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# Realizing Superior Luminescence in Oxyfluoride Glass-Ceramics by Enhancing Nano-Micro Phase Separation

J. Hu

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In this work, a novel series of oxyfluoride glasses-ceramics (GCs) is developed by enhancing the phase separation through the substitution of  $LaF_3$  for  $La_2O_3$ . The thus-derived GCs exhibit a remarkable 2700-fold increase in up-conversion (UC) luminescence of  $Er^{3+}$  ions compared to the precursor glass. From the <sup>19</sup>F Nuclear Magnetic Resonance analysis, this enhancement is attributed to the structural disorder-to-order transition in the fluoride-rich phase. Upon isothermal heat treatment, the translucent GCs transform into transparent ones, making UC luminescence even stronger. The enhanced UC luminescence leads to strong temperature-sensing ability of the studied glasses. The nano-micro phase separation is clarified by atomistic simulations and scanning electron microscopy. This study implies that phase separation engineering is a powerful way to achieve superior photonic performances.

# 1. Introduction

Transparent glass ceramics (GCs) combine the merits of crystals and glass matrices, enabling improved functionalization compared to either of them.<sup>[1]</sup> For instance, oxyfluoride glass matrices exhibit excellent optical transparency, good chemical, and thermal stabilities, and serve as a protection for the fluoride crystals, while the fluoride crystals exhibit favorable optical properties because of their low phonon energy.<sup>[2]</sup> Oxyfluoride GCs are traditionally produced via heat treatment (HT) of the parent oxyfluoride glass above the glass transition temperature ( $T_e$ ).<sup>[3]</sup> The formation

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of fluoride crystals in oxyfluoride glasses is initiated through phase separation into fluoride- and aluminosilicate-rich amorphous phases.<sup>[4-6]</sup> When rare-earth (RE) ions are doped into oxyfluoride glasses, they preferentially participate in the formation of fluoride crystals upon HT due to their similarities in both ionic radius and charge distribution to the alkali and alkaline earth ions in fluoride crystals.<sup>[7,8]</sup> Consequently, the RE ions are located in the low phonon energy environment of the fluoride crystals, thus reducing the non-radiative relaxation rate of RE ions and resulting in superior optical properties.<sup>[9,10]</sup> Among different kinds of fluoride crystals formed in oxyfluoride glasses,  $Ba_2LaF_7$  crystals possess ultralow phonon energy (270 cm<sup>-1</sup>) and high chemical stability.<sup>[11]</sup> Thus, RE-doped oxyfluoride GCs containing Ba<sub>2</sub>LaF<sub>7</sub> crystals are promising optical materials and have been extensively investigated for various applications, such as multicolor displays,<sup>[12]</sup> white light-emitting-diodes,<sup>[13]</sup> ultraviolet (UV) lasers,<sup>[14]</sup> up-conversion (UC) lasers,<sup>[15]</sup> and optical thermometry.<sup>[16,17]</sup>

The traditional approach for preparing oxyfluoride GCs is a time- and energy-intensive one owing to the additional HT process. Recently, some of the present authors developed a translucent oxyfluoride GC containing 40 vol.% large-sized flower-like Ba<sub>2</sub>LaF<sub>7</sub> crystals by melt-quenching.<sup>[18]</sup> Compared to traditional oxyfluoride GCs with Ba2LaF2 crystals, this melt-quenchingderived GC exhibits stronger tendency to phase separation and hence, enhanced UC luminescence. A subsequent isothermal HT strategy could be used to adjust the refractive index (n) of the glass matrix to match that of the fluoride crystal, thereby increasing the transparency of the GC. Moreover, the heat-treated GC accommodates more RE ions, leading to stronger UC luminescence. The phase separation was considered to be the primary origin of the formation of Ba<sub>2</sub>LaF<sub>7</sub> crystals from the oxyfluoride glass matrix during quenching. However, the relationship between structural heterogeneity, phase separation, crystal formation, and functionalities in oxyfluoride glass remains poorly understood, and this hinders the rational design of novel functional GCs.

The addition of network modifiers to a glass matrix, such as  $La_2O_3$  and  $LaF_3$  fluorides, can dissociate the  $[SiO_4]$  and  $[AlO_4]$  involved network. This induces the formation of phase-separated domains in oxyfluoride glasses, thereby reducing the crystal-lization activation energy to form fluoride crystals.<sup>[19]</sup> Despite progress in preparing the melt-quenching-derived oxyfluoride GCs with desired crystal type,<sup>[13,20,21]</sup> the formation mechanism of fluoride crystals in glass during quenching remains unknown, making it almost impossible to tailor the types of fluoride crystals through chemical composition tuning. It is thus important to further investigate the impact of chemical composition on both phase separation, crystallization behavior, and functionalities of melt-quenching-derived oxyfluoride glasses.

In this work, we prepared the oxyfluoride GCs exhibiting strong luminescence and temperature-sensing ability through

phase separation engineering. The phase separation engineering was realized by substituting  $LaF_3$  for  $La_2O_3$  in the precursor composition:  $45SiO_2 \cdot 15Al_2O_3 \cdot 12Na_2O \cdot 21BaF_2 \cdot 7La_2O_3 \cdot 0.5ErF_3 \cdot 1YbF_3$ , and subsequently by isothermal HT. We study the phase evolution and the disorder-to-order transition in the separated phases of the GCs with a substitution of  $LaF_3$  for  $La_2O_3$  by applying various analytical methods as well as molecular dynamics (MD) simulations detailed in the next section. The impact of the phase separation engineering on the UC luminescence and temperature-sensing ability of the GCs was investigated.

## 2. Results and Discussion

# 2.1. X-ray Diffraction (XRD), Raman, and Differential Scanning Calorimetry (DSC) Analyses

To obtain information on the formed crystal structures, the XRD patterns of the as-quenched samples (OLaF, 2LaF, 4LaF, 6LaF, and 7LaF) are collected in Figure 1a. No sharp Bragg's peak can be observed for the 0LaF sample besides two weak and broad humps, indicating the non-crystalline nature of this sample. However, with the addition of LaF<sub>3</sub>, sharp diffraction peaks start to appear, which can be assigned to the face-centered cubic (FCC) Ba<sub>2</sub>LaF<sub>7</sub> crystal (PDF#48-0099).<sup>[22]</sup> In the 2LaF sample, only three weak diffraction peaks at  $\approx 25.5^{\circ}$ ,  $42.2^{\circ}$ , and  $49.9^{\circ}$ appear together with the broad peak in the XRD pattern, implying that small amounts of tiny-sized crystals have already formed during quenching. With further increasing content of LaF<sub>3</sub>, ten distinct diffraction peaks of Ba2LaF2 crystal are observed in the XRD patterns of 4LaF, 6LaF, and 7LaF samples. These peaks become gradually sharper and more intense, implying the formation of more and larger Ba<sub>2</sub>LaF<sub>7</sub> crystals in the studied samples during the preparation process. The gradual increase in the content of Ba<sub>2</sub>LaF<sub>7</sub> crystals with the increasing LaF<sub>3</sub> concentration can be confirmed by the Debye–Scherrer equation.<sup>[23]</sup> However, we note that the peak positions in the studied samples slightly shift to a larger angle (Figure S1b,c, Supporting Information) compared with those in the standard PDF card. This is attributed to the slight shrinkage of the unit cell of Ba2LaF7 crystal, as induced by the substitution of the small-sized Er<sup>3+</sup> and Yb<sup>3+</sup> ions for larger-sized La<sup>3+</sup> ions.<sup>[11]</sup> Thus, RE ions doped GCs can be regarded as promising optical candidates as a result of the incorporation of Er<sup>3+</sup> and Yb<sup>3+</sup> ions into the fluoride crystals with low phonon energy. The heat-treated HT-0LaF sample shows precipitation of FCC Ba<sub>2</sub>LaF<sub>7</sub> crystals and the diffraction peaks become stronger in the other four heat-treated samples (Figure S1a. Supporting Information) without further formation of additional crystal phases. These results imply an increased crystallinity of the five samples upon HT.

