Tailoring the Glass Composition to Increase the Thermal Stability without Impacting the Crystallization Behavior of Oxyfluorophosphate Glass

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Abstract: Even though the (75 NaPO₃-25 CaF₂) (in mol%) glass can be heat-treated into transparent glass-ceramic with Er³⁺ doped CaF₂ crystals precipitating in the volume of the glass during heat-treatment, this glass was found to be a poor glass former, limiting its use as upconverter under 975 nm pumping. In this study, the impact of the glass composition on the thermal, optical and structural properties of the glass was investigated in order to understand how the glass composition can be tailored for the development of thermally stable upconverter glass-based material. The addition of MgO, Fe₂O₃ and Al₂O₃ in the NaPO₃-CaF₂ glass system increases the thermal stability of glass due to the depolymerization of the glass network. However, the changes in the glass composition also impacted on the nucleation and growth process. Indeed, CaF₂ and other crystals were found in the newly developed glasses after heat-treatment leading to glass-ceramics with lower intensity of upconversion than the (75 NaPO₃-25 CaF₂) glass-ceramic used as a reference. Glasses were also prepared with different concentrations of Er₂O₃ and ErF₃. These glasses were found to be promising as not only are they thermally stable, but they also exhibit green and red emission with high intensity under 975 nm pumping due to Er³⁺ clustering.

Keywords: crystallization; upconversion; oxyfluorophosphate glass; glass-ceramic; thermal stability

1. Introduction

Oxyfluorophosphate glasses have been gaining interest in recent years due to the combined properties of oxides and fluorides. These glasses possess low phonon energy and they allow high solubility of rare-earth (RE) ions as RE clustering occurs at very high RE content [1]. Additionally, the composition of the oxyfluorophosphate glasses can be easily tailored so that the glasses can be engineered with good chemical durability and thermal stability [2].

As the spectroscopic properties of RE ions can be tailored by controlling the local environment of the RE ions, glass-ceramics can possess higher absorption and emission cross-sections and energy transfer rates compared to their parent glasses if the RE ions are located in crystals with specific crystalline phase [3,4]. Due to their promising spectroscopic properties, RE doped GCs have found extensive use for numerous applications in optics, photonics, dental and bioactive fields, for example [5–7]. To be considered promising materials for these applications, the crystals should be homogeneously distributed in the volume of the glass matrix. Additionally, the crystals should be smaller than the incident light wavelength and they should have a similar refractive index than the glassy host for the glass-ceramic to be transparent. Therefore, the control of the growth of crystals with tailored composition, size and segregation within the volume of the glass is crucial especially for the technology related to transparent glass-ceramics.
Most studies on the development of new transparent GCs have been focused on silicate glasses. Wang and Ohwaki reported the first transparent RE doped GCs in 1993 [8]; The Er$^{3+}$, Yb$^{3+}$ codoped transparent glass-ceramic was reported with an upconversion efficiency higher than the parent glass due to the precipitation of (Pb, Cd)F$_2$ crystalline phase. Enhancement of the upconversion luminescence was also reported in transparent Er$^{3+}$ doped oxyfluoride aluminosilicate glass-ceramics due to the Er$^{3+}$ doped CaF$_2$ crystals precipitating in the volume of the glass [9]. Studies on transparent germanate and tellurite GCs have been also reported [10–13]. However, surprisingly, fewer studies can be found on transparent phosphate GCs.

