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Sensitized luminescence and energy transfer in Ce^{3+} and Eu^{2+} codoped calcium magnesium chlorosilicate

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Abstract

Ce^{3+} and Eu^{2+} ions codoped calcium magnesium chlorosilicate $[\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2]$ phosphors have been synthesized and characterized. Intense bluish-green light was observed under ultraviolet and blue light excitations. The diffuse reflection, excitation and emission spectra of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ were measured at room temperature, and enhancement of Eu^{2+} emission was confirmed. The fluorescence lifetimes of Ce^{3+} were measured, and the mechanism of nonradiative energy transfer from Ce^{3+} to Eu^{2+} is found to be electric dipole–dipole interaction. The probabilities and efficiencies of nonradiative energy transfer were also calculated, and the results indicate that the efficiency can be as high as 86% in this material system. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Solid-state green light sources are desirable for high density optical storage, color displays, medical diagnostics and undersea communications [1,2]. Many efforts have been spent on Er^{3+} doped fluoride materials due to their efficient green up-conversion [1–3]. However, these materials are not stable and may be not suitable for device applications. Calcium magnesium chlorosilicate $[\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2]$ is a new kind of luminescence

host with stable crystal structure and high thermal stability, and Eu^{2+} and Ce^{3+} singly doped $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$ have been demonstrated to be high efficient green and purplish-blue phosphors, respectively [4,5]. $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ phosphor emits bright green light when excited by ultraviolet and blue lights from near ultraviolet- and blue-emitting LEDs, and can be used to make efficient green light sources. In addition, this stable phosphor is important for the development of materials against counterfeiting [6] and efficient ultraviolet–visible transformation devices.

It is well known that the energy transfer from donor to acceptor plays an important role in luminescence and solid-state lasers [7,8]. The 4f–5d

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transitions of Ce^{3+} and Eu^{2+} are very sensitive to the nature of the host lattice, and the absorption and emission of Ce^{3+} and Eu^{2+} are efficient in many hosts [9–12]. In Ce^{3+} and Eu^{2+} codoped $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$ new system, strong coupling between Ce^{3+} and Eu^{2+} ions may occur, leading to variations in the excitation and emission spectra of Eu^{2+} . This is because the Ce^{3+} emission spectrum in the purplish-blue region overlaps considerably with the excitation spectrum of Eu^{2+} . Moreover, for practical applications it would be important if Ce^{3+} could greatly enhance the emission of Eu^{2+} , because cheaper CeO_2 could be used partly to replace expensive Eu_2O_3 .

In this paper, the luminescence properties of and the energy transfer process in $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ are reported. The diffuse reflection, excitation and emission spectra, and the fluorescence intensities of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ are compared to those of Eu^{2+} singly doped $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$. The enhanced green emission of Eu^{2+} is confirmed, and there is an efficient non-radiative energy transfer between Ce^{3+} and Eu^{2+} under ultraviolet light excitation. Fluorescence decay curves of Ce^{3+} in $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ system were obtained, and the experimental decay curves were fitted to the equations given by Inokuti and Hirayama (IH model) [13].

2. Experimental

Polycrystalline samples of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ were synthesized by high temperature solid state reaction. The starting materials were SiO_2 (GR), CaCO_3 (AR), MgO (4N), CaCl_2 (AR), Eu_2O_3 (4N), CeO_2 (4N), and Li_2CO_3 (AR). The synthesis procedure is similar to that described previously [4,5].

The crystal structure of the powder samples was examined using a D/max-rA X-ray diffractometer. The diffraction patterns indicate that the materials obtained were cubic calcium magnesium chlorosilicate. The excitation and fluorescence spectra of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ were measured at room temperature using a Hitachi MPF-4 spectrofluorometer and a 75-W xenon lamp source. The diffuse reflection spectra of the samples were

measured relative to MgO , and the wavelength resolution for all spectra was 0.5 nm.

The decay curves of the 5d level of Ce^{3+} ions in the $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ system were measured using time-correlated single-photon counting technique. The excitation source was a nanosecond flash lamp filled with nitrogen, and the excitation wavelength was 337 nm. The distortion of the fluorescence due to excitation source, photomultiplier and electronic system was removed by a suitable deconvolution procedure.

