

Article



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

Nirajan Ojha¹, Iuliia Dmitrieva¹, Wilfried Blanc² and Laeticia Petit^{1,*}

- ¹ Photonics Laboratory, Tampere University, Korkeakoulunkatu 3, FI-33720 Tampere, Finland; ojhanirajan@gmail.com (N.O.); jula2801@gmail.com (I.D.)
- ² Institut de Physique de Nice, UMR7010 CNRS, Université Côte d'Azur, Parc Valrose, CEDEX 2, 06018 Nice, France; wilfried.blanc@inphyni.cnrs.fr
- * Correspondence: laeticia.petit@tuni.fi

Abstract: Even though the (75 NaPO₃-25 CaF₂) (in mol%) glass can be heat-treated into transparent glass-ceramic with Er^{3+} 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 Er_2O_3 and ErF_3 . 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 Er^{3+} 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.



Citation: Ojha, N.; Dmitrieva, I.; Blanc, W.; Petit, L. Tailoring the Glass Composition to Increase the Thermal Stability without Impacting the Crystallization Behavior of Oxyfluorophosphate Glass. *Ceramics* 2021, *4*, 148–159. https://doi.org/ 10.3390/ceramics4020013

Academic Editors: Gilbert Fantozzi and Enrico Bernardo

Received: 15 March 2021 Accepted: 14 April 2021 Published: 16 April 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). 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)F₂ 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 CaF₂ 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 NaPO₃-CaF₂ system were successfully prepared with enhanced upconversion properties compared to the base glasses, due to the volume precipitation of Er^{3+} doped CaF₂ 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 NaPO₃-CaF₂ 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 NaPO₃-CaF₂ 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) (75NaPO₃-25CaF₂) - x (MgO /Al₂O₃ / Fe₂O₃)-0.25Er₂O₃ (in mol%) with x ranging from 0 to 6 and (100- y) (75NaPO₃-25CaF₂) - y (Er₂O₃/ErF₃) (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 labeled 0Fe when prepared in alumina crucible. NaPO₃ (technical grade), CaF₂ (99%), ErF₃ (99.9%) Er₂O₃ (99.9%), MgO (≥99%), Fe₂O₃ (≥99%) and Al₂O₃ (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_x) 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.

Glass Code	NaPO ₃	CaF ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	Er ₂ O ₃	ErF ₃
0Mg/Al	74.8	24.9				0.25	
1.5Mg	73.7	24.6		1.50		0.25	
3Mg	72.6	24.2		3.00		0.25	
4.5Mg	71.4	23.8		4.50		0.25	
6Mg	70.3	23.4		6.00		0.25	
0.5A1	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	
1Er ₂ O ₃	74.3	24.8				1.00	
$2Er_2O_3$	73.5	24.5				2.00	
3Er ₂ O ₃	72.8	24.2				3.00	
0.5ErF ₃	74.6	24.9					0.5
2ErF ₃	73.5	24.5					2.0
4ErF ₃	72.0	24.0					4.0
6ErF ₃	70.5	23.5					6.0
0Fe	74.8	24.9				0.25	
0.5Fe	74.4	24.8			0.5	0.25	
1Fe	74.1	24.7			1.0	0.25	

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

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-K_{α} 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 (λ_{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 Messtechnik 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 Er^{3+} 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 Al_2O_3 and Fe_2O_3 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 T_g, T_x and T_p—and more importantly to increase ΔT ($\Delta T = T_x - T_g$), 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).

		Thern	nal Properti	es	Maan Siza of the Crystallites	E-3+ 13 (1019)		
Glass Code	Т _g ±3 (°С)	T _x ±3 (°C)	Т _р ±3 (°С)	$\Delta T = T_x - T_g \\ \pm 6 (^{\circ}C)$	± 2 (nm)	$\pm 5\%$		
Prepared in Pt cucible								
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		
0.5A1	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 alumina 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		

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 are in agreement with the increase in T_g 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



Figure 1. Normalized IR spectra of the investigated Mg (**a**) Al (**b**) and Fe (**c**) glasses. The spectra are normalized to the maximum band at 1100 cm^{-1} .

