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# Stabilization of divalent $\text{Eu}^{2+}$ in fluorosilicate glass-ceramics *via* lattice site substitution†

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Yong Liu,<sup>a</sup> Xianping Fan,<sup>id</sup> <sup>a</sup> Guodong Qian,<sup>id</sup> <sup>a</sup> Xianghua Zhang<sup>c</sup> and Gaorong Han<sup>a</sup>

Fluorosilicate glasses and glass-ceramics with  $\text{MF}_2$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ),  $\text{ZnF}_2$  or  $\text{LaF}_3$  components were investigated to host divalent  $\text{Eu}^{2+}$  for photoluminescence (PL) application. X-ray diffraction phase identification and a series of spectroscopic analyses were performed to reveal the relationship between microstructure and the reduction of  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ . The precursor glasses were believed being constituted by silicate-rich phases and fluoride-rich phases, due to the immiscibility of fluoride-and-silicate mixed glass system. After heat treatment, the fluoride-rich glass phases could transform into fluoride crystalline phase in the glass-ceramics. Europium tended to enrich in the fluoride-rich phases in the glasses or in the precipitated fluoride crystalline phases in the glass-ceramics. Small amounts of  $\text{Eu}^{3+}$  were reduced to  $\text{Eu}^{2+}$  in the glasses where the electronegativity had a crucial impact. In contrast, large amounts of  $\text{Eu}^{3+}$  were reduced to  $\text{Eu}^{2+}$  in the glass-ceramics containing  $\text{MF}_2$  nanocrystals, where the reduction was determined by lattice site substitution. Using  $\text{ZnAl}_2\text{O}_4$  containing glass-ceramics as reference, it was evidenced that the similar and a little larger radii between sites and substitution ions are the prerequisite for  $\text{Eu}^{3+}/\text{M}^{2+}$  substitution. And using  $\text{LaF}_3$  containing glass-ceramics as reference, it was certified that unbalanced charge at substitution sites induce the  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reduction.

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## Introduction

As  $\text{Eu}^{2+}$  possesses ideal properties for light emission such as large absorption cross section, broad band spectrum, and highly efficient photoluminescence (PL), it has been widely adopted as active center in phosphor materials.<sup>1,2</sup> Owing to the exposure of 5d-shell of  $\text{Eu}^{2+}$  to ligands, it is also facile to tune its emission from violet to red by adjusting host lattice.<sup>3</sup> Thus,  $\text{Eu}^{2+}$ -doped inorganic phosphors have been widely used in commercial lighting and display devices, such as epoxy resin-or-silica mixed phosphor converted light emitting diodes (PC-LED) by mixing with resin or silica as spectrum transfer material.<sup>4</sup> However, such PC-LED structure usually suffers from thermal deterioration because of different thermal expansions and conductivities between phosphors and epoxy resin. In order to solve this problem, researchers recently developed glass-ceramics<sup>5–9</sup> with Eu-doped fluoride crystalline phases. It showed great advantages in thermal resistance, durability, and microstructure manipulation. Eu could enrich in fluoride phase, such

as  $\text{MF}_2$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ), of glass-ceramics to adapt itself with well-behaved PL performance.

However,  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  always coexist in the host, because Eu cation has variable valences. It thus becomes crucial to keep divalent  $\text{Eu}^{2+}$  as the majority. Generally, there are several ways to transform  $\text{Eu}^{3+}$  into  $\text{Eu}^{2+}$ : (i) adding reducing agents,<sup>10–12</sup> (ii) inputting reducing atmosphere during preparation processes,<sup>13,14</sup> (iii) adjusting optical basicity or electronegativity of host,<sup>15,16</sup> (iv) substituting  $\text{M}^{2+}$  sites in crystalline lattices.<sup>17,18</sup> As strategies (i) and (ii) accompany drawbacks such as introducing impurities into the system or leading to infeasibility for elaborated optimization of concentration and distribution of  $\text{Eu}^{2+}$ , strategies (iii) and (iv) are usually considered to be more executable. Using strategy (iv), silicate,<sup>19,20</sup> aluminosilicate,<sup>10,15,21</sup> borophosphate<sup>22,23</sup> and fluoride crystalline phases<sup>24–26</sup> have been reported as good stabilizers for divalent  $\text{Eu}^{2+}$ . Among them, fluoride crystalline phases show most advantages owing to their ultrasmall sizes down to several nanometers, similar refractive indices with silicate glasses, ideal host to selectively enrich  $\text{Eu}^{2+}$ . Hence, fluorosilicate glass-ceramics containing  $\text{Eu}^{2+}$ -enriched fluoride nanocrystals could achieve high transparency, large  $\text{Eu}^{3+}/\text{Eu}^{2+}$  reduction ratio, enhanced PL performance and ideal physico-chemical properties.

Our previous studies<sup>5–7</sup> have evidenced that alkaline earth fluoride ( $\text{MF}_2$ , where  $\text{M} = \text{Ca}; \text{Sr}; \text{Ba}$ ) nanocrystals could be good hosts to precipitate and enrich  $\text{Eu}^{2+}$  by  $\text{Eu}^{2+}/\text{M}^{2+}$  lattice substitution. But there is still a lack of systematical dissertation summarizing such lattice substitution strategy for stabilizing

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$\text{Eu}^{2+}$  in the fluorosilicate glass-ceramics. In this study, we prepared glass and glass-ceramic samples with the composition of  $50\text{SiO}_2\text{-}20\text{Al}_2\text{O}_3\text{-}20\text{MF}_x\text{-}7\text{NaF-}3\text{EuF}_3$  ( $\text{M} = \text{Ca, Sr, Ba, Zn}$ ) and  $50\text{SiO}_2\text{-}20\text{Al}_2\text{O}_3\text{-}20\text{LaF}_3\text{-}7\text{NaF-}3\text{EuF}_3$ . By comparative study of the valence state evolution and spectroscopic behaviors of Eu cations, we demonstrate the feasibility of the proposed site substitution strategy to stabilize the divalent  $\text{Eu}^{2+}$  in the fluorosilicate glass-ceramics containing  $\text{MF}_2$  nanocrystals.