3. Results and discussion

The polycrystalline $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$ samples were white in colour. $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ and $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ phosphors were yellowish-green in colour. The diffuse reflection spectra of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$ host, $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.006\text{Ce}^{3+}$, $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.03\text{Eu}^{2+}$ and $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.006\text{Ce}^{3+}, 0.03\text{Eu}^{2+}$ phosphors are shown in Fig. 1. Curve 1 indicates that the absorption of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$ host is strong in the 240–340 nm spectral region, weak in the ultraviolet long-wavelength region, and most of excitation energy is reflected in the visible light region. Comparison of curves 2 and 3 with 1 indicates that the absorption of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.006\text{Ce}^{3+}$ and $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.03\text{Eu}^{2+}$ in

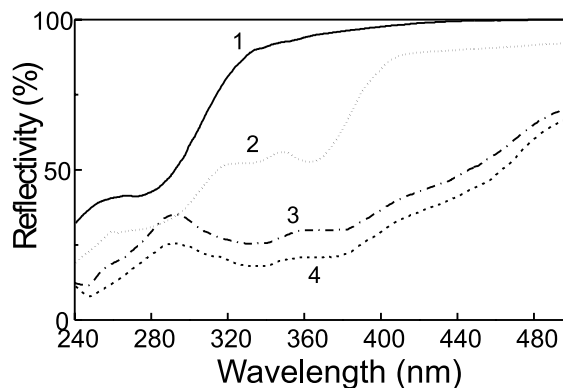


Fig. 1. Diffuse reflection spectra of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$ host (curve 1), $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.006\text{Ce}^{3+}$ (curve 2), $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.03\text{Eu}^{2+}$ (curve 3) and $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.006\text{Ce}^{3+}, 0.03\text{Eu}^{2+}$ (curve 4).

the 320–480 nm spectral range is much stronger than that of the $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$ host. The two diffuse reflection peaks of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.006\text{Ce}^{3+}$ are located at ~ 333 and 363 nm, and correspond to the $4f^1-4f^05d^1$ transitions of Ce^{3+} in $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$. The diffuse reflection of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.03\text{Eu}^{2+}$ consists of three broad bands, and the peaks are at 334 , 378 and ~ 450 nm. These absorption bands belong to the $4f^7-4f^65d^1$ transitions of Eu^{2+} and are strong in the ultraviolet and blue spectral regions. This is an essential condition for $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ to become an efficient green luminescence material. The diffuse reflection of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ (curve 4) shows that the absorption in the 240–500 nm spectral range is stronger than those of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$ and $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$, because the absorption is the net result of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2$ host and the $4f \rightarrow 5d$ band transition absorption of Eu^{2+} and Ce^{3+} . This efficient absorption of excitation energy increases the luminescence efficiency of phosphors.

The emission spectra of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:X\text{Ce}^{3+}, 0.03\text{Eu}^{2+}$ and $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.006\text{Ce}^{3+}$ at room temperature under 365 nm ultraviolet light excitation are shown in Fig. 2. It can be seen that $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ (curve 1) has a strong green band with the peak at 509 nm which is assigned to the octa-coordinated Eu^{2+} emission center [4]. The emission spectra of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4$

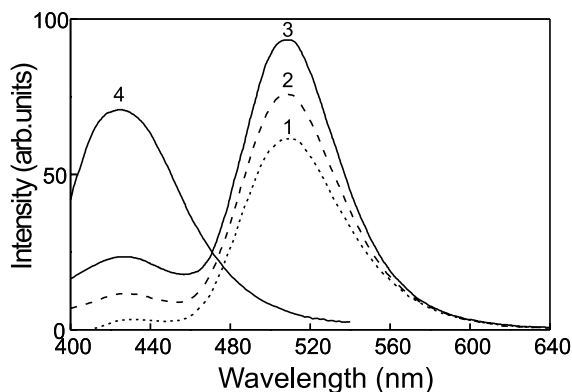


Fig. 2. Fluorescence spectra of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.03\text{Eu}^{2+}$ (curve 1), $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.006\text{Ce}^{3+}, 0.03\text{Eu}^{2+}$ (curve 2), $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.03\text{Ce}^{3+}, 0.03\text{Eu}^{2+}$ (curve 3) and $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.006\text{Ce}^{3+}$ (curve 4) under 365 nm excitation.

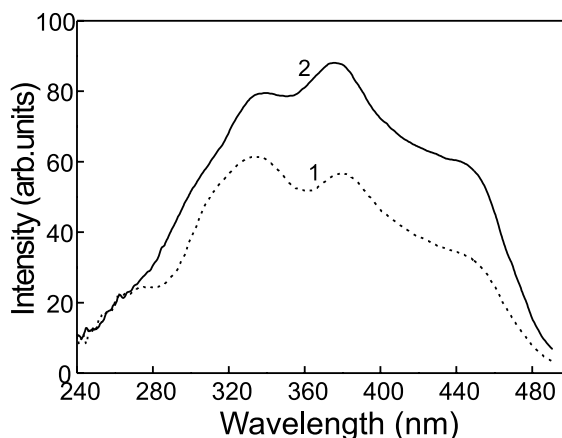


Fig. 3. Excitation spectra of Eu^{2+} (509 nm emission) in $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.03\text{Eu}^{2+}$ (curve 1) and $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.03\text{Ce}^{3+}, 0.03\text{Eu}^{2+}$ (curve 2).

