. The ALCHEMI technique was applied for the zone axis or around the zone axis determined from the SAED pattern. The peaks assigned to Ca, Zr and Eu were clearly detected in the EDS spectra of $\text{CaZrO}_3:\text{Eu}^{3+}$, as shown in Fig. 7(d). The fits of N_{Eu} to $\sum_i a_i N_i$ ($i = \text{Ca}$ or Zr) were examined for $\text{CaZrO}_3:\text{Eu}^{3+}$ and are plotted in Fig. 7(e). The data points lie on a straight line, which indicates the relatively high statistical accuracy of the experimental data.

Further analysis using the ALCHEMI technique was conducted on $\text{SrZrO}_3:\text{Eu}^{3+}$, Sr^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}$, and Mg^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}$, and the experimental results are summarized and shown in Figs. 8, 9, and 10, respectively. The results obtained for $\text{SrZrO}_3:\text{Eu}^{3+}$ also revealed relatively high statistical accuracy (Fig 8(e)). These analyses were successfully applied for the Sr^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}$. The fits of N_{Eu} to $\sum_i a_{i, Eu} N_i$ ($i = \text{Ca}$ or Zr) (Fig. 9(e)) and those of N_{Sr} to $\sum_i a_{i, Sr} N_i$ ($i = \text{Ca}$ or Zr) (Fig. 9(f)) for the $(\text{Ca}, \text{Sr})\text{ZrO}_3:\text{Eu}^{3+}$ sample have acceptable statistical accuracies. In the case of the Mg^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}$,

relatively high statistical accuracies was achieved for analysis of the Eu^{3+} substitution site (Fig. 8(e)), while that for the Mg^{2+} substitution site failed (Fig. 10(f)). The very small amount of Mg^{2+} in this sample meant that the relative peak intensity of the EDS spectra for Mg in Fig. 10(d) was too small to be used for the ALCHEMI analysis.

The values of the α_i ($i = \text{Ca}$ or Zr) coefficient derived from Eq. (1) were calculated using a least-squares method. The impurity concentrations c_x (Eq. (2)), and the site occupancies f_{ix} (Eq. (3)), for the impurities in the samples studied using the ALCHEMI technique were determined and are listed in Table 2. $f_{\text{Eu} \rightarrow \text{B}}$ in $\text{CaZrO}_3:\text{Eu}^{3+}$ and the $f_{\text{Eu} \rightarrow \text{A}}$ in the $\text{SrZrO}_3:\text{Eu}^{3+}$ were 80% and 87%, respectively. The dominant Eu^{3+} -substitution sites determined by ALCHEMI analysis were the B-sites in the CaZrO_3 and the A-sites in SrZrO_3 , which are consistent with the XRD analysis results, where Eu^{3+} -doping of CaZrO_3 (Fig. 4) resulted in lattice expansion and Eu^{3+} -doping of SrZrO_3 (Fig. 5) resulted in lattice shrinkage.

The results obtained for 40 mol% Sr^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}$ was also in good agreement with the XRD analysis results. The co-doped Sr^{2+} could occupy A sites (Ca^{2+}) as expected. $f_{\text{Eu} \rightarrow \text{A}}$ in the $\text{Ca}_{0.60}\text{Sr}_{0.40}\text{ZrO}_3$ was 83%, and the dominant Eu^{3+} substitution site was assigned as the A sites. In contrast, the site occupancies, $f_{\text{Eu} \rightarrow \text{A}}$

and $f_{Eu \rightarrow B}$ determined for 2 mol% Mg^{2+} -co-doped $CaZrO_3:Eu^{3+}_{0.05}$ (nominal composition of $(Ca_{0.98}Mg_{0.02})ZrO_3:Eu^{3+}_{0.05}$) were 32% and 68%, respectively. Thus, the dominant Eu^{3+} substitution site was found to be the B sites (Zr^{4+}).

These analytical results indicate that the dominant Eu^{3+} occupation site in $CaZrO_3$ is strongly influenced by the co-dopant, and the ionic radius of the co-dopant was one of the critical factors.