## Experimental methods

Oxyfluoride glasses (and a glass-ceramic sample) with the compositions of  $50\text{SiO}_2\text{-}20\text{Al}_2\text{O}_3\text{-}20\text{MF}_x\text{-}7\text{NaF-}3\text{EuF}_3$  in mol%, named as G1–4, GC5 ( $\text{M} = \text{Ca, Sr, Ba, La, or Zn}$ ;  $x$  is the valence of ion  $\text{M}$ ) was prepared by a melt-quenching method. Total weight of 50 g raw materials was weighed and mixed well in a RETSCH RM 200 mortar grinder. The batches of the raw materials were melted at  $1500^\circ\text{C}$  for 45 min in air. Plain glass was obtained by quenching the melt between two brass plates. The subsequent crystallization temperature of  $660^\circ\text{C}$  was selected between the first crystallization temperature ( $T_{c1}$ ) and the second crystallization temperature ( $T_{c2}$ ) for G1–4 (Fig. 1 (a)). The glass-ceramics GC1–4 were obtained by annealing the glasses at the above temperatures for 45 min in air. The compositions and crystallization temperatures of the groups are demonstrated below in Table 1. Note that the  $\text{ZnF}_2$ -based sample (GC5) loses its transparency due to an uncontrollable crystallization during the melt-quenching process.

Differential thermal analysis (DTA) measurement was carried out on a CDR-1 differential thermal analyzer with fixed specimen weight of 60 mg. XRD analysis was carried out on a PANalytical B.V. Empyrean 200895 X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ), and the scan speed was  $2.00 \text{ deg min}^{-1}$ . The excitation and emission spectra combining quantum yields were measured by an Edinburgh Instruments fluorospectrometer FLS 920 equipped with a red-sensitive photomultiplier (Hamamatsu R928P) in a Peltier-cooled housing in the single photon counting mode and with the aid of an integration sphere. A 450 W ozone-

**Table 1** The nominal compositions and the first and second crystallization temperature of glasses

Sample	Composition (mol%)	$T_{c1}$	$T_{c2}$
G1	$50\text{SiO}_2\text{-}20\text{Al}_2\text{O}_3\text{-}20\text{CaF}_2\text{-}7\text{NaF-}3\text{EuF}_3$	$602^\circ\text{C}$	$800^\circ\text{C}$
G2	$50\text{SiO}_2\text{-}20\text{Al}_2\text{O}_3\text{-}20\text{SrF}_2\text{-}7\text{NaF-}3\text{EuF}_3$	$598^\circ\text{C}$	$750^\circ\text{C}$
G3	$50\text{SiO}_2\text{-}20\text{Al}_2\text{O}_3\text{-}20\text{BaF}_2\text{-}7\text{NaF-}3\text{EuF}_3$	$597^\circ\text{C}$	$752^\circ\text{C}$
G4	$50\text{SiO}_2\text{-}20\text{Al}_2\text{O}_3\text{-}20\text{LaF}_3\text{-}7\text{NaF-}3\text{EuF}_3$	$650^\circ\text{C}$	$882^\circ\text{C}$
GC5	$50\text{SiO}_2\text{-}20\text{Al}_2\text{O}_3\text{-}20\text{ZnF}_2\text{-}7\text{NaF-}3\text{EuF}_3$	$815^\circ\text{C}$	

free xenon lamp was used as the excitation source for steady-state measurements. The calibrations for quantum yields were made by the Edinburgh Instrument and the measurements were repeated three times at room temperature for each excitation scheme and then averaged overall.