Figure 1b shows the normalized Raman spectra of the studied samples. The Raman spectra of 2LaF, 4LaF, 6LaF, and 7LaF samples were normalized by the intensity of the peak at 549 cm<sup>-1</sup>, whereas the spectrum of 0LaF sample was normalized by the maximum intensity at 474 cm<sup>-1</sup> owing to the absence of the peak at 549 cm<sup>-1</sup> (Figure S2a, Supporting Information). Two broad bands are found in the Raman spectrum of 0LaF, indicating the amorphous nature of 0LaF. A peak at 269 cm<sup>-1</sup> appears in the Raman spectra of 2LaF, 4LaF, 6LaF, and 7LaF, which becomes stronger with increasing LaF<sub>3</sub> content. This

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**Figure 1.** a) XRD patterns, b) normalized Raman spectra, c) DSC output curves, and MAS NMR spectra of d) <sup>29</sup>Si, e) <sup>27</sup>Al, and f) <sup>19</sup>F of 0LaF, 2LaF, 4LaF, 6LaF, and 7LaF samples. Note that the Raman peak positions are indicated in Figure 1b, the onset temperatures of the glass transition, the first, second, and main crystallization peaks, and the melting peak ( $T_g$ ,  $T_{c1}$ ,  $T_{c2}$ ,  $T_c$ , and  $T_m$ , respectively) are marked in Figure 1c, the hatched area in Figure 1c reflects the crystallization enthalpy. The stars in Figure 1d–f denote spinning sidebands.

confirms that Ba<sub>2</sub>LaF<sub>7</sub> crystals form and their fraction increases with LaF<sub>3</sub> content,<sup>[24]</sup> being in agreement with the XRD results (Figure 1a). The Raman peaks at 387, 416, 549, 616, and 688 cm<sup>-1</sup> are attributed to the symmetrical stretching vibration modes of [Si(Al)O<sub>4</sub>] inter-tetrahedra.<sup>[18]</sup> Upon HT, the Raman peak at 269 cm<sup>-1</sup> of Ba<sub>2</sub>LaF<sub>7</sub> crystal and other symmetric stretching vibrational peaks of [Si(Al)O<sub>4</sub>] inter-tetrahedra also appear in the HT-0LaF sample (Figure S2b, Supporting Information).<sup>[24,25]</sup> Additionally, the relative intensity ratios of the peaks at 269 cm<sup>-1</sup> in HT-2LaF, HT-4LaF, HT-6LaF, and HT-7LaF (Figure S2c, Supporting Information) are higher than those of the as-quenched samples, indicating an increase in the fraction of Ba<sub>2</sub>LaF<sub>7</sub> crystal.

Figure 1c shows the DSC curves of the as-quenched samples. The glass transition temperature ( $T_{\rm g}$ ) and the onset temperatures of the first, second, and main crystallization peaks ( $T_{c1}$ ,  $T_{c2}$ , and  $T_c$ , respectively), and the melting temperature ( $T_{\rm m}$ ) are determined from each DSC curve by the standard method given in<sup>[26]</sup> (see Table S2, Supporting Information). Both  $T_{\rm g}$  and  $T_{c1}$  first decrease, then increase, and finally decrease with increasing LaF<sub>3</sub> content and this non-monotonic trend matches the changing trend of the structural connectivity reported in,<sup>[27]</sup> being in contrast with those of oxide and oxyfluoride glasses.<sup>[28–31]</sup> This trend can be explained as follows. La<sub>2</sub>O<sub>3</sub> plays a role as a network modifier that lowers the glass network connectivity.<sup>[32,33]</sup> As shown in Figure S3 (Supporting Information), HT leads to an increase in both  $T_{\rm g}$  and  $T_{c1}$ . This is attributed to an increase in the

 $[SiO_4]/[AlO_4]$  ratio owing to the depletion of the Ba<sub>2</sub>LaF<sub>7</sub> crystals from the separated phase. In addition, it is seen that both  $T_g$  and  $T_{c1}$  of the heat-treated samples decrease with increasing LaF<sub>3</sub> content because of the volatilization of fluorides (SiF<sub>4</sub>) in melts (Figure S3, Supporting Information).

To investigate the formation of Ba<sub>2</sub>LaF<sub>7</sub>, the first crystallization enthalpy ( $\Delta H_1$ ) of the studied samples was calculated by integrating the area under the first exothermic peak, as shown in Figure 1c.  $\Delta H_1$  first sharply increases and then slowly increases with the LaF<sub>3</sub> concentration of the studied samples, while  $\Delta H_2$ for the second crystallization peak decreases or apparently disappears. As such, the crystallization event corresponding to the lower temperature exothermic peak is promoted by the addition of LaF<sub>3</sub>, while the one associated with the higher temperature exothermic peak is depressed. To further investigate the compositional effects on the crystallization behavior, the mass fractions (%) of the cations in the as-quenched samples were analyzed by Inductively coupled plasma optical emission spectrometer (ICP-OES). The obtained results are presented in Table S3 (Supporting Information). We can also observe that Ba<sub>2</sub>LaF<sub>7</sub> crystal starts to form in 2LaF in the melt. In this case, the molar fraction ratio between  $Ba^{2+}$  and  $La^{3+}$  is  $\approx 2$  as the atomic molar mass of Ba $(137.33 \text{ g mol}^{-1})$  is similar to that of La  $(138.91 \text{ g mol}^{-1})$ . This is coincident with the stoichiometric ratio of Ba2LaF2 crystal and could be a criterion for evaluating the formation of Ba<sub>2</sub>LaF<sub>7</sub> crystal.



**Figure 2.** Synchrotron radiation EXAFS measurements. a) Ba *K*-edge and b) La *K*-edge Fourier-transformed (FT) EXAFS spectra of 0LaF, 2LaF, 4LaF, 7LaF, HT-0LaF, HT-4LaF, and HT-7LaF, respectively. Note that  $BaF_2$  and  $BaAl_2O_4$  are reference samples for Ba *K*-edge FT EXAFS spectra in panel (a), while LaF<sub>3</sub> and LaTi<sub>2</sub>O<sub>7</sub> are reference samples for La *K*-edge FT EXAFS spectra in panel (b).

#### 2.2. Nuclear Magnetic Resonance (NMR) Analysis

Figure 1d shows the <sup>29</sup>Si magic angle spinning (MAS) NMR spectra of the as-quenched samples. Each <sup>29</sup>Si MAS NMR spectrum has only one resonance signal located at  $\approx$ -84 ppm, which can be assigned to  $Q^{(2)}$  species, where (2) denotes the sum of the numbers of Si-O-Si linkages per tetrahedral unit. We observe that this resonance signal gradually shifts from -84 to -88 ppm upon the replacement of La<sub>2</sub>O<sub>3</sub> by LaF<sub>3</sub>. This shift might be attributed to a decrease in the amount of Si-La bonds with the replacement. The glass network structure, e.g., the coordinating environment (NBO/T) of Si<sup>4+</sup> ions, does not undergo a pronounced change in composition. Figure 1e shows the <sup>27</sup>Al MAS NMR spectra of the as-quenched samples. The spectrum of 0LaF features the main resonance peak at about 58 ppm, which is attributed to four-fold coordinated aluminum (Al(IV)).<sup>[10]</sup> With the increasing content of LaF<sub>3</sub>, the position of the main resonance peak slightly shifts from 58 to 55 ppm, suggesting that no significant change in the coordination number of Al but a change in the coordination environment of Al. Al3+ ions can act as glass network intermediate and marginally exist in [Al(O,F)<sub>4</sub>] tetrahedra at the interface besides their primary structure role present in [AlO<sub>4</sub>] tetrahedra.<sup>10</sup> Namely, some Al-O linkages at the interface regions can be replaced by the Al-F linkages with the replacement of LaF<sub>3</sub> to La<sub>2</sub>O<sub>3</sub> in the studied samples, thereby altering the coordination environment of Al and causing the shift of the Al(IV) resonance peak. To detect the concentration variation of F<sup>-</sup> around Al<sup>3+</sup>, the <sup>27</sup>Al{<sup>19</sup>F} REDOR experiments were conducted on the 0LaF and 7LaF samples (Figure S4, Supporting Information). It is seen that the normalized REDOR signal intensity attenuations  $(S_0 - S)/S_0$ in 7LaF are larger than those in 0LaF during the evolution time *NTr*, indicating that more  $F^-$  ions around  $Al^{3+}$  are present in the former than in the latter.<sup>[34]</sup> Therefore, we infer that some O<sup>2-</sup> ions around Al<sup>3+</sup> are replaced by the F<sup>-</sup> ions when substituting LaF<sub>3</sub> for La<sub>2</sub>O<sub>3</sub> in the 0LaF sample. The peak of Al-F linkages is observed at  $\approx$  -194 ppm in the <sup>19</sup>F MAS NMR spectra (Figure 1f).