$\text{Cl}_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ (curve 2,3) exhibit a weak purplish-blue band at 427 nm which is due to the $5d-4f$ transition of Ce^{3+} , and a strong Eu^{2+} green emission band at 509 nm which is due to the simultaneous excitation of Eu^{2+} . Comparison of curves 1, 2 and 3 shows that codoping with a small amount of Ce^{3+} ions not only enhances the Eu^{2+} green emission band but also changes the luminescence colour of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ from green to bluish-green.

The excitation spectra of Eu^{2+} (509 nm emission) in both $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ and $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ are shown in Fig. 3. The Eu^{2+} emission intensity in $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ (curve 2) is higher than that in $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ (curve 1) under ultraviolet and blue light excitation from 270 to 480 nm spectral range. There are some differences between the spectrum shapes of the two phosphors. In order to show the differences clearly, the spectrum $[I(\text{curve 2}) - I(\text{curve 1})]$ is depicted as curve 1 in Fig. 4.

Curves 1 and 2 [excitation spectrum of $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Ce}^{3+}$] in Fig. 4 are similar in the $270-380$ nm spectral region. This means that variations of Eu^{2+} emission intensities are due to the Ce^{3+} excitation band under ultraviolet radiation from 270 to 380 nm, and there is a nonradiative energy transfer process from Ce^{3+} to Eu^{2+} in

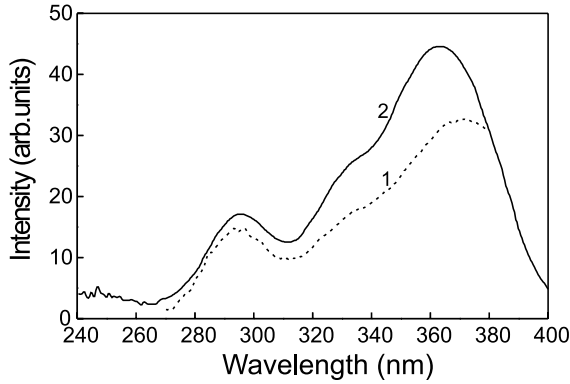


Fig. 4. Curve 1: Difference in excitation spectrum between $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.03\text{Ce}^{3+}, 0.03\text{Eu}^{2+}$ and $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.03\text{Eu}^{2+}$. Curve 2: Excitation spectrum of Ce^{3+} (425 nm emission) in $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.02\text{Ce}^{3+}$.

$\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ under ultraviolet light excitation.

Fluorescence decay curves for the $4f^05d^1 \rightarrow 4f^15d^0$ transition of Ce^{3+} in $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.02\text{Ce}^{3+}, Y\text{Eu}^{2+}$ samples with different Eu^{2+} concentrations (Y) are shown in Fig. 5. The decay curves are nonexponential with increasing Y . At low donor (Ce^{3+}) concentration, diffusion of excitation energy between Ce^{3+} ions can be neglected. Therefore, the Inokuti–Hirayama formula [13]

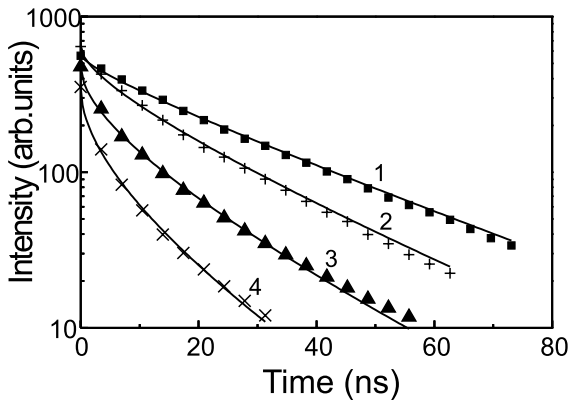


Fig. 5. Fluorescence decay curves of Ce^{3+} (400 nm emission) in $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.02\text{Ce}^{3+}, Y\text{Eu}^{2+}$. $Y = 0.02$ (no. 1), 0.04 (no. 2), 0.06 (no. 3), and 0.08 (no. 4). Solid curves: IH theoretical curves; symbols: Experimental data.