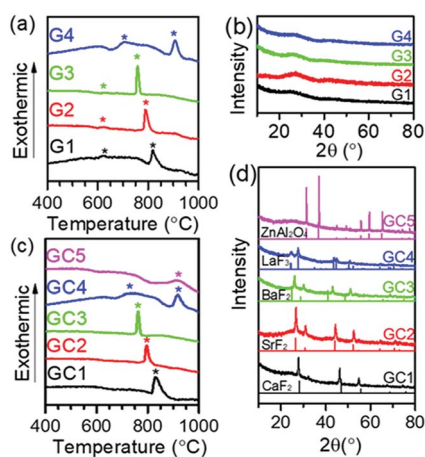
## Results and discussion

### Transition from glasses to glass-ceramics

Evidenced by differential thermal analysis (DTA, Fig. 1(a and c)) and X-ray diffraction (XRD, Fig. 1(b and d)), sample G1–4 referred to typical inorganic glasses without any crystalline phase, while sample GC5 was glass-ceramic constituted by the precipitated  $\text{ZnAl}_2\text{O}_4$  crystalline phases and residual glass phase. Glass samples G1–G4 have two exothermic DTA peaks, where the first peaks (which appeared at lower temperature) correspond to the precipitation of fluoride nanocrystals ( $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$ ,  $\text{LaF}_3$ ). Such kinds of crystalline phases were revealed by XRD patterns (Fig. 1(d)) of the glass-ceramics, GC1–GC4. These samples were obtained by annealing G1–G4 at  $660^\circ\text{C}$ , which were located between two crystallization peaks for 45 minutes. In contrast, the as-melt sample, GC5, was already glass-ceramic with opaque appearance due to the uncontrollable crystallization of  $\text{ZnAl}_2\text{O}_4$  during the quenching process of the melt. According to the Scherrer formula, the crystal sizes could be estimated from peak width of XRD patterns. As a result, the sizes of  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$ ,  $\text{LaF}_3$  and  $\text{ZnAl}_2\text{O}_4$  crystals in the glass-ceramics were evaluated as  $19.3 \pm 0.2 \text{ nm}$ ,  $14.6 \pm 0.2 \text{ nm}$ ,  $16.0 \pm 0.3 \text{ nm}$ ,  $17.9 \pm 2.7 \text{ nm}$  and  $>100 \text{ nm}$ , respectively. GC1–4 have high transparency, but GC5 lost its transparency. This is due to much smaller size of precipitated  $\text{MF}_x$  nanocrystals than the visible-near infrared wavelength, as well as similar refractive indices between  $\text{MF}_x$  nanocrystals and silicate hosts. So the fluorosilicate glass-ceramics show more optical merits than the reported oxide glass-ceramics.<sup>17–21</sup> The volume fractions of the precipitated nanocrystals (crystallinity) could also be evaluated by the integral intensity ratio of crystalline diffraction to all the diffraction. And the crystallinities were estimated to around 20% for all the glass-ceramic samples. Therefore, the glasses were converted into the glass-ceramics containing  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$ ,  $\text{LaF}_3$  nanocrystals except the  $\text{ZnF}_2$ -based GC5.

### Spectroscopic behaviors of $\text{Eu}^{3+}$ and $\text{Eu}^{2+}$

The sharp PL peaks in Fig. 2(a and b) were assigned to the  $4f\text{-}4f$  transitions of  $\text{Eu}^{3+}$ , while the broad PL bands in Fig. 2(c) could



**Fig. 1** DTA curves and XRD patterns of the G1–G4 glasses (a and b) and the GC1–GC5 glass-ceramics (c and d) with reference to the standard JCPDS cards.



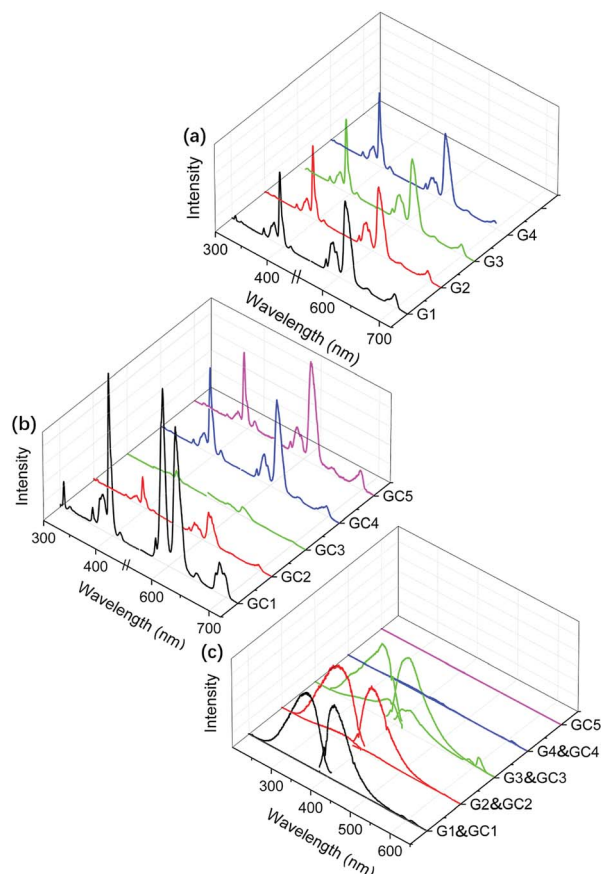


Fig. 2 PL excitation and emission spectra of the glasses (a) and the glass-ceramics (b) by monitoring and exciting with typical 4f–4f transitions of  $\text{Eu}^{3+}$  ( $\lambda_{\text{em}} = 612 \text{ nm}$ ,  $\lambda_{\text{ex}} = 393 \text{ nm}$ ), where the intensities of the glass in (a) are normalized by the maximum intensities and the intensity of the glass-ceramics in (b) are further normalized by those of the precursor glasses. In contrast, PL spectra (c) of the glasses and glass-ceramics are monitored and excited with typical 4f–5d transitions of  $\text{Eu}^{2+}$  ( $\lambda_{\text{em}} = 420 \text{ nm}$ ,  $\lambda_{\text{ex}} = 350 \text{ nm}$ ), where all the intensities are normalized by the maximum of the glass-ceramics except that G4, GC4 and GC5 have no intense PL spectra.

be assigned to  $4f^7\text{--}4f^65d^1$  transitions of  $\text{Eu}^{2+}$ . For  $\text{Eu}^{3+}$ , the PL excitation peaks of 363, 381, 393 and 414 nm were attributed to the transitions of  $^7\text{F}_0 \rightarrow ^5\text{D}_4$ ,  $^5\text{G}_4$ ,  $^5\text{L}_6$ ,  $^5\text{D}_3$ , respectively. And