Transparent glass-ceramics in the NaPO$_3$-CaF$_2$ system were successfully prepared with enhanced upconversion properties compared to the base glasses, due to the volume precipitation of Er$^{3+}$ doped CaF$_2$ crystals occurring during heat-treatment [14]. The onset of crystallization was reported to be largely different than the maximum nucleation temperature of glasses, independently of the glass composition, indicating that the nucleation and growth of the crystals can be controlled. Thus, transparent glass-ceramics can be obtained from this glass-system. However, glasses in this system possess low thermal stability against crystallization as evidenced by the low temperature difference between the crystallization and the glass transition temperatures. Thus, this glass has a high tendency to crystallize during heat treatment. One should remind that thermal stability is an important property the glass should possess for many applications, especially for the development of novel optical fibers, for example [15]. Indeed, uncontrolled crystallization could occur during the fiber drawing process of a poor glass former. Thus, it is important to advance the fundamental understanding of the impact of the glass composition on the thermal stability of glasses, especially of glasses within the NaPO$_3$-CaF$_2$ system, in order to develop promising transparent GCs. These GCs are of great interest not only from an optical fiber perspective but also with a view to finding new applications, for example for waste immobilization [16] or as sealing glasses [17,18]. Additionally, these GCs are promising upconverter materials which could be used to increase the efficiency of the solar cells [19,20].

The goal of this study is to understand how to tailor the glass composition in order to increase the thermal stability of the glass without modifying the volume precipitation of Er$^{3+}$ doped CaF$_2$ crystals inside the glass during heat-treatment, and so its upconversion property. Here, new glasses in the NaPO$_3$-CaF$_2$ glass system were prepared to investigate the effect of the glass composition on the thermal, optical, structural and crystallization properties.

2. Materials and Methods

The compositions of the investigated oxyfluorophosphate glasses are (100 − x − 0.25) (75NaPO$_3$-25CaF$_2$) − x (MgO / Al$_2$O$_3$ / Fe$_2$O$_3$)-0.25Er$_2$O$_3$ (in mol%) with x ranging from 0 to 6 and (100- y) (75NaPO$_3$-25CaF$_2$) − y (Er$_2$O$_3$ / ErF$_3$) (in mol%) with y ranging from 0.25 to 6. The composition of the glasses and their corresponding code are summarized in Table 1.

The glasses were prepared in air using standard melting condition. Platinum (Pt) crucible was used for the preparation of the Mg and Al glasses while the Fe glasses were prepared in an alumina crucible. The glass with x = 0 prepared in Pt crucible is labelled as 0Mg/Al, while it is labelled 0Fe when prepared in alumina crucible. NaPO$_3$ (technical grade), CaF$_2$ (99%), ErF$_3$ (99.9%), Er$_2$O$_3$ (99.9%), MgO (≥99%), Fe$_2$O$_3$ (≥99%) and Al$_2$O$_3$ (99%) were used as raw materials. The glasses were melted for 5 min between 900 and 1025 °C depending on the glass composition. After quenching in air, the glasses were annealed 40 °C below their respective glass transition temperature ($T_g$) for 6 h. The glasses were polished prior to the heat-treatment for 17h at 20 °C above their $T_g$ and then at their crystallization temperature ($T_p$) for 1 h.

The glass transition temperature ($T_g$), the onset of the crystallization ($T_c$) and the crystallization temperature ($T_p$) were determined using differential thermal analysis (DTA)
(TA instruments SDT Q600). The heating rate was 10 °C/min. Platinum pan and N₂ atmosphere were used for the measurement. $T_g$ was taken at the inflection point of the endotherm, $T_p$ at the maximum of the exothermic peak and $T_x$ at the onset of the crystallization peak. The accuracy of the measurement is ±3 °C.

Table 1. Composition (in mol%) and code of the investigated glasses.

| Glass Code | NaPO₃ | CaF₂ | Al₂O₃ | MgO | Fe₂O₃ | Er₂O₃ | ErF₃ |
|------------|-------|------|-------|-----|-------|-------|------|
| 0Mg/Al     | 74.8  | 24.9 | 1.5   | 0.25|
| 1.5Mg      | 73.7  | 24.6 | 3.0   | 0.25|
| 3Mg        | 72.6  | 24.2 | 4.5   | 0.25|
| 4.5Mg      | 71.4  | 23.8 | 6.0   | 0.25|
| 6Mg        | 70.3  | 23.4 |       | 0.25|
| 0.5Al      | 74.4  | 24.8 | 0.50  | 0.25|
| 1Al        | 74.1  | 24.7 | 1.00  | 0.25|
| 1.25Al     | 73.9  | 24.6 | 1.25  | 0.25|

Perkin Elmer Spectrum FTIR2000 spectrometer with Attenuated Total Reflection (ATR) mode was used to obtain the IR spectra of the glasses. For this measurement, the samples were crushed into powder. The IR spectra were recorded between 650 cm⁻¹ and 1500 cm⁻¹ with a resolution of 2 cm⁻¹ and 8 scan accumulation.