Figure 1f shows the <sup>19</sup>F MAS NMR spectra of the as-quenched samples. The spectra of 0LaF, 2LaF, 4LaF, 6LaF, and 7LaF samples exhibit two main broad resonance signals at  $\approx$ -12 and -194 ppm, which are denoted as F1 and F2, respectively. The

resonance signal F1 was assigned to F species in La-F and F-Ba linkages in Ba<sub>2</sub>LaF<sub>7</sub> crystals,<sup>[18]</sup> while the resonance signal F2 was related to F species in the F—Al linkages in Ba—F—Al or Na—F—Al.<sup>[35]</sup> In this work, a broad resonance signal (at  $\approx$ -27 ppm) with a small amplitude is observed in 0LaF sample, and shifts to the low-frequency region.<sup>[36]</sup> This broad resonance signal can be attributed to the strong electron paramagnetic resonance effect of Er<sup>3+</sup> and Yb<sup>3+</sup> ions on the surrounding F<sup>-</sup> ions in 0LaF. Specifically, Er<sup>3+</sup> and Yb<sup>3+</sup> ions tend to aggregate around F<sup>-</sup> ions. 0LaF has the lowest concentration of F<sup>-</sup> ions compared with other samples, and hence has the highest concentration of Er<sup>3+</sup> and Yb<sup>3+</sup> ions around F<sup>-</sup> ions, leading to the strongest paramagnetic resonance effect.<sup>[37]</sup>

#### 2.3. Extended X-Ray Absorption Fine Structure (EXAFS) Analysis

**Figure** 2a,b shows the Fourier-transformed (FT) *k*3-weighted  $\chi(k)$  EXAFS spectra of Ba *K*-edge and La *K*-edge in both the asquenched and HT samples, respectively. These measurements were performed to investigate the average coordination number (CN) of the Ba and La atoms. The FT EXAFS spectra of Ba *K*-edge (Figure 2a) display that the CN value of Ba<sup>2+</sup> first remains constant (for 0LaF and 2LaF samples) and then increases with the substitution of LaF<sub>3</sub> for La<sub>2</sub>O<sub>3</sub>.<sup>[38]</sup> We note that the *R*-value (2.67 Å) in 0LaF sample corresponds to Ba–O bond length and the *R*-value (2.63 Å) in the other samples containing LaF<sub>3</sub> is associated with Ba–F bond length. That is, upon further substitution of LaF<sub>3</sub> for La<sub>2</sub>O<sub>3</sub> or subsequent HT, Ba–F bonds account for the vast majority of the Ba–(O,F) bonds.<sup>[39]</sup>

Based on the FT EXAFS curves of La *K*-edge shown in Figure 2b, we find that the average CN of La<sup>3+</sup> increases with the substitution of LaF<sub>3</sub> for La<sub>2</sub>O<sub>3</sub>, which is estimated to be 8 in the HT-7LaF sample. This increase of the average CN of La<sup>3+</sup> could be attributed to the formation of Ba<sub>2</sub>LaF<sub>7</sub> crystals in the studied samples. Specifically, the peak position in the EXAFS spectrum of 0LaF slightly shifts to the position with small bond distance (2.47 Å) when increasing LaF<sub>3</sub> to 2 mol.% (2LaF sample), and then the bond distances remain constant with the further increasing concentration of LaF<sub>3</sub> in the samples.





**Figure 3.** a-e) MD simulated structures of 0LaF, 2LaF, 4LaF, 6LaF, and 7LaF, respectively. Note that [SiO<sub>4</sub>] and [AlO<sub>4</sub>] tetrahedra are shown in red color and magenta color, respectively; main network modifier domains are marked by black dash curves; atoms of Si, Al, O, Na, Ba, La, and F are represented by orange, magenta, red, purple, blue, green, and cyan balls, respectively. f-j) Scanning electron microscopy (SEM) images of 0LaF, 2LaF, 4LaF, 6LaF, and 7LaF, respectively, obtained by using secondary electron imaging mode. k-m) SEM images of 0LaF, 4LaF, and 7LaF obtained from the backscattered electron imaging mode of SEM. n) An enlarged structural domain taken from a fluoride-rich phase in (e). o) Cubic lattice structure of a Ba<sub>2</sub>LaF<sub>7</sub> crystal unit.

As such, the bond mostly transformed from La–O (2.47 Å) to La–F (2.43 Å) based on the bond distances in reference La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and LaF<sub>3</sub> crystals. However, the bond at 2.43 Å is likely due to a mixture of La–(O,F) bonds. In addition, we find that the peaks become sharper and that the peak positions remain constant at  $\approx$ 2.43 Å with increasing fraction of Ba<sub>2</sub>LaF<sub>7</sub> crystals upon HT. This indicates that the structure of the La units in the studied samples is similar to that in the Ba<sub>2</sub>LaF<sub>7</sub> crystal.<sup>[40]</sup>

### 2.4. Molecular Dynamics (MD) Simulations and Scanning Electronic Microscopy (SEM) Analysis

To understand changes in the glass structure features with composition on the atomic level, MD simulations of these glasses were performed. Snapshots of the simulated structures are shown in **Figure** 3a–e. These show typical signs of phase-separated features, forming aluminosilicate oxide-rich and fluoride-rich phases, where the former consists of glass network formers ([SiO<sub>4</sub>] and [AlO<sub>4</sub>] tetrahedra) and the latter is composed of glass network modifiers. Most Ba<sup>2+</sup> and La<sup>3+</sup> ions (network modifier cations) are enriched in the fluoride-rich phase, which can be explained by Poulain's ionic glass model.<sup>[41]</sup> In addition, we find that the proportion of the fluoride-rich phase increases with the replacement of La<sub>2</sub>O<sub>3</sub> by LaF<sub>3</sub>, and the chemical compo-

sition of the fluoride-rich phase evaluated from Figure 3n is close to the stoichiometric composition of Ba<sub>2</sub>LaF<sub>7</sub> crystal (Figure 3o). This highlights the great tendency of Ba<sub>2</sub>LaF<sub>7</sub> crystals to precipitate from the fluoride-rich phase upon HT or even during quenching. Moreover, it was reported that  $[MO_xF_y]$  (M = Na<sup>+</sup>, Ba<sup>2+</sup>, and La<sup>3+</sup>) and [Al(O,F)<sub>4</sub>] polyhedra units are generally distributed at the interface between aluminosilicate oxide-rich and fluoride-rich phases.<sup>[10]</sup> That is, these units play a critical role in connecting [SiO<sub>4</sub>] and [AlO<sub>4</sub>] tetrahedra in the aluminosilicate oxide-rich phase.

To explore the short-range structure and atomic bonds in the simulated structure, we calculate the pair distribution function (PDF) and average coordination number (CN) for cation-oxygen and cation-fluorine pairs (Figures S5 and S6, Supporting Information). The observed bond lengths and used cutoff values are listed in Table S4 (Supporting Information). These bond distances in each cation-oxygen and cation-fluorine correlation exhibit small changes with composition. However, the bond intensities of La—F and Ba—F in PDF sharply increase, while those of Na—F and Al—F slightly increase and those of cation-oxygen (La—O, Ba—O, Na—O, and Al—O) decrease with composition. In addition, the average CN of Na, Al, La, and Ba to F increases with composition, which is consistent with the PDF results. This indicates that Ba<sup>2+</sup> and La<sup>3+</sup> ions prefer to bond to F<sup>-</sup> ions in the fluoride-rich phase rather than to O2<sup>-</sup> ions at the interface

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**Figure 4.** a,d) Optical transmittance spectra, b) UC luminescence, c) average lifetime decay curves of  ${}^{2}H_{11/2}$  level of Er<sup>3+</sup> ions, e) refractive index of 0LaF, 2LaF, 4LaF, 6LaF, and 7LaF samples (in panels (a-c) and black dots in panel (e) and HT-0LaF, HT-2LaF, HT-4LaF, HT-6LaF, and HT-7LaF samples (in panel (d) and red dots in panel (e)). f) <sup>139</sup>La WURST-QCPMG NMR spectra of both 7LaF-RE-Free and HT-7LaF-RE-Free samples.

region, thereby increasing the possibility of forming  ${\rm Ba_2LaF_7}$  crystals.

We next analyzed the microstructure of the oxyfluoride glasses and GCs by performing SEM measurements. This was done using secondary electron imaging mode on the studied samples subjected to etching in 7% hydrofluoric (HF) acid for 20-25 s. Two distinct regions including both white droplets (white dashed circles) and black domains (black arrows) are observed in the SEM images of OLaF (Figure 3f) and 2LaF (Figure 3g). Thus, we infer that the black domains are the aluminosilicate oxiderich phase owing to the depletion of the aluminosilicate oxiderich phase upon HF acid etching, resulting in the aluminosilicate oxide-rich phase having a low contrast. The expected corrosion reactions are shown in Supporting Information. Consequently, the fluoride-rich phases are observed as the white droplet domains. Two types of white domains can be seen in 4LaF (Figure 3h), 6LaF (Figure 3i), and 7LaF (Figure 3g), namely, interpenetrating regions (white arrows) and irregular shaped regions (sphere- and flower-like, red-arrows). The fractions of both the interpenetrating regions and the crystals increase with increasing LaF<sub>3</sub>. To further distinguish the two types of white domains, SEM measurements in backscattered electron imaging mode were conducted for 0LaF, 4LaF, and 7LaF samples without etching by HF. The obtained SEM images are shown in Figure 3k-m, respectively. Only some irregular shaped white domains are observed in the glass matrix and these grow with increasing concentration of LaF<sub>3</sub>. The XRD and Raman results indicate that the irregular shaped white domains can be attributed to Ba<sub>2</sub>LaF<sub>7</sub> crystals, while the interpenetrating white domains are the fluoride-rich phase. Upon HT, some spherical Ba<sub>2</sub>LaF<sub>7</sub> nanocrystals (≈25 nm)

precipitate from the fluoride-rich phase (white droplet domains) in HT-0LaF (Figure S7a, Supporting Information). The existing flower-like Ba<sub>2</sub>LaF<sub>7</sub> crystals grow from 100 nm to  $\approx$ 120 nm in size and some tiny Ba<sub>2</sub>LaF<sub>7</sub> nanocrystals with the approximate size of 15 nm form in the fluoride-rich phase of HT-4LaF (Figure S7b, Supporting Information). The crystallization behavior in the HT-7LaF sample is similar to that in HT-4LaF except that the flower-like Ba<sub>2</sub>LaF<sub>7</sub> crystals are larger (Figure S7c, Supporting Information).<sup>[18]</sup> This indicates that the fluoride-rich phase assists the formation of Ba<sub>2</sub>LaF<sub>7</sub> nanocrystals and the fraction of Ba<sub>2</sub>LaF<sub>7</sub> crystals increases upon HT.