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 1.5μ m, measured at ~2.01 × 10⁻²¹ cm² and $6.32 × 10^{-21}$ cm², respectively, indicating that the site of the Er³⁺ ions is similar in all the investigated glasses. Thus, Al, Mg and Fe are not expected to be in the shell of Er³⁺ 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 CaF₂ crystals (ICDD PDF #00-035-0816) were found in all the glasses, other crystals such as NaPO₃ (ICDD PDF#04-011-3120) and Na₂Ca₂(P₂O₇)F₂ (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%. Ca₂P₂O₇ 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, Al₂O₃ and Fe₂O₃ promotes the precipitation of new crystals at the expense of CaF₂ 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, Al₂O₃ and Fe₂O₃ as discussed earlier. The size of the crystallites size was determined by XRD using the following Scherrer's equation [27]:

$$D = K\lambda/\beta\cos\theta \tag{1}$$

where K = 0.9 is the numerical factor, $\lambda = 0.154056$ nm represents the wavelength of the X-ray (Cu K_{\alpha} radiation), β is the full width at half maximum of the X-ray diffraction peak in radians and θ 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.

1

As shown in Table 2, the crystallites grow in size as the concentration of MgO, Al₂O₃ and Fe₂O₃ 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 TiO₂, 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 heattreatment and are depicted in Figure 4.



Figure 3. XRD spectra of the investigated glasses heat-treated at ($T_g + 20$ °C) for 17h and at T_p for 1h Mg (**a**) Al (**b**) and Fe (**c**) [Peaks correspond to * CaF₂ (ICDD PDF #00-035-0816), + NaPO₃ (ICDD PDF#04-011-3120), x Na₂Ca₂(P₂O₇)F₂ (ICDD PDF#04-012-1844), o Ca₂P₂O₇ (ICDD PDF #00-009-0345)].

The spectra exhibit green and red emission bands which correspond to ${}^{2}H_{11/2}$ (525 nm) ${}^{4}S_{3/2}$ (550 nm) $\rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ 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 CaF₂ 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 NaPO₃, Na₂Ca₂(P₂O₇)F₂ and/or Ca₂P₂O₇ crystals at the expense of CaF₂ 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_2O_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.



Figure 4. Upconversion spectra of the Mg (**a**) Al (**b**) and Fe (**c**) glasses measured prior to (solid line) and after heat-treatment at (T_g + 20 °C) for 17 h and at T_p 1 h (bold line) (λ_{exc} = 975 nm).

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_2O_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_2O_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^{3+} ions are suspected to act as modifier, breaking the P-O-P bands to form P-O⁻. Er^{3+} ionic linkages between the PO₄ 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 $0.25Er_2O_3$ glass.

Glass Code	Thermal Properties				Moon Size of the Crystallites	E-3+ I3 (10 ¹⁹)
	Т _g ±3 (°С)	T _x ±3 (°C)	Т _р ±3 (°С)	$\begin{array}{c} \Delta T = T_x - T_g \\ \pm 6 \ (^{\circ}C) \end{array}$	(nm)	±5%
0Mg/Al	269	323	338	54	17	8.19
$1Er_2O_3$	281	357	376	76	26	33.02
$2Er_2O_3$	289	375	415	86	37	65.84
$3Er_2O_3$	298	384	466	86	NA	99.52
0.5ErF ₃	266	337	352	71	17	8.29
2 ErF_3	267	354	368	87	28	32.99
4 ErF ₃	286	382	408	96	33	66.95
6 ErF ₃	296	396	456	100	NA	101.43



Figure 5. Normalized IR spectra of the investigated ErF_3 (**a**) and Er_2O_3 (**b**) glasses. Note that the 0Mg/Al corresponds to 0.25Er₂O₃ glass.