The highest PL red emission intensity at 614 nm was achieved for Mg^{2+} -co-doped $CaZrO_3:Eu^{3+}_{0.05}$ with $f_{Eu \rightarrow B}$ of 68%, which was lower than that for $CaZrO_3:Eu^{3+}_{0.05}$ (80%). These results suggest that in addition to the amount of Eu^{3+} at the B-sites, there must be another material parameter that has an influence on the intensity of the PL red emission.

4. Conclusions

Eu^{3+} -doped $CaZrO_3$, $SrZrO_3$ and Mg^{2+} -or Sr^{2+} -doped $CaZrO_3$ were synthesized and their PL properties were characterized. Eu^{3+} substitution in $CaZrO_3$, $SrZrO_3$ and Mg^{2+} - or Sr^{2+} -doped $CaZrO_3$ was investigated using XRD analysis and the ALCHEMI technique. Eu^{3+} cations were identified to occupy mainly the B sites (Zr^{4+}) in $CaZrO_3$. The dominant Eu^{3+} substitution site in $CaZrO_3$ was strongly

influenced by the co-dopant, and the ionic radius of the co-dopant was an influential factor. The dominant Eu^{3+} substitution site could be changed to the A sites (Ca^{2+} , Sr^{2+}) with Sr^{2+} as a co-dopant with a larger ionic radius relative to Ca^{2+} , while the dominant Eu^{3+} substitution site could remain as the B sites by co-doping of Mg^{2+} with a smaller ionic radius than Ca^{2+} in Eu^{3+} -doped CaZrO_3 . To achieve further improvement in the red luminescence properties of Eu^{3+} -doped CaZrO_3 -based compounds, it is necessary to recognize the effects of various material parameters, including the influence of the two different dominant Eu^{3+} substitution sites on the red luminescence properties. Further study is in progress, and the results will be reported as Part II.

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Table 1. Relationship between coordination number and ionic radius [14].

Cation	Zr ⁴⁺	Eu ³⁺	Mg ²⁺	Eu ³⁺	Ca ²⁺	Sr ²⁺
Coordination number	6	6	8	8	8	8
Ionic radius (nm)	0.072	0.095	0.089	0.107	0.112	0.126

[14] R. D. Shannon, *Acta Crystal.*, **A32**, (1976) 751-767.

Table 2. Impurity concentrations c_x , and the fraction of site occupancies f_{ix} , determined by the ALCHEMI technique.

	CaZrO ₃	SrZrO ₃	(Ca _{0.60} Sr _{0.40})ZrO ₃		(Ca _{0.98} Mg _{0.02})ZrO ₃	
M	Eu	Eu	Eu	Sr	Eu	Mg
$a_{A,M}$	0.01	0.07	0.11	0.6	0.03	-
$a_{B,M}$	0.04	0.01	0.01	0.0	0.05	-
c_M	0.02	0.02	0.02	0.25	0.03	-
$f_{M \rightarrow A}$	0.20	0.87	0.83	1.0	0.32	-
$f_{M \rightarrow B}$	0.80	0.13	0.17	0.0	0.68	-

Figure and table captions

Fig. 1. SEM images of (a) $\text{CaZrO}_3:\text{Eu}^{3+}$, (b) $\text{SrZrO}_3:\text{Eu}^{3+}$, (c) Mg^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}$ and (d) Sr^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}$.

Fig. 2. PL excitation spectra for $\text{CaZrO}_3:\text{Eu}^{3+}$, $\text{SrZrO}_3:\text{Eu}^{3+}$, $(\text{Ca}_{0.98}\text{Mg}_{0.02})\text{ZrO}_3:\text{Eu}^{3+}$ and $(\text{Ca}_{0.60}\text{Sr}_{0.40})\text{ZrO}_3:\text{Eu}^{3+}$.