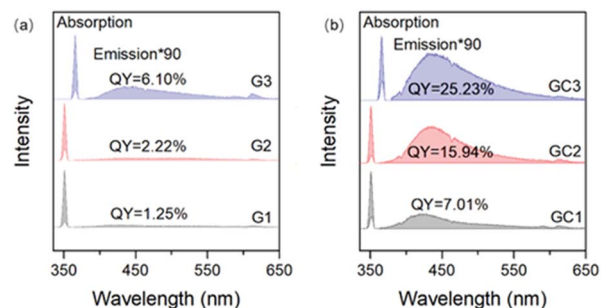


Fig. 3 The integral sphere collected PL spectra of  $\text{Eu}^{2+}$  in the  $\text{MF}_2$ -based (a) glasses and (b) glass-ceramics. The excitation spectra were monitored at 350 nm, and the emission spectra were excited at 420 nm.

the PL emission peaks were ascribed to  $^5\text{D}_0 \rightarrow ^7\text{F}_J$  where  $J = 1, 2, 3$  and 4 correspond to 590, 612, 650 and 689 nm, respectively. As the 4f electron shell was shielded by the outer shells (5d and 6s), the 4f–4f transition was less influenced by coordination surroundings, which led the parabolas of  $4f^n$  excited states to be located in parallel and directly above the ground state in the configuration coordinate. Therefore, the band widths of  $\text{Eu}^{3+}$  PL peaks appeared as narrow linear shapes. On the contrary, the PL bands of  $\text{Eu}^{2+}$  have large band width covering more than 100 nm with the maxima at 350 and 420 nm. As d shell is exposed to ligands, there was offset between the equilibrium position of both the  $4f^65d^1$  and  $4f^7$  states of  $\text{Eu}^{2+}$ . Therefore, the f–d transition presented large Stokes shift, and electron–phonon coupling further broadened the PL bands.<sup>27</sup> Such a Stokes shift and spectral broadening are depicted in Fig. S1.† It shows that  $\text{Eu}^{2+}$  has similar PL bands in the glasses and glass-ceramics. But there are large Stokes shifts on the PL excitation and emission spectra. Between the glass and glass-ceramic samples, more or less Stokes difference exists, where GC3 exhibits the largest Stokes shift ( $4712 \text{ cm}^{-1}$ ) among all the samples. These are attributed to the different coordination environments around  $\text{Eu}^{2+}$  in the glass and glass-ceramics. In the glass samples,  $\text{Eu}^{2+}$  is mainly surrounded by both  $\text{O}^{2-}$  and  $\text{F}^-$ , while  $\text{Eu}^{2+}$  ions are predominantly enriched in fluoride phase in glass-ceramics. With the enrichment of  $\text{Eu}^{2+}$  in different nanocrystals, the Stokes shifts of  $\text{Eu}^{2+}$  also appear to have some differences due to the lattice difference of  $\text{MF}_2$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}$ ) nanocrystals. With configuration coordinates, Fig. S2† illustrates Stokes shift order of  $\Delta\text{stokes}(\text{G3}) < \Delta\text{stokes}(\text{GC3})$  and  $\Delta\text{stokes}(\text{G3}) < \Delta\text{stokes}(\text{GC1}) < \Delta\text{stokes}(\text{GC2})$ .

All the glasses and glass-ceramics showed PL feature of both  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$ , except that the  $\text{LaF}_3$ -based samples only exhibited the PL feature of  $\text{Eu}^{3+}$ . For comparison, the PL intensities of each group were normalized according to glasses for  $\text{Eu}^{3+}$  and glass-ceramics for  $\text{Eu}^{2+}$ . Compared to the glasses, most of the glass-ceramics possessed stronger PL for  $\text{Eu}^{2+}$ , owing to the reduction of  $\text{Eu}^{3+}$  into  $\text{Eu}^{2+}$  during the treatment. The  $\text{Eu}^{2+}$  bands also existed in glass samples and increased by the sequence of G1 to G3 according to Fig. 2(c). The appearance of PL bands implied that reduction of  $\text{Eu}^{3+}$  started in the glass forming stage. However, the PL of  $\text{Eu}^{3+}$  displayed intricate changes before and after heat treatment. The  $\text{Eu}^{3+}$  PL peaks of  $\text{CaF}_2$  and  $\text{LaF}_3$  based glass-ceramics (GC1 and GC4) strengthened after heat treatment, while the PL peaks of  $\text{SrF}_2$  and  $\text{BaF}_2$  based glass-ceramics (GC2 and GC3) were weaker than those of the glasses. In addition, sample G4, GC4 and GC5 almost had no intense PL bands of  $\text{Eu}^{2+}$  according to Fig. 2(c), which indicates the absence of  $\text{Eu}^{2+}$  in those samples. The evolution of PL intensity could be also evidenced by the integral sphere collected spectra (Fig. 3(a and b)). We believe that the PL behavior of the material was mainly influenced by: (i) the ratio diversification of  $\text{Eu}^{3+}/\text{Eu}^{2+}$  due to the  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reduction; (ii) the coordination of  $\text{Eu}^{2+}/\text{Eu}^{3+}$  into the precipitated crystalline phases. These two factors will be discussed in subsequent passages.