Panalytical EMPYREAN multipurpose X-ray Diffractometer (XRD) with Nickel filtered Cu-Kα radiation was used to determine the crystal phases in the heat-treated glasses. The spectra were obtained using the Bragg-Brentano geometry and by rotating the sample holder around the Phi-axis at a constant speed of 16 revolutions per minute. The scan range was from 20° to 80° using a step size of 0.026. The MAUD software was used to analyze the XRD-patterns of the heat-treated glasses.

The upconversion spectra of the glasses were measured from glasses crushed into powder to allow one to compare the intensity of the emission between the samples. The glasses were excited using a TEC-cooled fiber-coupled multimode laser (II-VI Laser Enterprise) with a center emission wavelength ($\lambda_{exc}$) at ~975 nm and power of ~23.5 mW. The spectra were measured using a Spectro 320 optical spectrum analyzer equipped with a photomultiplier tube capable of measuring wavelengths between 500 nm and 700 nm (Instrument Systems Optische Messmethnik GmbH, Munich, Germany) at room temperature. The luminescence light was collected from the samples to the spectrum analyzer using a lens and a liquid light guide.

3. Results and Discussion

Recently, the nucleation and growth behavior of glasses in the NaPO₃-CaF₂ system was reported by Ojha et al. [14]. A small addition of TiO₂, ZnO or MgO (1.5 mol%) was found to be enough to impact the nucleation and growth process: although Er³⁺ doped CaF₂ crystals precipitate in all the glasses during heat-treatment, the Maximum Nucleation Temperature ($T_{n max}$) and the crystal growth rates were found to depend on the glass composition. However, the changes in the glass composition were too little to impact the thermal stability of the glasses. Thus, in this study, new glasses with a larger amount of
MgO were investigated. Glasses were also prepared with Al₂O₃ and Fe₂O₃ as they were found to prevent the tendency of phosphate glasses in other systems to crystallize [21,22].

As shown in Table 2, MgO, Al₂O₃ and Fe₂O₃ can be added in the NaPO₃-CaF₂ system to increase Tₘ, Tₓ and Tₚ—and more importantly to increase ∆T (ΔT = Tₓ − Tₙ), which is used as a gauge to the glass resistance against crystallization. Thus, it is clearly shown here that the addition of MgO, Al₂O₃ and Fe₂O₃ increases the thermal stability of the glass in the NaPO₃-CaF₂ system. While most of the Mg glasses are poor glass formers due to their low ΔT (<90 °C), the Al and Fe glasses can be considered as good glass formers due to their ΔT larger than 90 °C.

### Table 2. Thermal properties of the investigated glasses (NA: the peak intensity is too small to estimate the size of the crystallite).

| Glass Code | Tₙ ± 3 (°C) | Tₓ ± 3 (°C) | Tₚ ± 3 (°C) | ΔT = Tₓ − Tₙ ± 6 (°C) | Mean Size of the Crystallites ±2 (nm) | Er³⁺ Ions/cm³ (10¹⁹) ±5% |
|------------|-------------|-------------|-------------|--------------------------|---------------------------------------|--------------------------|
| 0Mg/Al     | 269         | 323         | 338         | 54                       | 17                                    | 8.19                     |
| 1.5Mg      | 279         | 345         | 365         | 66                       | 24                                    | 8.36                     |
| 3Mg        | 290         | 377         | 410         | 87                       | 30                                    | 8.43                     |
| 4.5Mg      | 297         | 381         | 410         | 84                       | 36                                    | 8.50                     |
| 6Mg        | 302         | 381         | 405         | 79                       | 45                                    | 8.61                     |
| 0.5Al      | 281         | 378         | 420         | 97                       | 30                                    | 8.31                     |
| 1Al        | 295         | 393         | 420         | 98                       | 41                                    | 8.31                     |
| 1.25Al     | 299         | 399         | 429         | 100                      | NA                                    | 8.31                     |
| Prepared in Pt crucible |
| 0Fe        | 270         | 343         | 360         | 73                       | 18                                    | 8.19                     |
| 0.5Fe      | 300         | 390         | 435         | 86                       | 31                                    | 8.28                     |
| 1Fe        | 330         | 499         | 538         | 169                      | NA                                    | 8.35                     |
| Prepared in alumina crucible |