Fig. 3. PL emission spectra for $\text{CaZrO}_3:\text{Eu}^{3+}$, $\text{SrZrO}_3:\text{Eu}^{3+}$, $(\text{Ca}_{0.98}\text{Mg}_{0.02})\text{ZrO}_3:\text{Eu}^{3+}$ and $(\text{Ca}_{0.60}\text{Sr}_{0.40})\text{ZrO}_3:\text{Eu}^{3+}$.

Fig. 4. XRD patterns for (a) CaZrO_3 and $\text{CaZrO}_3:\text{Eu}^{3+}_{0.05}$ calcined at 1400 °C for 6 h, and (b) magnified XRD patterns for the region from 74 to 75° (dashed line indicates the XRD peak position for CaZrO_3 without Eu^{3+}).

Fig. 5. XRD patterns for (a) SrZrO_3 and $\text{SrZrO}_3:\text{Eu}^{3+}_{0.05}$ calcined at 1400 °C for 6 h, and (b) magnified XRD patterns for the region from 72 to 73° (dashed line indicates the XRD peak position for SrZrO_3 without Eu^{3+}).

Figure and table captions

Fig. 6. XRD patterns for (a) Mg^{2+} - or Sr^{2+} -doped CaZrO_3 and Mg^{2+} - or Sr^{2+} -doped $\text{CaZrO}_3:\text{Eu}^{3+}_{0.05}$, and (b) magnified XRD patterns for the region from 73 to 75° (dashed lines indicate the XRD peak position for the doped perovskite without Eu^{3+}).

Fig. 7. (a) Bright field and (b) dark field TEM images, and (c) SAED pattern for $\text{CaZrO}_3:\text{Eu}^{3+}$. (d) EDS spectrum for $\text{CaZrO}_3:\text{Eu}^{3+}$ and (e) fit of N_{Eu} to $\sum_i a_i N_i$ ($i = \text{Ca}, \text{Zr}$) for CaZrO_3 , together with a linear fit to the data.

Fig. 8. (a) Bright field and (b) dark field TEM images, and (c) SAED pattern for $\text{SrZrO}_3:\text{Eu}^{3+}$. (d) EDS spectrum for $\text{SrZrO}_3:\text{Eu}^{3+}$ and (e) fit of N_{Eu} to $\sum_i a_i N_i$ ($i = \text{Sr}, \text{Zr}$) for SrZrO_3 , together with a linear fit to the data.

Fig. 9. (a) Bright field and (b) dark field TEM images, and (c) SAED pattern for Sr^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}$. (d) EDS spectrum for Sr^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}$ and (e, f) Fit of N_j to $\sum_i a_{i,j} N_i$ ($i = \text{Ca}, \text{Zr}; j = \text{Eu}, \text{Sr}$) for $(\text{Ca}, \text{Sr})\text{ZrO}_3$, together with a

linear fit to the data.

Fig. 10. (a) Bright field and (b) dark field TEM images, and (c) SAED pattern for Mg^{2+} -co-doped $\text{CaZrO}_3:\text{Eu}^{3+}$. (d) EDS spectrum and (e,f) Fit of N_j to $\sum_i a_{i,j} N_i$ ($i = \text{Ca}, \text{Zr}; j = \text{Eu}, \text{Mg}$) for $(\text{Ca},\text{Mg})\text{ZrO}_3$, together with a linear fit to the data.

Table 1. Relationship between coordination number and ionic radius [14].

Table 2. Impurity concentrations c_x , and the fraction of site occupancies f_{ix} , determined by the ALCHEMI technique.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

CaZrO₃ (Orthorhombic)

The site substituted by Eu³⁺ cation

Host	By XRD	By ALCHEMI
CaZrO ₃	B-site	B-site
SrZrO ₃	A-site	A-site
(Ca, Sr)ZrO ₃ ^{*1}	A-site	A-site
(Ca, Mg)ZrO ₃ ^{*2}	-	B-site

^{*1} Sr²⁺ cations could occupy into A-site.

^{*2} The amount of Mg²⁺ was too low to be determined.