## Electronegativity related reduction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ in the glasses

The reduction of  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  in glass is usually believed to relate with the optical basicity. This parameter was primarily used to describe the “electron donor ability” of oxygen as well as the concentration of non-bridging oxygen.<sup>28,29</sup> From Fig. 2(c), the PL of  $\text{Eu}^{2+}$  increased by the consequence of  $G1 < G2 < G3$ . However, this trend contradicted the well-developed theory of optical basicity that the lower optical basicity ( $A(\text{Ca}^{2+}) < A(\text{Sr}^{2+}) < A(\text{Ba}^{2+})$ ) determined the higher reduction ratio of  $\text{Eu}^{2+}$  ( $G1 > G2 > G3$ ).<sup>15</sup> (Herein, due to relatively small concentration of  $\text{Eu}^{2+}$ , it could be assumed to still be lower than the PL quenching concentration and thus be correlated with PL intensity.) We believed that the contradiction was primarily because the investigated glasses were fluoride and oxide mixed glass system. Oxide (silicate) glass is covalent bond majored “random tetrahedral network” and linked by sharing corners, while fluoride glass is ionic bond majored “random polyhedral packing” and linked by sharing corners, edges and planes. In the high fluoride content (30 mol%) mixed system, we have revealed that the glass was indeed constructed by separated fluoride-rich glass phases and silicate-rich glass phases.<sup>30</sup> Thus, the  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reduction could not be well interpreted by optical basicity, but we tried to relate it with “electronegativity”, which was the primary origin of “optical basicity”.

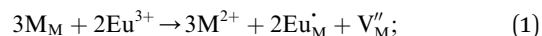
Electronegativity,  $\chi$ , is a chemical property that describes the tendency of an atom or ion to attract electron clouds towards itself.<sup>31</sup> Due to the electronegativity differences between  $\text{Eu}^{3+}$  and other cations,  $\text{Eu}^{3+}$  tended to attract more electron density around its neighboring cations with lower electronegativity, and eventually captured an electron from fluorine. Thus, the  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reduction was more likely to happen where electronegativity of neighboring cations of  $\text{Eu}^{3+}$  were lower. In the glass samples, there were indeed two kinds of separated glass phases: fluoride-rich glass phases and silicate-rich glass phases.<sup>30</sup> It has been well evidenced that lanthanides, such as europium, could selectively enrich in fluoride rich phases.<sup>32</sup> According to the “random polyhedral packing” model,  $[\text{AlF}_6]$  coordination octahedra could form the skeleton of fluoride rich glass phases, and other metal ions such as  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Eu}^{2+/3+}$  filled the pores of  $[\text{AlF}_6]$  framework.<sup>33</sup> In G1–G3, the electronegativity decreases as per the sequence  $\chi(\text{Ca}^{2+}) > \chi(\text{Sr}^{2+}) > \chi(\text{Ba}^{2+})$ ,  $\text{Eu}^{2+}$  ions were more likely to form in the latter groups. In G4,  $\chi(\text{Eu}^{3+})$  is close to  $\chi(\text{La}^{3+})$ , and in GC5  $\chi(\text{Zn}^{2+})$  is much larger than  $\chi(\text{Eu}^{3+})$ , so only slight amounts of  $\text{Eu}^{2+}$  were found in G4 and no  $\text{Eu}^{2+}$  was detected in GC5, as shown in Fig. 2(c).

## Stabilization of $\text{Eu}^{2+}$ in the glass-ceramics via lattice site substitution

Lattice site substitution has been considered as a facile  $\text{Eu}^{2+}$  doping strategy to avoid other impurities, uncontrollable redox reaction and large aggregation. The conversion ratio of reduction through this method was mainly influenced by two crucial factors: the charge and radius of the site. In order to form stable divalent  $\text{Eu}^{2+}$ , the lattice sites should meet the following

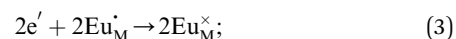
criteria: (i) the sites should be originally divalently charged, (ii) the radii of the sites should be close to the radii of  $\text{Eu}^{2+}$ .<sup>34,35</sup>

The site charge requisition of  $\text{Eu}^{2+}$  substitution could be examined by comparison between the  $\text{MF}_2$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}$ )-based (G1, G2, G3) and the  $\text{LaF}_3$ -based (G4) samples. The crystalline phases of G4 were  $\text{LaF}_3$ . The trivalent  $\text{La}^{3+}$  sites rather than divalent ones led to no transition of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  and absence of the  $\text{Eu}^{2+}$  PL (Fig. 2(c)), although the radii of  $\text{La}^{3+}$  was close to  $\text{Eu}^{2+}$  ( $R_{\text{La}^{3+}}(1.160 \text{ \AA}) < R_{\text{Eu}^{2+}}(1.25 \text{ \AA})$ ). Thus, the divalent sites were required for reduction. As previously reported, the mechanism of the  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reduction was expressed by a series of defect equations. When  $\text{Eu}^{3+}$  enters the lattice containing  $\text{M}^{2+}$  with similar radii, a cation vacancy with two negative charges is formed



where  $\text{M}_\text{M}$  stands for metal ion which occupied its own lattice,  $\text{Eu}_\text{M}^\bullet$  for the doping  $\text{Eu}^{3+}$  ion which occupied the lattice of metal ion with one extra positive charge, and  $\text{V}_\text{M}''$  for the vacancy of metal ion with two negative charges.

As the vacancy act as electron donor,  $\text{Eu}^{3+}$  was reduced to  $\text{Eu}^{2+}$ .



where  $\text{V}_\text{M}^\times$  stands for the vacancy of metal ion with no extra charge,  $\text{Eu}_\text{M}^\times$  for the doping  $\text{Eu}^{3+}$  with no extra charge.