One should notice that the 0Mg/Al and 0Fe glasses exhibit different thermal properties, although these glasses have the same composition (75NaPO₃-25CaF₂, in mol%). Their different thermal properties can be related to the crucibles used for the glass melting. Indeed, 1 mol% of Al₂O₃ is expected in the Fe glasses due to the contamination from the alumina crucible occurring during the glass melting, as confirmed using SEM coupled with EDS. This confirms the increase in the thermal properties of the glass due to the addition of Al₂O₃ in the NaPO₃-CaF₂ system.

In order to understand the different thermal properties of the investigated glasses, their structure was investigated using FTIR. The normalized IR spectra of the glasses are presented in Figure 1.

The IR spectra are similar to those reported in [14,23] and a detailed attribution of the IR bands can be found in [24]. In summary, the progressive decrease in the intensity of the bands at 700, 950, ~1000 and 1250 associated with the slight increase in the intensity of the shoulder at 1100 cm⁻¹ as compared to the main band can be seen when x increases in the 3 glass systems. These changes indicate that the progressive addition of MgO, Al₂O₃ and Fe₂O₃ leads to a depolymerization of the glass network associated with an increase in the Q¹ units and a decrease in the Q² units, the Q¹ and Q² units being units with 1 and 2 bridging oxygens per tetrahedron, respectively. P-O-Fe/Al/Mg bonds are also expected to form at the expense of P-O-P bonds, as suggested in [14,23]. Therefore, the addition of MgO, Al₂O₃ and Fe₂O₃ is expected to lead to the distortion and compaction of the glass network. These changes in the glass structure associated with the progressive addition of MgO, Al₂O₃ and Fe₂O₃ are in agreement with the increase in Tₙ and also in the thermal stability of the glasses. Similar impact of the addition of Al₂O₃ and Fe₂O₃ on the structure and thermal stability of phosphate glasses were reported in [23,25]. One can notice that the changes in the IR spectra are more distinct when adding Fe₂O₃ than when adding...
MgO or Al$_2$O$_3$ in the network probably due to the Al contamination from the crucible as discussed earlier. Additionally, one should also mention that the structure of the Fe glasses is expected to be more polymerized compared to the other glasses, due to the fact that the Fe$^{3+}$ ions could crosslink three oxygen more than that bonded to Mg$^{2+}$ as reported in [26].

Despite the fact that the changes in the glass composition have a noticeable impact on the structure, the glasses exhibit similar absorption and cross-sections at 975 nm and 1.5µm, measured at $\sim 2.01 \times 10^{-21}$ cm$^2$ and $6.32 \times 10^{-21}$ cm$^2$, respectively, indicating that the site of the Er$^{3+}$ ions is similar in all the investigated glasses. Thus, Al, Mg and Fe are not expected to be in the shell of Er$^{3+}$ ions although they clearly have an impact on the phosphate network.

The glasses were heat-treated at ($T_g$ + 20 °C) for 17 h and at their respective $T_p$ for 1 h as performed in [14]. All the investigated glasses became translucent after heat-treatment. They look similar to those reported in [14]. The decrease in the transmittance was evidenced by the decrease in the transmittance of the heat-treated glasses (Figure 2).