# 2.5. Optics, Refractive Index, Fluorescence Lifetime, and <sup>139</sup>La NMR Analyses

**Figure** 4a,d shows the optical transmittance (%) spectra in the wavelength range of 275–800 nm of the as-quenched and heattreated samples, respectively. The optical transmittance spectra normalized to 1 mm thickness are derived from the optical absorption spectra (Figure S8a,b, Supporting Information) by using Equation (6). Figure 4a shows that the optical transmittance decreases with the substitution of LaF<sub>3</sub> for La<sub>2</sub>O<sub>3</sub>. This trend can also be visualized in samples 0LaF, 2LaF, 4LaF, 6LaF, and 7LaF from left to right in the inset of Figure 4a. The decrease in optical transmittance can be clarified as follows. On the one hand, the fluoride-rich phase, size, and fraction of Ba<sub>2</sub>LaF<sub>7</sub> crystal increase with the replacement of La<sub>2</sub>O<sub>3</sub> by LaF<sub>3</sub>, with the size of Ba<sub>2</sub>LaF<sub>7</sub> crystal up to  $\approx$ 200 nm in 7LaF sample. This results in strong light scattering and absorption, thus lowering

the optical transmittance. On the other hand, the refractive index  $(n_d)$  at the wavelength of 588 nm of the as-quenched samples (Figure 4e) decreases from 1.5856 to 1.5473 with increasing the content of LaF<sub>3</sub>. Hence, the differences in  $n_d$  ( $\Delta n_d$ ) between pure  $Ba_2LaF_7$  crystal ( $\approx 1.54$ ) and the as-quenched samples decrease from 0.0340 to 0.0073 (Table S5, Supporting Information) with increasing the content of LaF<sub>3</sub>, and thereby increasing the optical transmittance. Thus, we infer the increase in the fluoride-rich phase fraction and in both the Ba2LaF7 crystal size and fraction are responsible for the decrease of the optical transmittance, i.e., the decrease of  $\Delta n_d$  is not the determining factor. Moreover, it is shown in Table S5 (Supporting Information) that the density  $(\rho)$  of the studied samples exhibits the same variational trend as that in  $n_d$  since  $n_d$  is proportional to  $\rho$ .<sup>[42,43]</sup> After HT, the optical transmittance of HT-0LaF (inset of Figure 4d) is similar to that of 0LaF, i.e., the formation of small spherical Ba2LaF7 crystals hardly influences the light scattering. Although  $\Delta n_d$  decreases from 0.0340 to 0.0252 (Table S5, Supporting Information) after HT, the optical transmittance of HT-2LaF (inset of Figure 4d) becomes lower than that of 2LaF as the increase of both size and fraction of Ba<sub>2</sub>LaF<sub>7</sub> crystal causes an increase of the light scattering. Interestingly, the optical transmittances of 4LaF, 6LaF, and 7LaF samples (see inset of Figure 4d) increase with decreasing  $\Delta n_d$  (Table S5, Supporting Information) upon HT, while the size and fraction of Ba2LaF7 crystals increase. This implies that a decrease of  $\Delta n_d$  causes an enhanced optical transmittance. According to a previous study,<sup>[18]</sup> the diffusion of La<sup>3+</sup> ions from glass phase to Ba<sub>2</sub>LaF<sub>7</sub> phase during HT leads to a decrease of  $\Delta n_d$ . To this end, we further probe the spatial distribution of La<sup>3+</sup> ions by performing <sup>139</sup>La NMR measurements on both 7LaF-RE-Free and HT-7LaF-RE-Free samples (Figure 4f). The <sup>139</sup>La NMR spectra were obtained using the scheme of the Wideband Uniform-Rate Smooth Truncation-Quadrupolar Carr-Purcell-Meiboom-Gill (WURST-QCPMG) pulse.[44] We note that some broad <sup>139</sup>La NMR signals, which are affected by magnetic shielding anisotropy and quadrupole interaction, are observed in the spectrum of the 7LaF-RE-Free sample.<sup>[45]</sup> However, the band in the spectrum of the HT-7LaF-RE-Free sample becomes narrower as Ba2LaF7 crystals precipitate from glass matrix during HT. In addition, the normalized <sup>19</sup>F single pulse NMR spectra in Figure S9 (Supporting Information) demonstrate that the F2 signal of the Na-F-Al or Ba-F-Al linkages in HT-7LaF-RE-Free is weaker than that in 7LaF-RE-Free. This suggests that F<sup>-</sup> ions are transferred from the F-Al linkages to Ba2LaF7 crystal phase, and thus their bonded La<sup>3+</sup> ions migrate towards the precipitating sites of Ba<sub>2</sub>LaF<sub>7</sub> crystals, thereby enhancing the growth of these crystals. Thus, the decrease of  $\Delta n_d$  is ascribed to the diffusion of La<sup>3+</sup> ions from the glass phase to the Ba2LaF2 crystal phase upon HT, leading to an increase of the optical transmittance.[46]

To understand the energy transfer from Yb<sup>3+</sup> to Er<sup>3+</sup> ions, the energy level scheme of Er<sup>3+</sup> and Yb<sup>3+</sup> ions in the studied samples is demonstrated in Figure S10 (Supporting Information), implying a UC luminescence mechanism.<sup>[47]</sup> As shown in Figure 4b, under the excitation of the 980 nm laser, the samples with high LaF<sub>3</sub> concentration exhibit much stronger UC luminescence. For instance, the UC luminescence intensity of 7LaF sample is about 2700 times higher than that of 0LaF sample. Note that the UC luminescence of the studied samples arises from the transitions of <sup>2</sup>H<sub>11/2</sub>  $\rightarrow$  <sup>4</sup>I<sub>15/2</sub> (523 nm), <sup>4</sup>S<sub>3/2</sub>  $\rightarrow$  <sup>4</sup>I<sub>15/2</sub> (541 nm), and <sup>4</sup>F<sub>9/2</sub>  $\rightarrow$ 

**Table 1.** The absolute internal up-conversion photoluminescence quantum yield (UPLQY) of 0LaF, HT-0LaF, 7LaF, and HT-7LaF samples.

Samples	UPLQY (%)
0LaF	0.0000293
7LaF	0.01879
HT-0LaF	0.000236
HT-7LaF	0.0617

<sup>4</sup>I<sub>15/2</sub> (653 nm) of Er<sup>3+</sup> ions. This enhancement in UC luminescence can be explained by the following two aspects. First, Er<sup>3+</sup> and Yb<sup>3+</sup> ions in the 0LaF sample are present in the glass matrix phase, which possesses higher maximum phonon energy (≈1100 cm<sup>-1</sup>) than Ba<sub>2</sub>LaF<sub>7</sub> crystals  $\approx$ 270 cm<sup>-1</sup>) and the non-radiative relaxation rate of Er<sup>3+</sup> in the former is higher than that in the latter.<sup>[11]</sup> Hence, the UC luminescence of 0LaF sample is much weaker than that of the LaF<sub>3</sub>-doped samples containing Ba<sub>2</sub>LaF<sub>7</sub> crystals. Second, owing to the similarity in ionic radius among Er<sup>3+</sup>, Yb<sup>3+</sup>, and La<sup>3+</sup> ions, some La<sup>3+</sup> ions can be substituted by Er<sup>3+</sup> and/or Yb<sup>3+</sup> ions in the Ba<sub>2</sub>LaF<sub>7</sub> crystal. As such, the distance between Er<sup>3+</sup> and Yb<sup>3+</sup> ions in Ba<sub>2</sub>LaF<sub>7</sub> crystals becomes shorter, thereby increasing the energy transfer possibility from Yb<sup>3+</sup> to Er<sup>3+</sup> ions. In addition, the fraction of Ba<sub>2</sub>LaF<sub>7</sub> crystal increases with increasing LaF3, allowing more  $\mathrm{Er}^{3+}$  and  $\mathrm{Yb}^{3+}$  ions to enter into Ba2LaF7 crystals, thus enhancing the UC luminescence.