$$I(t) = I(0) \exp \left[-\frac{t}{\tau_0} - \frac{4}{3} \pi \Gamma \left(1 - \frac{3}{s} \right) N_A R_0^3 \left(\frac{t}{\tau_0} \right)^{3/s} \right] \quad (1)$$

can be used to describe the density of the donor (Ce^{3+}) in the presence of the acceptor (Eu^{2+}), where τ_0 is the intrinsic lifetime of donor ion, N_A is the concentration of acceptor ions, Γ is the gamma function, R_0 is the critical transfer distance, and the interaction parameter $s = 6$ for electric dipole–dipole, $s = 8$ for dipole–quadrupole, and $s = 10$ for quadrupole–quadrupole interaction.

The experimental decay curves were fitted to Eq. (1) by the standard least-squares method. All the root-mean-square (rms) errors are listed in Table 1. The fittings were good in the case of electric dipole–dipole interaction (solid lines in Fig. 5), but became distinctly poorer for the dipole–quadrupole and quadrupole–quadrupole interactions for all these curves. In the last two cases, the rms errors were systematically larger than that for the dipole–dipole interaction by at least a factor of two. The results indicate that dipole–dipole interaction is the dominant mechanism governing the nonradiative energy transfer from Ce^{3+} to Eu^{2+} in $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ under ultraviolet radiation.

The critical energy-transfer distance (R_0) is an adjustable parameter and has an average value of 1.5 nm. The values of the measured lifetime and the derived values of the critical distance are given in Table 2. The probability (P) and the efficiency (η) of nonradiative energy transfer were calculated from the lifetime data using the expressions

$$P = 1/\tau - 1/\tau_0, \quad (2)$$

$$\eta = \frac{P}{1/\tau} = 1 - \frac{\tau}{\tau_0}, \quad (3)$$

where τ_0 is the intrinsic lifetime of the donor and τ is the lifetime of the donor in the presence of acceptor. The values of P and η obtained at room temperature are also presented in Table 2, and the efficiency of nonradiative energy transfer can be as high as 86%.

Table 1

Root-mean-square error of fittings on experimental decay curves using Inokuti–Hirayama formula

Sample	$S = 6$ (%)	$S = 8$ (%)	$S = 10$ (%)
$\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.02\text{Ce}^{3+}, 0.02\text{Eu}^{2+}$	2.82	8.41	6.63
$\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.02\text{Ce}^{3+}, 0.04\text{Eu}^{2+}$	2.51	6.84	9.73
$\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.02\text{Ce}^{3+}, 0.06\text{Eu}^{2+}$	2.42	6.85	10.24
$\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:0.02\text{Ce}^{3+}, 0.08\text{Eu}^{2+}$	1.69	5.86	8.83

Table 2

Fluorescence lifetimes and energy-transfer parameters of Ce^{3+} in $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:X\text{Ce}^{3+}, Y\text{Eu}^{2+}$

Ce^{3+} conc. (X)	Eu^{2+} conc. (Y)	τ (ns)	rms (%)	η (%)	P ($\times 10^7 \text{ s}^{-1}$)	R_0 (nm)
0.02	0	35.47				
0.02	0.02	24.10	4.14	32	1.33	1.41
0.02	0.04	14.96	10.41	58	3.87	1.48
0.02	0.06	8.85	15.11	75	8.48	1.52
0.02	0.08	5.01	13.69	86	17.14	1.58

4. Conclusion

In summary, $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ has been demonstrated to be an efficient bluish-green emission phosphor under ultraviolet light excitation. In this material system, Ce^{3+} and Eu^{2+} act as donor and acceptor, respectively, and the efficiency of nonradiative energy transfer from Ce^{3+} to Eu^{2+} can be as high as 86%. Comparison of the excitation and emission spectra indicates that Ce^{3+} is a sensitizer in this system. The fluorescence decay curves of Ce^{3+} in this material system were fitted to the Inokuti–Hirayama formula, and the dominant nonradiative energy transfer mechanism from Ce^{3+} to Eu^{2+} is found to be electric dipole–dipole interaction. Both $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Eu}^{2+}$ and $\text{Ca}_8\text{Mg}(\text{SiO}_4)_4\text{Cl}_2:\text{Ce}^{3+}, \text{Eu}^{2+}$ emit efficient green and bluish-green lights under near ultraviolet and blue-emitting LED excitations. Hence, they are suitable for the development of fluorescent display devices, efficient green light sources and anti-counterfeiting materials.

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