The decrease in the transmittance property after heat-treatment can be related to the precipitation of crystals occurring during the heat-treatment, which was confirmed by
measuring the XRD pattern of the glasses after heat-treatment. The XRD patterns of the heat-treated glasses, in Figure 3, exhibit peaks confirming the precipitation of crystals during heat-treatment.

**Figure 2.** Transmittance spectrum of the as-prepared 1.5 Mg glass taken as an example as all the as-prepared glasses exhibit similar transmittance spectra (solid line) and of some heat-treated (HT) glasses (dashed line).

Although CaF$_2$ crystals (ICDD PDF #00-035-0816) were found in all the glasses, other crystals such as NaPO$_3$ (ICDD PDF#04-011-3120) and Na$_2$Ca$_2$(P$_2$O$_7$)F$_2$ (ICDD PDF#04-012-1844) were detected in the XRD pattern of the Al glasses and also in the XRD pattern of the Mg glasses with x > 1.5mol%. Ca$_2$P$_2$O$_7$ crystals (ICDD PDF #00-009-0345) are also suspected in the heat-treated 1Fe glass. Thus, it is shown here that the progressive addition of MgO, Al$_2$O$_3$ and Fe$_2$O$_3$ promotes the precipitation of new crystals at the expense of CaF$_2$ during heat-treatment. The precipitation of these new crystals is thought to be due to the distortion and compaction of the glass network induced by the addition of MgO, Al$_2$O$_3$ and Fe$_2$O$_3$ as discussed earlier. The size of the crystallites size was determined by XRD using the following Scherrer’s equation [27]:

$$D = \frac{K\lambda}{\beta\cos\theta}$$

where K = 0.9 is the numerical factor, $\lambda = 0.154056$ nm represents the wavelength of the X-ray (Cu K$_\alpha$ radiation), $\beta$ is the full width at half maximum of the X-ray diffraction peak in radians and $\theta$ is the Bragg angle. Here, the strongest diffraction peak at $2\theta = 47^\circ$, which corresponds to the (220) crystal planes, was used for the calculation.

As shown in Table 2, the crystallites grow in size as the concentration of MgO, Al$_2$O$_3$ and Fe$_2$O$_3$ increases, which is in agreement with the decrease in the transmittance observed after heat-treatment (Figure 2). Similar growth of the crystallite size was reported when adding 1.5mol% of TiO$_2$, ZnO and MgO in the base glass [14]. One should mention that the crystal volume fraction in all the heat-treated glasses—which is estimated from the ratio of integrating area of the peaks to total integrated area of the XRD patterns as in [28]—is about (3.5 ± 0.1)%, indicating that the decrease in the transmittance of the Mg, Al and Fe glasses after heat-treatment can be related to the precipitation of different crystals and also to the precipitation of large crystals which cause strong light scattering.

The upconversion spectra of the glasses were measured prior to and after heat-treatment and are depicted in Figure 4.
Although CaF\(_2\) crystals (ICDD PDF #00-035-0816) were found in all the glasses, other crystals such as NaPO\(_3\) (ICDD PDF#04-011-3120) and Na\(_2\)Ca\(_2\)(P\(_2\)O\(_7\))F\(_2\) (ICDD PDF#04-012-1844) were detected in the XRD pattern of the Al glasses and also in the XRD pattern of the Mg glasses with \(x > 1.5\)mol%. Ca\(_2\)P\(_2\)O\(_7\) crystals (ICDD PDF #00-009-0345) are also suspected in the heat-treated Fe glass. Thus, it is shown here that the progressive addition of MgO, Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) promotes the precipitation of new crystals at the expense of CaF\(_2\) during heat-treatment. The precipitation of these new crystals is thought to be due to the distortion and compaction of the glass network induced by the addition of MgO, Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) as discussed earlier. The size of the crystallites size was determined by XRD using the following Scherrer’s equation [27]:

\[
\text{D} = \frac{K \lambda}{\beta \cos \theta}
\]

where \(D\) is the crystallite size, \(K\) is a shape factor (usually taken as 0.9), \(\lambda\) is the wavelength of the X-ray (1.54 Å for Cu K\(_\alpha\)), \(\beta\) is the full width at half maximum (FWHM) of the peak in radians, and \(\theta\) is the Bragg angle.