It is interesting to point out that the intensity of the bands at 880 and ~965 cm⁻¹ is lower when using ErF_3 than Er_2O_3 , indicating that (1) the network of the ErF_3 glasses contains a lower amount of Q² units than the network of the Er_2O_3 glasses which is also evidenced by the position of the band at ~1100 cm⁻¹ being shifted to lower wavenumber in the spectra of the ErF_3 glasses and (2) the long chain structure of the phosphate network is cut to smaller rings in the ErF_3 glasses. Similar changes in the structure were reported in [24,35] when replacing CaO by CaF₂ in the NaPO₃-CaO-CaF₂ network. It is possible to think that the ErF_3 glasses are more thermally stable than the Er_2O_3 glasses as their network is more depolymerized and contains a larger number of small rings.

As shown in Figure 6, the ErF_3 and Er_2O_3 raw materials have a similar impact on the crystallization properties of the glasses; CaF_2 , $NaPO_3$ and $Na_2Ca_2(P_2O_7)F_2$ crystals were found in the highly Er^{3+} concentrated glasses after heat-treatment. The crystallites have similar sizes in the ErF_3 and Er_2O_3 glasses when prepared with the same amount of Er^{3+} ions (Table 3).



Figure 6. XRD spectra of the glasses prepared with ErF_3 (**a**) and Er_2O_3 (**b**) after heat-treatment (Tg + 20 °C) for 17 h and at T_p for 1 h (λ_{exc} = 975 nm) [Peaks correspond to * CaF₂ (ICDD PDF #00-035-0816), +NaPO₃ (ICDD PDF#04-011-3120), x Na₂Ca₂(P₂O₇) F₂ (ICDD PDF#04-012-1844), o Ca₂P₂O₇ (ICDD PDF #00-009-0345)]. Note that the 0Mg/Al corresponds to 0.25Er₂O₃ glass.





Figure 7. Upconversion spectra of the glasses prepared with ErF_3 (**a**) and Er_2O_3 (**b**) after heat-treatment at (T_g + 20 °C) for 17 h and at T_p for 1 h (λ_{exc} = 975 nm). Note that the 0Mg/Al corresponds to 0.25Er₂O₃ glass.

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 CaF₂ 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 ${}^{4}F_{9/2}$ 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 $\sim 66 \times 10^{19}$ and $100 \times 10^{19} Er^{3+}$ ions/cm³ in both glass systems. Finally, it is interesting to point out that the $3Er_2O_3$ 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 $3Er_2O_3$ glass than in the $6ErF_3$ glass, probably due to the less strong bonding of Er^{3+} ions with non-bringing oxygens in the Er_2O_3 glasses than in the ErF_3 glasses as discussed earlier.

4. Conclusions

To conclude, novel Er^{3+} doped oxyfluorophosphate glasses in the NaPO₃-CaF₂ system were prepared with various amounts of MgO, Fe₂O₃, Al₂O₃, Er₂O₃ and ErF₃ 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. I.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.

Funding: Academy of Finland (Flagship Programme, Photonics Research and Innovation PREIN-320165 and Academy Project -326418) is greatly acknowledged for the financial support.