To further characterize the energy transfer from Yb<sup>3+</sup> to Er<sup>3+</sup> ions, the UC luminescence decay curves of the studied samples for  $^2H_{11/2} \rightarrow ^4I_{15/2}$  (523 nm),  $^4S_{3/2} \rightarrow ^4I_{15/2}$  (541 nm), and  $^4F_{9/2} \rightarrow ^4I_{15/2}$  (653 nm) transitions of Er<sup>3+</sup> ions are shown in Figure 4c and Figure S11a,b (Supporting Information), respectively. The corresponding decay curves can be well-fitted by a second-order exponential decay mode equation,

$$I = A_1 e^{(-t/\tau_1)} + A_2 e^{(-t/\tau_2)}$$
(1)

where *I* is the UC luminescence intensity,  $A_1$  and  $A_2$  are the fitting parameters, *t* is the time,  $\tau_1$  and  $\tau_2$  are the slow and fast decay components (long and short lifetime), respectively. Based on Equation (3), the average lifetime  $\tau$  can be calculated as,

$$\tau = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2)$$
<sup>(2)</sup>

Figure 4c and Figure S9a,b (Supporting Information) show that the values of the average lifetime for  ${}^{2}H_{11/2}$ ,  ${}^{4}S_{3/2}$ , and  ${}^{4}F_{9/2}$  states increase with increasing LaF<sub>3</sub>, implying that the samples with higher concentrations of LaF<sub>3</sub> have a higher probability of energy transfer between  $Er^{3+}$  and  $Yb^{3+}$  ions. Moreover, the increased probability of energy transfer between  $Er^{3+}$  and  $Yb^{3+}$  ions is verified by the absolute internal up-conversion photoluminescence quantum yield (UPLQY in %) (Table 1). It is seen that, despite its rather small value, the absolute internal UPLQY of 7LaF is around 641 times higher than that of 0LaF. The absolute internal UPLQY of 0LaF increases by 8.1 times, while that of 7LaF increases by 3.3 times upon HT.

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#### 2.6. Optical Thermometry Mechanism and Performance

Due to the small energy gap ( $\Delta E$ ) of thermally coupled energy levels (TCLs) of  ${}^{2}H_{11/2}$  and  ${}^{4}S_{3/2}$  for Er<sup>3+</sup> ions, electrons at  ${}^{4}S_{3/2}$  (lower energy level) can be populated to  ${}^{2}H_{11/2}$  (upper energy level) with increasing thermal excitation temperature by absorbing phonon energy from the glass matrix (Figure S10, Supporting Information). In addition, the fluorescence intensity of the radiative transition level.<sup>[48]</sup> Thus, the fluorescence intensity ratio (FIR) between  ${}^{2}H_{11/2}$  and  ${}^{4}S_{3/2}$  levels of Er<sup>3+</sup> ions increases with the electron transition from  ${}^{4}S_{3/2}$  levels of Er<sup>3+</sup> ions follows the Boltzmann distribution,<sup>[27,49,50]</sup> the FIR is related to the absolute temperature (*T*) as,

$$FIR = \frac{I_{\rm H}}{I_{\rm S}} = Ce^{-\frac{\Delta E}{k_{\rm B}T}}$$
(3)

where  $I_{\rm H}$  and  $I_{\rm S}$  are the intensities of the fluorescence from the upper ( ${}^{2}H_{11/2}$ ) and lower ( ${}^{4}S_{3/2}$ ) energy levels, respectively,  $\Delta E$ is the effective energy gap between  ${}^{2}H_{11/2}$  and  ${}^{4}S_{3/2}$  levels, C is a temperature-independent constant, and  $k_{\rm B}$  is the Boltzmann constant.<sup>37</sup> For temperature-sensing applications, we note that the 0LaF sample cannot be applied in an optical temperature sensor due to its extremely weak UC luminescence even at room temperature (Figure S12, Supporting Information). On the other hand, HT-0LaF, 7LaF, and HT-7LaF samples exhibit remarkable UC luminescence and could potentially be applied. Their UC luminescence spectra were measured at the ambient temperature range of 313-513 K and are shown in Figure 5a-c, respectively. To quantify the effect of temperature variation on the intensity of the peak at 523 nm, we have normalized the intensities of the green UC luminescence spectra by that of the peak at 541 nm. As shown in Figure 5g-i, the calculated FIR values represented by the black square increase monotonously with increasing temperature, in agreement with the Boltzmann distribution theory. The black fitting curves in Figure 5g-i represent the temperature dependence of the FIR, from which it is seen that the HT-7LaF and HT-0LaF samples have the highest and lowest degree of coincidence, respectively.

The experimental relation between Ln (FIR) and the inverse absolute temperature (1/*T*) of HT-0LaF, 7LaF, and HT-7LaF is depicted in Figure 5d–f, respectively. This relation can be linearly fitted by the following equation,

$$\ln (FIR) = \ln C - \frac{\Delta E}{k_{\rm B}T}$$
<sup>(4)</sup>

The intercept (ln*C*) and slope ( $\Delta E/k_{\rm B}$ ) of the Equation (6) for HT-0LaF, 7LaF, and HT-7LaF are determined to be 1.38, 1.61, and 1.8 and -923.3, -961.7, and -974.7, respectively. Thus, the obtained C and  $\Delta E$  values are 3.98, 5.01, and 6.05 and 644.4, 668.7, and 677.8 cm<sup>-1</sup>, respectively. The regression coefficients ( $R^2$ ) for the linear fits are 0.980, 0.993, and 0.999, respectively, indicating that the HT-7LaF exhibits the highest accuracy in sensing temperature. To better assess the optical thermometry performance

of the FIR method, the relative temperature sensitivity  $(S_R)$  of the studied samples is evaluated as,

$$S_{\rm R} = \left| \frac{1}{FIR} \frac{d(FIR)}{dT} \right| = \frac{\Delta E}{k_{\rm B} T^2}$$
(5)

According to Equation (7), by fitting the experimental data,  $S_{\rm R}$  values of TCLs ( ${}^{2}{\rm H}_{11/2}$  and  ${}^{4}{\rm S}_{3/2}$ ) in HT-0LaF, 7LaF, and HT-7LaF are calculated as shown in Figure 5g–i, respectively. The  $S_{\rm R}$  values of HT-0LaF, 7LaF, and HT-7LaF are in the range of 0.0035–0.00942, 0.0036–0.00982, and 0.0037–0.00995 K<sup>-1</sup>, respectively, in the temperature range between 513 and 313 K. Specifically, the maximum  $S_{\rm R}$  values of HT-0LaF, 7LaF, and HT-7LaF are determined to be 0.00942, 0.00982, and 0.00995 K<sup>-1</sup> at 313 K, respectively. The comparisons in  $S_{\rm R}$  are made in **Table 2** between the studied samples (HT-0LaF, 7LaF, and HT-7LaF) and other materials are shown. It is seen that the  $S_{\rm R}$  values of the studied samples are larger in some cases and smaller in other cases.

To determine the structural-thermal stability of the UC luminescence for temperature detection, the studied samples are subjected to the cycling process of heating and cooling in the temperature range from 313 to 513 K. The temperature-dependent 2D UC luminescence maps of the samples are shown in Figure 5j-l, respectively. Compared with HT-0LaF and 7LaF, the UC luminescence intensity of HT-7LaF at 523 and 541 nm nearly recovers to its original state during cooling from 513 to 313 K, i.e., the temperature-dependent UC luminescence behavior of HT-7LaF is reversible during the cycling process. This reversibility could be assigned to both the protecting role of the oxide glass matrix and the increase of optical transmittance upon HT. Thus, the high-crystallized, transparent HT-7LaF sample containing Ba<sub>2</sub>LaF<sub>7</sub> nanocrystals shows promise to be used in optical temperature sensors with excellent thermal stability. Moreover, it should be mentioned that phase separation has a strong effect on mechanical properties of the phase-separated oxyfluoride glasses according to a previous study.[56] This effect needs to be investigated in the future.

### 3. Conclusions

We prepared a series of functional oxyfluoride glasses and glassceramics by phase separation engineering, i.e., by gradually substituting La<sub>2</sub>O<sub>3</sub> with LaF<sub>3</sub> in 45SiO<sub>2</sub>-15Al<sub>2</sub>O<sub>3</sub>-12Na<sub>2</sub>O-21BaF<sub>2</sub>-7La<sub>2</sub>O<sub>3</sub>-0.5ErF<sub>3</sub>-1.0YbF<sub>3</sub> and by isothermal heat-treatment. The as-quenched samples are prone to undergo phase separation, resulting in aluminosilicate oxide-rich and fluoride-rich phases. They contain Ba<sub>2</sub>LaF<sub>7</sub> crystals, and their fraction and size increase with increasing the LaF<sub>3</sub> content, leading to the transformation of the transparent glass into translucent glass-ceramics, and hence to the enhanced UC luminescence. The critical Ba<sup>2+</sup>/La<sup>3+</sup> ratio for the formation of Ba<sub>2</sub>LaF<sub>7</sub> crystal was found to be  $\approx$ 2, which is consistent with that in the Ba<sub>2</sub>LaF<sub>7</sub> crystal.