These substitution effects were illustrated in Fig. 4. Accordingly, the  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reduction took place and alkaline earth cation vacancies formed in GC1–3 (Fig. 4(a–c)), and broad PL bands of  $\text{Eu}^{2+}$  were found. The lattice constants were calculated by Bragg's Law, as listed in Table 2. The site substitution can be further verified according to lattice constant change. The expansion of  $\text{CaF}_2$  lattice in GC1 corresponded with smaller radius of  $\text{Ca}^{2+}(1.12 \text{ \AA})$  compared to that of  $\text{Eu}^{2+}(1.25 \text{ \AA})$ , and the shrinkage of  $\text{SrF}_2/\text{BaF}_2$  lattice in GC2 and GC3 for larger radii of  $\text{Sr}^{2+}(1.26 \text{ \AA})$  and  $\text{Ba}^{2+}(1.42 \text{ \AA})$ . Also, the  $\text{Eu}^{3+}/\text{La}^{3+}$  substitution took place in  $\text{LaF}_3$  lattice of GC4 without the  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reduction. The very small deviation from standard lattice constant of  $\text{LaF}_3$  in GC4 was due to the very similar radii of  $\text{La}^{3+}(1.160 \text{ \AA})$  and  $\text{Eu}^{3+}(1.066 \text{ \AA})$ .

When the site was divalently charged, the radius difference between substitution cation pairs would play a prime role for the  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reduction. By reference to  $\text{ZnF}_2$ -based sample (GC5), the influence of the radius difference on the lattice site substitution could be clearly observed. The ionic radii<sup>36</sup> with 8 coordination number were demonstrated as below:  $R_{\text{Zn}^{2+}}(0.60 \text{ \AA}) < R_{\text{Eu}^{3+}}(1.066 \text{ \AA}) < R_{\text{Ca}^{2+}}(1.12 \text{ \AA}) < R_{\text{Eu}^{2+}}(1.25 \text{ \AA}) < R_{\text{Sr}^{2+}}(1.26 \text{ \AA}) < R_{\text{Ba}^{2+}}(1.42 \text{ \AA})$ . Due to the huge difference between doping cations ( $R_{\text{Eu}^{3+}}(1.066 \text{ \AA})$ ;  $R_{\text{Eu}^{2+}}(1.25 \text{ \AA})$ ) and lattice cations ( $R_{\text{Zn}^{2+}}(0.60 \text{ \AA})$ ), a barrier was created in the  $\text{Eu}^{3+}/\text{Zn}^{2+}$  substitution. Moreover, less deviation of  $\text{ZnAl}_2\text{O}_4$  lattice constant in GC5 also confirmed the above theory. Furthermore, the radius differences between  $\text{Eu}^{3+}$  and  $\text{M}^{2+}$  sites would determine how much  $\text{Eu}^{3+}$  would be reduced into  $\text{Eu}^{2+}$ . The PL intensity of  $\text{Eu}^{2+}$  increased by the order of  $\text{GC1} < \text{GC2} < \text{GC3}$ , while that of  $\text{Eu}^{3+}$



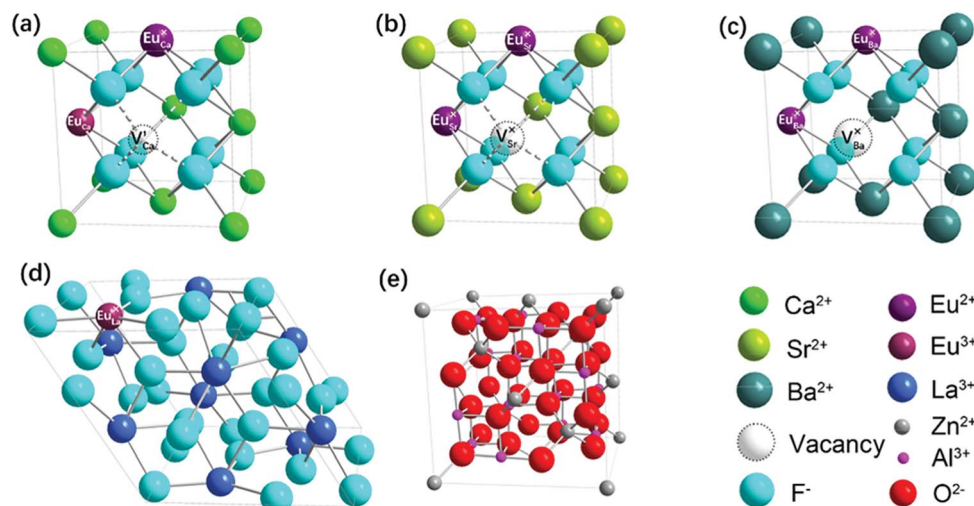


Fig. 4 Schematic model to describe site substitution of  $\text{Eu}^{2+}$  or  $\text{Eu}^{3+}$  in different primitive cells. (a–c)  $\text{Eu}^{2+}$ -doped cubic  $\text{MF}_2$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}$ ) cell, (d)  $\text{Eu}^{3+}$ -doped hexagonal  $\text{LaF}_3$  cell, (e)  $\text{Eu}^{3+}$ -doped cubic  $\text{ZnAl}_2\text{O}_4$  cell.