Figure 3. XRD spectra of the investigated glasses heat-treated at \((T_g + 20 \, ^\circ\text{C})\) for 17h and at \(T_p\) for 1h Mg (a) Al (b) and Fe (c) [Peaks correspond to * CaF\(_2\) (ICDD PDF #00-035-0816), + NaPO\(_3\) (ICDD PDF#04-011-3120), x Na\(_2\)Ca\(_2\)(P\(_2\)O\(_7\))F\(_2\) (ICDD PDF#04-012-1844), o Ca\(_2\)P\(_2\)O\(_7\) (ICDD PDF #00-009-0345)].

The spectra exhibit green and red emission bands which correspond to \(^2\text{H}_{11/2}\) (525 nm) \(^4\text{S}_{3/2}\) (550 nm) \(\rightarrow ^4\text{I}_{15/2}\) and \(^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}\) transitions of Er\(^{3+}\), respectively [29]. The heat-treatment increases significantly the intensity of the visible emission confirming the presence of Er\(^{3+}\) ions in the CaF\(_2\) crystals as explained in [14,30]. However, the increase in the intensity of the upconversion after heat-treatment depends on the glass composition: the newly heat-treated glasses exhibit lower intensity of upconversion than the heat-treated 0Mg/Al glass. Thus, it is clearly shown that the progressive precipitation of the NaPO\(_3\), Na\(_2\)Ca\(_2\)(P\(_2\)O\(_7\))F\(_2\) and/or Ca\(_2\)P\(_2\)O\(_7\) crystals at the expense of CaF\(_2\) crystals as \(x\) increases leads to lower intensity of upconversion.

Although the 0Mg/Al and 0Fe glass are similar in composition, the heat-treated 0Fe glass exhibits lower intensity of upconversion confirming that the addition of Al\(_2\)O\(_3\) in the
NaPO$_3$-CaF$_2$ glass, due to the contamination from the alumina crucible discussed earlier, limits the precipitation of CaF$_2$ crystals during the heat-treatment and so the increase in intensity of the upconversion.

\[ D = \frac{K \lambda}{\beta \cos \theta} \]

where $K = 0.9$ is the numerical factor, $\lambda = 0.154056$ nm represents the wavelength of the X-ray (Cu K$_{\alpha}$ radiation), $\beta$ is the full width at half maximum of the X-ray diffraction peak in radians and $\theta$ is the Bragg angle. Here, the strongest diffraction peak at $2\theta = 47^\circ$, which corresponds to the (220) crystal planes, was used for the calculation.

As shown in Table 2, the crystallites grow in size as the concentration of MgO, Al$_2$O$_3$ and Fe$_2$O$_3$ increases, which is in agreement with the decrease in the transmittance observed after heat-treatment (Figure 2). Similar growth of the crystallite size was reported when adding 1.5mol% of TiO$_2$, ZnO and MgO in the base glass [14]. One should mention that the crystal volume fraction in all the heat-treated glasses—which is estimated from the ratio of integrating area of the peaks to total integrated area of the XRD patterns as in [28]—is about $(3.5 \pm 0.1)$%, indicating that the decrease in the transmittance of the Mg, Al and Fe glasses after heat-treatment can be related to the precipitation of different crystals and also to the precipitation of large crystals which cause strong light scattering.

The upconversion spectra of the glasses were measured prior to and after heat-treatment and are depicted in Figure 4.