Acknowledgments: This work made use of Tampere Microscopy Center facilities at Tampere University.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Boetti, N.G.; Scarpignato, G.C.; Lousteau, J.; Pugliese, D.; Bastard, L.; Broquin, J.-E.; Milanese, D. High concentration Yb-Er co-doped phosphate glass for optical fiber amplification. *J. Opt.* **2015**, *17*, 65705. [CrossRef]
- Bunker, B.C.; Arnold, G.W.; Wilder, J.A. Phosphate glass dissolution in aqueous solutions. J. Non Cryst. Solids. 1984, 64, 291–316. [CrossRef]
- 3. Gonçalves, M.C.; Santos, L.F.; Almeida, R.M. Rare-earth-doped transparent glass ceramics. *Comptes Rendus Chim.* 2002, *5*, 845–854. [CrossRef]
- 4. De Pablos-Martín, A.; Durán, A.; Pascual, M.J. Nanocrystallisation in oxyfluoride systems: Mechanisms of crystallisation and photonic properties. *Int. Mater. Rev.* 2012, *57*, 165–186. [CrossRef]
- 5. Zanotto, E.D. A bright future for glass-ceramics. *Am. Ceram. Soc. Bull.* 2010, 89, 19–27.
- 6. Shang, F.; Chen, Y.; Xu, J.; Yang, T.; Yang, Y.; Chen, G. Up-conversion luminescence and highly sensing characteristics of Er³⁺/Yb³⁺ co-doped borophosphate glass-ceramics. *Opt. Commun.* **2019**, *441*, 38–44. [CrossRef]
- Saad, M.; Elhouichet, H. Good optical performances of Eu³⁺/Dy³⁺/Ag nanoparticles co-doped phosphate glasses induced by plasmonic effects. *J. Alloys Compd.* 2019, 806, 1403–1409. [CrossRef]
- 8. Wang, Y.; Ohwaki, J. New transparent vitroceramics codoped with Er³⁺ and Yb³⁺ for efficient frequency upconversion. *Appl. Phys. Lett.* **1993**, *63*, 3268–3270. [CrossRef]
- Qiao, X.; Fan, X.; Wang, J.; Wang, M. Luminescence behavior of Er³⁺ ions in glass–ceramics containing CaF₂ nanocrystals. *J. Non Cryst. Solids* 2005, 351, 357–363. [CrossRef]
- 10. Kang, S.; Xiao, X.; Pan, Q.; Chen, D.; Qiu, J.; Dong, G. Spectroscopic properties in Er³⁺-doped germanotellurite glasses and glass ceramics for mid-infrared laser materials. *Sci. Rep.* **2017**, *7*, 43186. [CrossRef] [PubMed]
- 11. Ren, J.; Lu, X.; Lin, C.; Jain, R.K. Luminescent ion-doped transparent glass ceramics for mid-infrared light sources. *Opt. Express* **2020**, *28*, 21522–21548. [CrossRef] [PubMed]
- Xing, Z.; Gao, S.; Liu, X.; Sun, S.; Yu, C.; Xiong, L.; Li, K.; Liao, M. Study on the structure, mechanical properties, and 2-μm fluorescence of Ho³⁺-doped transparent TeO₂-based glass–ceramics. *J. Alloys Compd.* **2016**, *660*, 375–381. [CrossRef]
- Liu, X.; Zhou, J.; Zhou, S.; Yue, Y.; Qiu, J. Transparent glass-ceramics functionalized by dispersed crystals. *Prog. Mater. Sci.* 2018, 97, 38–96. [CrossRef]