decreased by  $\text{GC1} > \text{GC2} > \text{GC3}$  (Fig. 2(b)). Thus, the ratio of  $\text{Eu}^{2+}/\text{Eu}^{3+}$  should be  $\text{GC1} < \text{GC2} < \text{GC3}$  assuming that the concentrations of  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  were lower than the PL quenching concentrations. The  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reduction was indeed driven by the radius difference between different  $\text{Eu}^{3+}/\text{M}^{2+}$  pairs. On the one hand, for  $\text{Eu}^{3+}/\text{Ca}^{2+}$  substitution with small radius difference ( $\text{Ca}^{2+}(1.12 \text{ \AA})$  vs.  $\text{Eu}^{3+}(1.066 \text{ \AA})$ ) and  $\text{Ca}^{2+}$  sites with smaller radii than  $\text{Eu}^{2+}(1.25 \text{ \AA})$ , it only drove  $\text{Eu}^{3+}$  to be partially reduced to  $\text{Eu}^{2+}$ , so  $\text{Eu}^{3+}/\text{Eu}^{2+}$  coexisted in GC1. The inversion of PL peak intensities at 590 nm and 612 nm for G1 (Fig. 2(a)) and GC1 (Fig. 2(b)) well verified the  $\text{CaF}_2$  crystalline coordination environment of  $\text{Eu}^{3+}$  in GC1. The PL enhancement of  $\text{Eu}^{3+}$  (Fig. 2(b)) was due to lower phonon energy and lower multi-phonon transition ratio of  $\text{Eu}^{3+}$  in  $\text{CaF}_2$  lattice of GC1. As both the  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  were enriched in the  $\text{CaF}_2$  nano-crystals, the strengthened cross relaxation transition between  $\text{Eu}^{2+}/\text{Eu}^{3+}$  coincidentally eliminated the weakening of multi-phonon transition, so the PL lifetime of GC1 had no significant change compared to G1 (Fig. 5 and Table 3). On the other hand,  $\text{Eu}^{3+}/\text{Ba}^{2+}$  or  $\text{Eu}^{3+}/\text{Sr}^{2+}$  substitution with large radius difference ( $\text{Sr}^{2+}(1.26 \text{ \AA})/\text{Ba}^{2+}(1.42 \text{ \AA})$  vs.  $\text{Eu}^{3+}(1.066 \text{ \AA})$ ) and  $\text{Sr}^{2+}/\text{Ba}^{2+}$  sites with larger radii than  $\text{Eu}^{2+}(1.25 \text{ \AA})$  drove more  $\text{Eu}^{3+}$  to be reduced to  $\text{Eu}^{2+}$ . Accordingly, large amounts of  $\text{Eu}^{3+}$  remained trivalent in GC1, while small amounts remained in GC2 and GC3. No inversion of PL peak intensities at 590 nm and 612 nm

for G2 and G3 (Fig. 2(a)) and GC2 and GC3 (Fig. 2(b)) implied that all  $\text{Eu}^{3+}$  in GC2 and GC3 corresponded to those remaining in the glassy phase, which exhibited much shorter PL lifetimes (Fig. 5; Table 3).

#### Quantum yield (QY) improvement and PL enhancement of $\text{Eu}^{2+}$

After heat treatment, large quantities of  $\text{Eu}^{2+}$  formed by  $\text{Eu}^{3+}/\text{M}^{2+}$  substitution in GC1–GC3, QY of the  $\text{Eu}^{2+}$  PL (Fig. 3) was improved to about 4–7 times of QY of precursor glasses. QY is dominated by two competitive processes: radiative transition (RT) and non-radiative transition (NRT). Theoretically, the probability of RT and NRT,  $W_{\text{RT}}$  and  $W_{\text{NRT}}$  have the following relationships:

$$\tau = \frac{1}{W_{\text{RT}} + W_{\text{NRT}}}; \quad (4)$$

$$\eta = \frac{W_{\text{RT}}}{W_{\text{RT}} + W_{\text{NRT}}} = \tau W_{\text{RT}}; \quad (5)$$

where  $\eta$  and  $\tau$  represent QY and lifetime of PL, respectively. Accordingly, the QY improvement depended on lower NRT or longer PL life time.  $\text{Eu}^{2+}$  ions were mainly enriched in the separated fluoride glass phases filled with large content of quenching defects, unsaturated bonds and interfaces. Thus,

Table 2 The calculated lattice constants and standard values of precipitated nanocrystals in glass-ceramics

Crystalline phase	Lattice constant ( $\text{\AA}$ )	Standard value ( $\text{\AA}$ )
$\text{CaF}_2$ in GC1	5.545	5.463 (PDF#35-0816)
$\text{SrF}_2$ in GC2	5.760	5.800 (PDF#06-0262)
$\text{BaF}_2$ in GC3	5.929	6.200 (PDF#04-0452)
$\text{LaF}_3$ in GC4	$7.184 \times 7.184 \times 7.351$	$7.187 \times 7.187 \times 7.35$ (PDF#32-0483)
$\text{ZnAl}_2\text{O}_4$ in GC5	8.072	8.089 (PDF#05-0669)



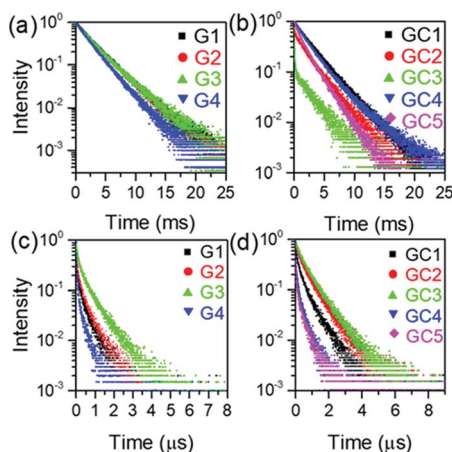


Fig. 5 PL Decay curves of samples. (a and b) the glass and glass-ceramics samples excited at 393 nm and monitored at 612 nm for  $\text{Eu}^{3+}$  (c and d) Excited at 350 nm and monitored at 420 nm for  $\text{Eu}^{2+}$ .