The structure evolution with phase separation and the mechanism of crystallization in the studied samples were revealed by performing DSC, SEM, XRD, NMR, and EXAFS characterizations as well as MD simulations. Isothermal heat treatment (HT) leads to a further increase in the fraction of Ba<sub>2</sub>LaF<sub>7</sub> crystals, light transmittance, and UC luminescence intensity in the www.advancedsciencenews.com

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**Figure 5.** Normalized UC luminescence spectra of a) HT-0LaF, b) 7LaF, and c) HT-7LaF samples under the excitation of the 980 nm diode laser at various temperatures from 313 to 513 K. Temperature dependence of FIR (black fitting curve) between  ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$  and  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$  transitions of  $Er^{3+}$  ions and the sensitivity  $S_R$  (red fitting curve) of g) HT-0LaF, h) 7LaF, and i) HT-7LaF samples. Logarithmic plot of the FIR as a function of the inverse absolute temperature of d) HT-0LaF, e) 7LaF, and f) HT-7LaF samples. Temperature-induced switching of FIR of heat-treated GC (alternating between 313 and 473 K). Temperature-dependent emission mapping of j) HT-0LaF, k) 7LaF, and l) HT-7LaF samples. Note that the emission was obtained upon the cycling process of heating and cooling at the temperature range from 313 to 513 K.

studied samples. The increase in light transmittance upon HT is attributed to the minimization in light scattering due to the decrease of the difference in refractive index between the residual glass matrix and the Ba<sub>2</sub>LaF<sub>7</sub> crystals. HT-7LaF sample exhibits more temperature-sensitive UC luminescence compared with 7LaF sample. Our work demonstrates that optimizing both glass composition and HT conditions enables fabricating the oxyfluoride glass ceramics with outstanding optical and photonic performances for temperature-sensing applications.

### 4. Experimental Section

Materials and Samples Preparation: All the chemicals (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, BaF<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, LaF<sub>3</sub>, ErF<sub>3</sub> and YbF<sub>3</sub> with purity of 99.99%) used for preparing the studied samples were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. Ethanol (C<sub>2</sub>H<sub>5</sub>OH, 99%) and hydrofluoric acid (HF, 40%) solution were obtained from VWR International S.A.S and TH. Geyer Honeywell, respectively.

All the oxyfluoride glasses and glass ceramics were prepared by using a traditional melt-quenching method. The molar compositions of

Sensing materials	Temperature range [K]	$\Delta E [\text{cm}^{-1}]$	S <sub>R</sub> [%K <sup>-1</sup> ]	Refs.
$Ba_2LaF_7$ : $Er^{3+}$ , $Yb^{3+}$ heat-treated 7LaF	313-513	677.8	974.7/T <sup>2</sup>	This work
Ba <sub>2</sub> LaF <sub>7</sub> : Er <sup>3+</sup> , Yb <sup>3+</sup> 7LaF	313-513	668.7	961.7/T <sup>2</sup>	This work
Ba <sub>2</sub> LaF <sub>7</sub> : Er <sup>3+</sup> , Yb <sup>3+</sup> heat-treated 0LaF	313-513	644.4	923.3/T <sup>2</sup>	This work
BaYF <sub>5</sub> : Er <sup>3+</sup> , Yb <sup>3+</sup> heat-treated GC	313–473	787	1134/T <sup>2</sup>	[27]
Sr <sub>2</sub> YbF <sub>7</sub> : Er <sup>3+</sup> GC	300–500	786	1129.8/T <sup>2</sup>	[51]
NaYF <sub>4</sub> : Er <sup>3+</sup> , Yb <sup>3+</sup> GC	298–693	774	1117.4/T <sup>2</sup>	[52]
NaYF <sub>4</sub> : Er <sup>3+</sup> , Yb <sup>3+</sup> phosphors	290–320	715	1028/T <sup>2</sup>	[53]
TeO <sub>2</sub> -WO <sub>3</sub> : Er <sup>3+</sup> , Yb <sup>3+</sup> glasses	300–690	679	976.8/T <sup>2</sup>	[54]
silicate glass: Er <sup>3+</sup> , Yb <sup>3+</sup>	296–723	413	593/T <sup>2</sup>	[55]

**Table 2.**  $\Delta E$  and  $S_R$  of FIR-based optical temperature sensors based on UC luminescence from  ${}^{2}H_{11/2}$  and  ${}^{4}S_{3/2}$  levels of Er<sup>3+</sup> ions.

the studied samples were 45SiO<sub>2</sub>-15Al<sub>2</sub>O<sub>3</sub>-12Na<sub>2</sub>O-21BaF<sub>2</sub>-(7-x)La<sub>2</sub>O<sub>3</sub> $xLaF_3-0.5ErF_3-1YbF_3$  (x = 0, 2, 4, 6, and 7, respectively). In addition to the studied samples, a sample was prepared for measuring the <sup>139</sup>La and <sup>19</sup>F solid-state NMR spectra with the molar composition of 45SiO<sub>2</sub>-15Al<sub>2</sub>O<sub>3</sub>-12Na<sub>2</sub>O-21BaF<sub>2</sub>-7LaF<sub>3</sub>. Specifically, 10 g raw material of each sample was mixed in proportion and put into an alumina crucible with a lid, and then melted in a muffle furnace under an air atmosphere at 1450 °C for 45 min. Then each melt was cast onto a steel plate preheated at 300 °C to obtain the fast melt-quenched sample. Each sample was annealed at 500 °C for 8 h and then slowly cooled down to room temperature. Afterward, all the studied samples were cut into small pieces and polished for further characterization. The derived samples were denominated as 0LaF, 2LaF, 4LaF, 6LaF, and 7LaF according to the molar fractions of LaF<sub>3</sub> (0%, 2%, 4%, 6%, and 7%, respectively). These samples were heat-treated at 913 K for 2 h, and named as HT-0LaF, HT-2LaF, HT-4LaF, HT-6LaF, and HT-7LaF, respectively. The sample used for <sup>139</sup>La and <sup>19</sup>F solid-state NMR measurement was named as 7LaF-RE-Free, while this sample was heat-treated at 913 K for 2 h, denominated as HT-7LaF-RE-Free.

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*Material Characterizations: Crystallization Behavior*: To study the crystallization behavior of the studied samples, the DSC (embedded in NET-ZSCH STA 449F3 Jupiter) was used to observe the enthalpic responses of the samples to a heating process at 10 K min<sup>-1</sup> up to 1273 K in nitrogen. The XRD measurements were performed to identify the crystallization phases by a PANalytical diffractometer, operated at 40 kV and 40 mA, with Cu-K $\alpha$  ( $\lambda$  = 1.5406 Å) radiation during the 2 $\theta$  range of 10°–90° with a step size of 0.013°.

Morphology and Chemical Composition: The morphologies of the spontaneously precipitated crystals in the as-quenched samples were characterized by field-emission SEM (QUANTA 200) in the back-scattering electron mode using a voltage of 30 kV. To better visualize the microstructures of the surface layer, the as-quenched samples were etched in 7% HF solution for 20–25 s before conducting the SEM (Zeiss Gemini 500) analysis. To determine the chemical compositions of the studied glasses, the glass samples were dissolved in HF acid and then quantified by ICP-OES PerkinElmer 7300 V, US).

Structure Analyses: The short-range structure of the studied samples was characterized by solid-state NMR spectroscopy (Bruker Avance III HD 500 MHz spectrometer (11.7 T)) at 25 °C. The single-pulse MAS <sup>19</sup>F NMR signals of OLaF, 2LaF, 4LaF, 6LaF, and 7LaF were recorded at a resonance frequency of 470.5 MHz, using a 2.5 mm MAS NMR probe. The spinning rate was 24 kHz, and the 90° pulse length of 2  $\mu s$  was used. The relaxation delay of <sup>19</sup>F was 4 s. The <sup>19</sup>F single pulse NMR signals of the 7LaF-RE-Free and HT-7LaF-RE-Free samples were recorded using a 4.0 mm NMR probe. The spinning rate was 12 kHz and the 90° pulse length was 2.2 µs, while the relaxation delay of <sup>19</sup>F was 128 s. The <sup>19</sup>F chemical shifts were referenced to CFCl<sub>3</sub>, using AlF<sub>3</sub> ( $\delta = -172.5$  ppm) as a secondary standard. <sup>27</sup>Al MAS NMR spectra of OLaF, 2LaF, 4LaF, 6LaF, and 7LaF were obtained at the resonance frequency of 130.2 MHz, operating with a 2.5 mm MAS probe at a spinning rate of 12 kHz. The typical pulse length was 0.83 µs (10° liquid flip angle). The relaxation delay was 0.5 s for all the samples. The chemical shifts of  $^{27}$ Al were referenced to Al(NO<sub>3</sub>)<sub>3</sub> (1 M) aqueous solution. <sup>29</sup>Si MAS NMR spectra of 0LaF, 2LaF, 4LaF, 6LaF, and 7LaF were acquired at the resonance frequency of 99.4 MHz using a 4 mm probe at a spinning rate of 6 kHz. A spin echo pulse scheme with the 90° pulse length of 6  $\mu$ s was used to acquire the spectrum. The relaxation delays of the studied samples were set as 300 s. The chemical shifts were referenced to tetrakis (trimethylsilyl) silane standard ( $\delta = -9.7$  ppm). Line shape deconvolutions were done with the DMFIT package.<sup>[57]</sup>

To compare the signal intensity of  $F^-$  around  $AI^{3+}$  between the OLaF and 7LaF samples, the <sup>27</sup>Al{<sup>19</sup>F} heteronuclear dipole-dipole interaction experiment was conducted using a rotational echo double resonance (REDOR) method.<sup>[58]</sup> This experiment included two steps: 1) a rotor-synchronized spin echo signal of the observed nuclei was recorded, yielding the intensity  $S_0$ ; 2) the spin echo signal of the observed nuclei was measured with  $\pi$ pulses added to the dephaser channel during the rotor period, thereby obtaining the attenuated intensity S. The  $\pi$  pulses could recouple heteronuclear dipolar interactions with the observed nuclei (<sup>27</sup>Al nuclei), which were averaged by MAS. Then the normalized REDOR signal intensity difference  $(S_0 - S)/S_0$  was plotted as a function of dipolar evolution time NTr<sup>[59]</sup> where N is the number of rotor cycles and Tr is the rotor period. The resonance frequencies of <sup>27</sup>Al nuclei and <sup>19</sup>F nuclei were 130.3 and 500.1 MHz, respectively. The operating spinning rate is 12 kHz. The  $\pi$ pulse lengths of <sup>27</sup>Al and <sup>19</sup>F were 5.4 µs. The relaxation delay was 0.5s. The chemical shifts of <sup>27</sup>Al were referenced to the Al(NO<sub>3</sub>)<sub>3</sub> aqueous solution.