As the newly developed glasses exhibit lower intensity of upconversion than the 0Mg/Al glass after heat treatment, glasses were prepared with a larger amount of Er$^{3+}$ ions, as it is well known that heavy Er$^{3+}$-doping in glass leads to clustering of Er$^{3+}$ ions and so to cooperative upconversion [31]. As shown in Table 3, an increase in the number of Er$^{3+}$ ions increases the $T_g$, $T_x$ and $T_p$ and also the thermal stability of the glasses, suggesting that the Er$^{3+}$ ions also strengthen the glass structure. Similar results were also reported in [32]. Surprisingly, the ErF$_3$ glasses are more thermally stable than the Er$_2$O$_3$ glasses when prepared with the same amount of Er$^{3+}$ ions. As suggested by [33], strong bonding of Er$^{3+}$ ions with non-bringing oxygens is thus expected in the ErF$_3$ glasses, increasing the rigidity of the network.

In order to understand the impact of the raw material on the thermal properties of the glasses, the IR spectra of the Er$_2$O$_3$ and ErF$_3$ glasses were measured and compared. As depicted in Figure 5, the progressive addition of Er$^{3+}$ ions in the glass leads to similar changes in the IR spectra than those observed in Figure 1—indicating that as for Al, Mg and Fe, the addition of Er$^{3+}$ ions leads to the depolymerization of the phosphate network.
Thus, the Er\textsuperscript{3+} ions are suspected to act as modifier, breaking the P-O-P bands to form P-O\textsuperscript{2-}.Er\textsuperscript{3+} ionic linkages between the PO\textsubscript{4} units increasing \( T_g \) as suggested in [34].

**Table 3.** Thermal properties of the investigated glasses (NA: the peak intensity is too small to estimate the size of the crystallites). Note that the 0Mg/Al corresponds to 0.25Er\textsubscript{2}O\textsubscript{3} glass.

| Glass Code | \( T_g \) ± 3 (°C) | \( T_x \) ± 3 (°C) | \( T_p \) ± 3 (°C) | \( \Delta T = T_x - T_g \) ± 6 (°C) | Mean Size of the Crystallites (nm) | Er\textsuperscript{3+} Ions/cm\textsuperscript{3} (10\textsuperscript{19}) ± 5% |
|------------|-------------------|-------------------|-------------------|---------------------|---------------------|---------------------|
| 0Mg/Al     | 269               | 323               | 338               | 54                  | 17                  | 8.19                |
| 1Er\textsubscript{2}O\textsubscript{3} | 281               | 357               | 376               | 76                  | 26                  | 33.02               |
| 2Er\textsubscript{2}O\textsubscript{3} | 289               | 375               | 415               | 86                  | 37                  | 65.84               |
| 3Er\textsubscript{2}O\textsubscript{3} | 298               | 384               | 466               | 86                  | NA                  | 99.52               |
| 0.5Er\textsubscript{3}F\textsubscript{3} | 266               | 337               | 352               | 71                  | 17                  | 8.29                |
| 2 Er\textsubscript{3}F\textsubscript{3} | 267               | 354               | 368               | 87                  | 28                  | 32.99               |
| 4 Er\textsubscript{3}F\textsubscript{3} | 286               | 382               | 408               | 96                  | 33                  | 66.95               |
| 6 Er\textsubscript{3}F\textsubscript{3} | 296               | 396               | 456               | 100                 | NA                  | 101.43              |

**Figure 5.** Normalized IR spectra of the investigated Er\textsubscript{3}F\textsubscript{3} (a) and Er\textsubscript{2}O\textsubscript{3} (b) glasses. Note that the 0Mg/Al corresponds to 0.25Er\textsubscript{2}O\textsubscript{3} glass.

It is interesting to point out that the intensity of the bands at 880 and \( \sim 965 \) cm\textsuperscript{-1} is lower when using Er\textsubscript{3}F\textsubscript{3} than Er\textsubscript{2}O\textsubscript{3}, indicating that (1) the network of the Er\textsubscript{3}F\textsubscript{3} glasses contains a lower amount of Q\textsuperscript{2} units than the network of the Er\textsubscript{2}O\textsubscript{3} glasses which is also evidenced by the position of the band at \( \sim 1100 \) cm\textsuperscript{-1} being shifted to lower wavenumber in the spectra of the Er\textsubscript{3}F\textsubscript{3} glasses and (2) the long chain structure of the phosphate network is cut to smaller rings in the Er\textsubscript{3}F\textsubscript{3} glasses. Similar changes in the structure were reported in [24,35] when replacing CaO by CaF\textsubscript{2} in the NaPO\textsubscript{3}-CaO-CaF\textsubscript{2} network. It is possible to think that the Er\textsubscript{3}F\textsubscript{3} glasses are more thermally stable than the Er\textsubscript{2}O\textsubscript{3} glasses as their network is more depolymerized and contains a larger number of small rings.