Table 3 The lifetime of luminescence emitted by  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$

Sample	$\text{Eu}^{3+}$ ( $\mu\text{s}$ )	$\text{Eu}^{2+}$ (ns)	Sample	$\text{Eu}^{3+}$ ( $\mu\text{s}$ )	$\text{Eu}^{2+}$ (ns)
G1	3.06	174	GC1	3.03	321
G2	3.29	206	GC2	2.32	476
G3	3.08	342	GC3	1.77	612
G4	2.48	112	GC4	2.58	168
			GC5	1.96	85

$\text{Eu}^{2+}$  in the glasses had high  $W_{\text{RT}}$  and low QY (<10%), which was also evidenced by the shorter lifetimes of  $\text{Eu}^{2+}$  (Fig. 5(c)). On the contrary,  $\text{Eu}^{2+}$  in the glass-ceramics were incorporated in  $\text{MF}_2$  crystalline phases, where the concentration of PL quenching centers were much lower than those in glass phases. Therefore, PL lifetimes of  $\text{Eu}^{2+}$  in the glass-ceramics (Fig. 5(d)) appeared much longer than those of the precursor glasses. It supports the glass-ceramics, GC1–GC3, achieved much higher QY of the  $\text{Eu}^{2+}$  PL.

Besides a high QY value, strong PL still requires high concentration of the active center ( $\text{Eu}^{2+}$ ) without serious concentration quenching. The  $\text{BaF}_2$ -based glass-ceramics possessed high solubility of  $\text{Eu}^{2+}$  rather than  $\text{SrF}_2$  or  $\text{CaF}_2$ -based glass-ceramics. Larger radii as well as large radius difference were found to play almost equal roles when reducing  $\text{Eu}^{3+}$  into  $\text{Eu}^{2+}$ . Therefore, the  $\text{BaF}_2$ -based rather than the  $\text{SrF}_2$ -based glass-ceramics got the highest QY and the strongest PL, simultaneously. It also demonstrates that the proposed  $\text{MF}_2$  lattice site substitution strategy is very suitable for alkaline earth fluorosilicate glass-ceramics showing great advantages in large amount (3–5 mol%) of Eu introduction, high reduction ratio of  $\text{Eu}^{3+}/\text{Eu}^{2+}$  than in other hosts and efficiently enhanced PL of  $\text{Eu}^{2+}$  compared to that of oxide glass-ceramics.<sup>19–23</sup>

We also evaluate the reproducibility and applicability of the present lattice substitution method for fabrication of  $\text{Eu}^{2+}$ -doped fluorosilicate glass-ceramics. From Fig. S3,<sup>†</sup> it is evidenced that the glass-ceramics could be well reproduced with

a highly similar PL bands and the PL performance could also be well maintained even after 3 years. Moreover, the lattice substitution strategy primarily relies on the annealing processes, which has been widely applied in the glass and ceramic industry. Therefore, the proposed preparation method has good applicability in large scale applications.

## Conclusions

The separated fluoride glass phases formed in the precursor fluorosilicate glasses transformed into fluoride nanocrystals in the glass-ceramics after heat treatment. The inclined precipitation of alkaline earth fluoride nanocrystals and the  $\text{Eu}^{3+}/\text{M}^{2+}$  lattice site substitution enabled the facile  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reduction and stabilization of  $\text{Eu}^{2+}$  in the fluorosilicate glass-ceramics. The Eu tended to enrich in fluoride-rich phases of the glasses and in the fluoride nanocrystalline phases of the glass-ceramics. In glasses, the  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reduction depended on the electronegativity of fluoride glass phases, while in glass-ceramics, the  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reduction depended on the lattice site substitution in fluoride crystalline phases. The lattice site substitution depended on two key factors: the radii and the valency difference between sites and substitution ions. The similar radii between sites and ions were the prerequisites of the doping. Too small radii of doping ions (like  $\text{Zn}^{2+}$ ) were not preferred for  $\text{Eu}^{3+}/\text{M}^{2+}$  substitution, while comparably larger radii (like  $\text{Ba}^{2+}$ ) were more facile for both  $\text{Eu}^{3+}/\text{M}^{2+}$  substitution and  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reduction. And to some extent, larger the radii, easier it was for the  $\text{Eu}^{3+}/\text{M}^{2+}$  substitution to take place. The unbalanced charge at the substitution sites drove the reduction of  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ . The  $\text{Eu}^{3+}/\text{M}^{2+}$  substitution was attributed to the  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reduction, while  $\text{Eu}^{3+}/\text{La}^{3+}$  substitution led to almost no reduction of  $\text{Eu}^{3+}$ . High  $\text{Eu}^{2+}$  doping concentration and enhanced luminescent QY of  $\text{Eu}^{2+}$  were simultaneously achieved in  $\text{BaF}_2$ -based glass-ceramic.

## Conflicts of interest

There are no conflicts to declare.

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