To compare the distribution density of the La<sup>3+</sup> ions between the 7LaF-RE-Free and HT-7LaF-RE-Free samples, <sup>139</sup>La NMR measurements were also compared. The static <sup>139</sup>La NMR spectra were obtained at a resonance frequency of 71.2 MHz via the WURST-QCPMG technique. Further details of NMR measurements for <sup>139</sup>La could be found elsewhere.<sup>[60,46]</sup>

Ba and La K-edge EXAFS spectra were acquired for the 0LaF, 2LaF, 4LaF, 7LaF, HT-0LaF, HT-4LaF, and HT-7LaF samples at the BL14B2 beamline at SPring-8 (Hyogo, Japan), wherein BaF<sub>2</sub> and LaF<sub>3</sub> were used as the reference samples, respectively. The preparation of the measured samples was obtained by mixing each studied sample with boron nitride to an optimal concentration of the target ion. A Si(111) double crystal monochromator was used in all the EXAFS experiments and all the data were collected in the standard transmission mode using an ion chamber detector at 300 K. Athena program was used to process the obtained EXAFS data, and the spectra were theoretically fitted by using the first shell model with FEFF calculation using FEFF6 embedded in Artemis program.<sup>[61,62]</sup> The Raman spectra in the range of 170 to 1200 cm<sup>-1</sup> were acquired using a micro-Raman spectrometer (inVia, Renishaw) with a 532 nm green diode pumped solid-state laser at room temperature.

*Optical Performances and Temperature-Sensing Ability*: UV-vis absorption spectra in the wavelength range from 275 to 800 nm were collected by a UV-vis spectrophotometer (Varian Cary 50). The optical transmittance was obtained by using the equation derived from the Beer–Lambert Law, as follows:

$$Transmittance = 10^{\left(2 - \frac{A}{THK}\right)}$$
(6)

where Transmittance is the light transmittance (%) at a given wavelength, A is the absorbance, and THK is the sample thickness (in mm). The refractive index (n) of the samples was measured at various wavelengths by KALNEW Precision Refractometer KPR-2000 at 25 °C. The density ( $\rho$ ) of the studied samples was determined at 298 K by the Archimedes' principle, using ethanol as an immersion liquid. The UC luminescence spectra in the wavelength range of 500-700 nm were recorded with a HITACHI F-7000 fluorescence spectrophotometer under the 980 nm laser excitation. The excitation power was 0.5 W and the slit was 1 nm. The lifetime measurements were carried out using the method described elsewhere.<sup>[63]</sup> The upconversion photoluminescence quantum yield (UPLQY) was measured by using an optical integrating sphere coupled to a fiber optic spectrometer (NQ512-1.7, 900-1700 nm, Ocean Optics). The optical response of the instrument was calibrated with a standard tungsten halogen lamp. Subsequently, the samples were put in a cuvette with optical length of 1 mm. The absolute internal UPLQY is defined as:

$$\eta_{int} = \frac{N_1}{N_2} \times 100\% \tag{7}$$

where  $\eta_{\rm int}$  is internal UPLQY,  $N_1$  is the number of emitted photos, and  $N_2$  is the number of emitted photos. Statistical analysis was performed through the Origin software.

To investigate the temperature dependence of the UC luminescence for the potential application of temperature-sensing, the samples were placed in a temperature-controlled copper cylinder and heated from 313 to 513 K in a heating tube. The temperature was monitored by a temperature controller (TAP-02) with a type-K thermocouple. The excitation power was 0.5 W, and the excitation and emission slits were 2.5 nm. The UC luminescence decay curves of the sample were recorded by FLSP-980 spectrophotometer (Edinburgh Instruments Ltd., Edinburgh, UK). The excitation source was 980 nm laser with a frequency of 500 Hz.

MD Simulations: The short- and medium-range structures of the studied samples were simulated by conducting classical MD simulations that involve effective partial charge pairwise potentials. Specifically, the simulation was performed using the DL POLY 2.20 package, [10,64] where the potentials had the Buckingham form. The structures of the glasses with the composition 45SiO<sub>2</sub>-15Al<sub>2</sub>O<sub>3</sub>-12Na<sub>2</sub>O-21BaF<sub>2</sub>-(7-x)La<sub>2</sub>O<sub>3</sub>-xLaF<sub>3</sub>-0.5ErF<sub>3</sub>-1YbF<sub>3</sub> (mol%) were simulated, where La<sup>3+</sup> ions represent  $Er^{3+}$  and Yb<sup>3+</sup> ions. The input density (g  $cm^{-3}$ ) as well as the simulation cell dimension and final density after equilibrium are listed in Table S1 (Supporting Information). The initial density was calculated and starting atom positions were randomly generated.<sup>[10]</sup> After generating the initial simulation box, the samples were relaxed at 0 K, followed by a melting procedure by stepwise heating to 2000, 4000, and finally, 6000 K, where a 100 ps NVT run was followed by a 60 ps NVE run at each temperature. Then the glass melt was gradually cooled down to 300 K with a nominal cooling rate of 5 K ps<sup>-1</sup>. At 300 K, constant pressure relaxation for 100 ps with the NPT ensemble was used to allow the system to relax to its equilibrium volume. This was followed by NVE relaxations for another 60 ps, and this final configuration was then used for the structural analysis. The total simulation time of each glass composition is  $\approx$  1.8 ns. A fixed timestep of 1 fs was used, and the Berendsen thermostat and barostat were used to control temperature and pressure, respectively, during NVT or NPT MD simulations. Further details of MD simulations of oxyfluoride glasses could be found in recent papers.<sup>[10,65]</sup>

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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# **Conflict of Interest**

The authors declare no conflict of interest.

# **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### **Keywords**

nanocrystals, phase separation engineering, temperature-sensing, transparent glass-ceramics, up-conversion luminescence

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- P. P. Fedorov, A. A. Luginina, A. I. Popov, J. Fluor. Chem. 2015, 172, 22.
- [2] C. Bocker, J. Wiemert, C. Rüssel, J. Eur. Ceram. Soc. 2013, 33, 1737.
- [3] C. Bocker, C. Rüssel, I. Avramov, Int. J. Appl. Glas. Sci. 2013, 4, 174.
- [4] M. Stoica, M. Brehl, C. Bocker, A. Herrmann, C. Rüssel, Mater. Chem. Phys. 2018, 207, 36.
- [5] C. Lin, C. Rüssel, S. Dai, Prog. Mater. Sci. 2018, 93, 1.
- [6] K. Sun, D. Tan, X. Fang, X. Xia, D. Lin, J. Song, Y. Lin, Z. Liu, M. Gu, Y. Yue, J. Qiu, *Science* **2022**, *375*, 307.
- [7] M. J. Weber, R. W. Bierig, Phys. Rev. 1964, 134, A1492.
- [8] A. D. Sontakke, K. Annapurna, J. Appl. Phys. 2012, 112, 013510.
- [9] T. Ouyang, S. Kang, Z. Zhang, D. Yang, X. Huang, Q. Pan, J. Gan, J. Qiu, G. Dong, Adv. Opt. Mater. 2019, 7, 1900197.
- [10] J. Zhao, R. Ma, X. Chen, B. Kang, X. Qiao, J. Du, X. Fan, U. Ross, C. Roiland, A. Lotnyk, L. Kienle, X. Zhang, J. Phys. Chem. C 2016, 120, 17726.
- [11] X. Fan, J. Wang, X. Qiao, M. Wang, J. L. Adam, X. Zhang, J. Phys. Chem. B 2006, 110, 5950.
- [12] Z. Li, D. Zhou, Y. Yang, P. Ren, J. Qiu, Sci. Rep. 2017, 7, 1.
- [13] X. Yang, M. Zhang, H. Ma, X. Xu, X. Yu, ECS J. Solid State Sci. Technol. 2019, 8, R127.
- [14] T. Wang, B. Liu, Y. Lin, Q. Yang, W. Gao, M. J. Li, J. Qiu, X. Yu, X. Xu, S. F. Yu, Opt. Lett. 2020, 45, 5986.
- [15] X. Xu, W. Zhang, D. Yang, W. Lu, J. Qiu, S. F. Yu, Adv. Mater. 2016, 28, 8045.
- [16] Z. Zhao, F. Hu, Z. Cao, F. Chi, X. Wei, Y. Chen, C. K. Duan, M. Yin, *Ceram. Int.* 2017, 43, 14951.
- [17] L. Qiu, J. Mao, Z. Zhao, P. Wang, M. T. Abbas, X. Wei, F. Chi, Y. Chen, M. Yin, *Ceram. Int.* **2021**, *47*, 6244.
- [18] Z. Li, C. Chen, W. Shen, D. Zhou, L. R. Jensen, X. Qiao, J. Ren, J. Du, Y. Zhang, J. Qiu, Y. Yue, *Adv. Opt. Mater.* **2022**, *10*, 2102713.
- [19] C. Lin, C. Bocker, C. Rüssel, Nano Lett. 2015, 15, 6764.
- [20] D. Chen, Y. Zhou, Z. Wan, H. Yu, H. Lu, Z. Ji, P. Huang, Phys. Chem. Chem. Phys. 2015, 17, 7100.