As shown in Figure 6, the Er\textsubscript{3}F\textsubscript{3} and Er\textsubscript{2}O\textsubscript{3} raw materials have a similar impact on the crystallization properties of the glasses; CaF\textsubscript{2}, NaPO\textsubscript{3} and Na\textsubscript{2}Ca\textsubscript{2}(P\textsubscript{2}O\textsubscript{7})F\textsubscript{2} crystals were found in the highly Er\textsuperscript{3+} concentrated glasses after heat-treatment. The crystallites have similar sizes in the Er\textsubscript{3}F\textsubscript{3} and Er\textsubscript{2}O\textsubscript{3} glasses when prepared with the same amount of Er\textsuperscript{3+} ions (Table 3).
Ceramics 2021, 4

As expected, an increase in the number of Er$^{3+}$ ions in the ErF$_3$ and Er$_2$O$_3$ glasses increases significantly the intensity of the upconversion as depicted in Figure 7.

Interestingly, the intensity ratio of the red to green emissions increases with an increase in the concentration of Er$^{3+}$ ions. This can be due to the reduction in the distance between Er$^{3+}$ ions located in the CaF$_2$ nanocrystals. Indeed, the interionic interactions are favored when the concentration of the Er$^{3+}$ ions increases resulting in an efficient cross-relaxation process between erbium–erbium pairs [36]. With increasing the content of Er$^{3+}$ into the crystals, the cross-relaxation probability gives rise to the populating of the $^4F_{9/2}$ level,
increasing the intensity ratio of the red emission over the green one. Similar results were reported by Chen et al. [36]. It is clearly shown that the optimum amount of Er$^{3+}$ ions for the preparation of glass with high intensity of visible upconversion seems to be between $66 \times 10^{19}$ and $100 \times 10^{19}$ Er$^{3+}$ ions/cm$^3$ in both glass systems. Finally, it is interesting to point out that the 3Er$_2$O$_3$ glass exhibits slightly larger red and green emissions than the 6ErF$_3$ glass while having the same amount of Er$^{3+}$ ions. Thus, a larger number of Er$^{3+}$ ions is expected in the CaF$_2$ crystals precipitating in the 3Er$_2$O$_3$ glass than in the 6ErF$_3$ glass, probably due to the less strong bonding of Er$^{3+}$ ions with non-bridging oxygens in the Er$_2$O$_3$ glasses than in the ErF$_3$ glasses as discussed earlier.

4. Conclusions

To conclude, novel Er$^{3+}$ doped oxyfluorophosphate glasses in the NaPO$_3$-CaF$_2$ system were prepared with various amounts of MgO, Fe$_2$O$_3$, Al$_2$O$_3$, Er$_2$O$_3$ and ErF$_3$ in order to prepare thermally stable glasses which can be heat-treated into glass-ceramic with strong visible upconversion under 975 nm pumping. It is shown here that it is possible to tailor the glass composition to increase the thermal stability of the glass. However, due to changes in the glass structure, the tailoring of the glass composition has also a significant impact on the nucleation and growth and so on the intensity of the upconversion under 975 nm pumping. We demonstrate that it is possible to increase significantly the intensity of the green and red emissions by increasing the number of Er$^{3+}$ ions in the glass.

Author Contributions: L.P. and W.B. designed the study. L.D. prepared the Fe, Mg and Al containing glasses. N.O. prepared the Er containing glasses and performed all experimental study and wrote the manuscript. All authors have read and agreed to the published version of the manuscript.

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