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- [21] W. Shen, Y. Yang, Z. Li, M. I. Khan, E. Cao, D. Zhou, J. Qiu, J. Non. Cryst. Solids 2019, 523, 119579.
- [22] Z. Li, D. Zhou, Y. Yang, P. Ren, R. Zhu, T. Han, J. Qiu, J. Alloys Compd. 2018, 731, 1044.
- [23] A. Astruc, S. Célérier, E. Pavon, A. S. Mamede, L. Delevoye, S. Brunet, Appl. Catal. B Environ. 2017, 204, 107.
- [24] Z. Li, L. Tan, C. Chen, D. Zhou, L. R. Jensen, J. Ren, Y. Zhang, J. Qiu, Y. Yue, J. Non. Cryst. Solids 2022, 593, 121773.
- [25] Q. Liu, Y. Tian, C. Wang, F. Huang, X. Jing, J. Zhang, X. Zhang, S. Xu, Phys. Chem. Chem. Phys. 2017, 19, 29833.
- [26] Q. Zheng, Y. Zhang, M. Montazerian, O. Gulbiten, J. C. Mauro, E. D. Zanotto, Y. Yue, *Chem. Rev.* 2019, 119, 7848.
- [27] Z. Li, D. Zhou, L. R. Jensen, J. Qiu, Y. Zhang, Y. Yue, J. Am. Ceram. Soc. 2021, 104, 4471.
- [28] J. Chung, H. Inoue, K. Yoshimoto, A. Masuno, Y. Watanabe, J. Am. Ceram. Soc. 2021, 104, 3963.
- [29] A. Gaddam, H. R. Fernandes, D. U. Tulyaganov, J. M. F. Ferreira, J. Non. Cryst. Solids 2019, 505, 18.
- [30] S. V. Smiljanić, S. R. Grujić, M. B. Tošić, V. D. Živanović, J. N. Stojanović, S. D. Matijašević, J. D. Nikolić, *Ceram. Int.* 2014, 40, 297.
- [31] J. Chung, Y. Watanabe, Y. Yananba, Y. Nakatsuka, H. Inoue, J. Am. Ceram. Soc. 2020, 103, 167.
- [32] B. O. Mysen, G. D. Cody, A. Smith, Geochim. Cosmochim. Acta 2004, 68, 2745.
- [33] L. Lin, G. Ren, M. Chen, Y. Liu, Q. Yang, Opt. Mater. 2009, 31, 1439.
- [34] L. M. Funke, O. Janka, R. Pöttgen, L. Glebov, M. R. Hansen, H. Eckert, J. Phys. Chem. C 2019, 123, 12411.
- [35] F. Muñoz, A. De Pablos-Martín, N. Hémono, M. J. Pascual, A. Durán,
   L. Delevoye, L. Montagne, J. Non. Cryst. Solids 2011, 357, 1463.
- [36] T. J. Kiczenski, L. S. Du, J. F. Stebbins, J. Non. Cryst. Solids 2004, 337, 142.
- [37] T. Story, C. H. W. Swüste, P. J. T. Eggenkamp, H. J. M. Swagten, W. J. M. de Jonge, *Phys. Rev. Lett.* **1996**, *77*, 2802.
- [38] Z. Sun, Q. Liu, T. Yao, W. Yan, S. Wei, Sci. China Mater. 2015, 58, 313.
- [39] X. Li, D. Chen, F. Huang, G. Chang, J. Zhao, X. Qiao, X. Xu, J. Du, M. Yin, *Laser Photonics Rev.* 2018, 12, 1800030.
- [40] A. De Pablos-Martín, M. A. García, A. Muñoz-Noval, G. R. Castro, M. J. Pascual, A. Durán, J. Non. Cryst. Solids 2014, 384, 83.
- [41] M. Poulain, Nature 1981, 293, 279.

- [42] Y. Y. Huang, A. Sarkar, P. C. Schultz, J. Non. Cryst. Solids 1978, 27, 29.
- [43] H. N. RITLAND, J. Am. Ceram. Soc. 1955, 38, 86.
- [44] X. Zhang, L. Hu, J. Ren, J. Phys. Chem. C 2020, 124, 1594.
- [45] B. Herreros, P. Man, J. Manoli, J. Fraissarda, J. Chem. Soc. Chem. Commun. 1992, 464.
- [46] T. Zhao, L. Hu, J. Ren, J. Phys. Chem. C 2021, 125, 26901.
- [47] Y. Shi, M. Yuan, J. Li, F. Li, W. Cui, X. Jiao, Y. Peng, Y. Huang, L. Chen, Inorg. Chem. 2022, 61, 5309.
- [48] D. Chen, S. Liu, Z. Wan, Y. Chen, J. Alloys Compd. 2016, 672, 380.
- [49] Q. Min, W. Bian, Y. Qi, W. Lu, X. Yu, X. Xu, D. Zhou, J. Qiu, J. Alloys
- Compd. 2017, 728, 1037.
   [50] J. Zhong, D. Chen, Y. Peng, Y. Lu, X. Chen, X. Li, Z. Ji, J. Alloys Compd. 2018, 763, 34.
- [51] X. Li, J. Cao, Y. Wei, Z. Yang, H. Guo, J. Am. Ceram. Soc. 2015, 98, 3824.
- [52] J. Sha, P. Zeng, L. Liao, S. Tian, H. Guo, Y. Chen, C. Duan, M. Yin, J. Alloys Compd. 2014, 617, 538.
- [53] F. Vetrone, R. Naccache, A. Zamarrón, A. J. Fuente, F. Sanz-Rodríguez, L. Maestro, E. Rodriguez, D. Jaque, J. Solé, D. Jaque, ACS Nano 2010, 4, 3254.
- [54] A. Pandey, S. Som, V. Kumar, V. Kumar, K. Kumar, V. Rai, H. Swart, Sens. Actuators B: Chem. 2014, 202, 1305.
- [55] C. Li, B. Dong, S. Li, C. Song, Chem. Phys. Lett. 2007, 443, 426.
- [56] K. V. Tian, B. Yang, Y. Yue, J. Mayers, D. T. Bowron, R. S. Donnan, C. Dobo-Nagy, J. W. Nicholson, D. Fang, A. L. Greer, A. Chass, G. N. Greaves, *Nat. Commun.* 2015, *6*, 8631.
- [57] X. Zhang, R. Zhang, L. Hu, J. Ren, J. Mater. Chem. C 2019, 7, 6728.
- [58] J. R. Garbow, T. Gullion, Chem. Phys. Lett. **1992**, 192, 71.
- [59] X. Zhang, L. Hu, J. Ren, J. Phys. Chem. C 2020, 124, 8919.
- [60] L. A. O'Dell, R. W. Schurko, Chem. Phys. Lett. 2008, 464, 97.
- [61] B. Ravel, M. Newville, J. Synchrotron Rad. 2005, 12, 537.
   [62] K. Shinozaki, H. Tsuchiya, T. Honma, K. Ohara, H. Masai, T. Ina, T.
- [62] K. Shinozaki, H. Isuchiya, I. Honma, K. Ohara, H. Masai, I. Ina, I. Komatsu, J. Phys. Condens. Matter. 2020, 32, 055705.
- [63] R. Wang, D. Zhou, J. Qiu, Y. Yang, C. Wang, J. Alloys Compd. 2015, 629, 310.
- [64] J. Zhao, X. Xu, K. Ren, Z. Luo, X. Qiao, J. Du, J. Qiu, X. Fan, G. Qian, Adv. Theory Simul. 2019, 2, 1970034.
- [65] J. Zhao, X. Xu, P. Li, X. Li, D. Chen, X. Qiao, J. Du, G. Qian, X. Fan, J. Phys. Chem. B 2019, 123, 3024.

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