- 14. Ojha, N.; Szczodra, A.; Boetti, N.G.; Massera, J.; Petit, L. Nucleation and growth behavior of Er³⁺ doped oxyfluorophosphate glasses. *RSC Adv.* **2020**, *10*, 25703–25716. [CrossRef]
- 15. Stolov, A.; Simoff, D.A.; Li, J. Thermal Stability of Specialty Optical Fibers. J. Light. Technol. 2008, 26, 3443–3451. [CrossRef]
- 16. Donald, I.W.; Metcalfe, B.L.; Taylor, R.N.J. The immobilization of high level radioactive wastes using ceramics and glasses. *J. Mater. Sci.* **1997**, *32*, 5851–5887. [CrossRef]
- 17. Donald, I.W. Preparation, properties and chemistry of glass- and glass-ceramic-to-metal seals and coatings. *J. Mater. Sci.* **1993**, *28*, 2841–2886. [CrossRef]
- 18. Wei, T.Y.; Hu, Y.; Hwa, L.G. Structure and elastic properties of low-temperature sealing phosphate glasses. *J. Non Cryst. Solids* **2001**, *288*, 140–147. [CrossRef]
- 19. De Wild, J.; Meijerink, A.; Rath, J.K.; van Sark, W.G.J.H.M.; Schropp, R.E.I. Upconverter solar cells: Materials and applications. *Energy Environ. Sci.* 2011, *4*, 4835–4848. [CrossRef]
- Van Sark, W.G.; de Wild, J.; Rath, J.K.; Meijerink, A.; Schropp, R.E.I. Upconversion in solar cells. *Nanoscale Res. Lett.* 2013, 8, 81. [CrossRef]
- Bingham, P.A.; Hand, R.J.; Forder, S.D. Doping of iron phosphate glasses with Al₂O₃, SiO₂ or B₂O₃ for improved thermal stability. *Mater. Res. Bull.* 2006, 41, 1622–1630. [CrossRef]
- Marasinghe, G.K.; Karabulut, M.; Ray, C.S.; Day, D.E.; Allen, P.G.; Bucher, J.J.; Shuh, D.K.; Badyal, Y.; Saboungi, M.L.; Grimsditch, M.; et al. Environment Issues and Waste Management Technologies IV (special issue). *Ceram. Trans.* 1999, 93, 195.
- Zhang, L.; Ghussn, L.; Schmitt, M.L.; Zanotto, E.D.; Brow, R.K.; Schlesinger, M.E. Thermal stability of glasses from the Fe₄(P₂O₇)₃– Fe(PO₃)₃ system. J. Non Cryst. Solids 2010, 356, 2965–2968. [CrossRef]
- 24. Cui, S.; Massera, J.; Lastusaari, M.; Hupa, L.; Petit, L. Novel fluorophosphates glasses and glass-ceramics. *J. Non Cryst. Solids* **2016**, 445, 40–44. [CrossRef]
- 25. Takebe, H.; Suzuki, Y.; Uemura, T. The effects of B₂O₃ and Al₂O₃ additions on the structure of phosphate glasses. *Phys. Chem. Glas. Eur. J. Glas. Sci. Technol. Part B* **2014**, *55*, 207–210.
- 26. Raguenet, B.; Tricot, G.; Silly, G.; Ribes, M.; Pradel, A. The mixed glass former effect in twin-roller quenched lithium borophosphate glasses. *Solid State Ionics* **2012**, *208*, 25–30. [CrossRef]
- 27. Holzwarth, U.; Gibson, N. The Scherrer equation versus the "Debye-Scherrer equation". *Nat. Nanotechnol.* **2011**, *6*, 534. [CrossRef] [PubMed]
- 28. Li, X.; Xu, D.; Liu, X.; Guo, H. Dual valence Eu-doped phospho-alumino-silicate glass-ceramics containing Ba₃AlO₃PO₄ nanocrystals for W-LEDs. *RSC Adv.* **2017**, *7*, 53839–53845. [CrossRef]
- 29. Auzel, F. Upconversion and Anti-Stokes Processes with f and d Ions in Solids. Chem. Rev. 2004, 104, 139–174. [CrossRef]
- 30. Szczodra, A.; Mardoukhi, A.; Hokka, M.; Boetti, N.G.; Petit, L. Fluorine losses in Er³⁺ oxyfluoride phosphate glasses and glass-ceramics. *J. Alloys Compd.* **2019**, *797*, 797–803. [CrossRef]
- 31. Seneschal, K.; Smektala, F.; Bureau, B.; Floch, M.L.; Jiang, S.; Luo, T.; Lucas, J.; Peyghambarian, N. Properties and Structure of High Erbium Doped Phosphate Glass for Short Optical Fibers Amplifiers. *Mater. Res. Bull.* **2005**, *40*, 1433–1442. [CrossRef]
- 32. Ersundu, A.E.; Karaduman, G.; Çelikbilek, M.; Solak, N.; Aydın, S. Effect of Rare-Earth Dopants on the Thermal Behavior of Tungsten Tellurite Glasses. *J. Alloys Compd.* 2010, 508, 266–272. [CrossRef]
- Nazabal, V.; Todoroki, S.; Nukui, A.; Matsumoto, T.; Suehara, S.; Hondo, T.; Araki, T.; Inoue, S.; Rivero, C.; Cardinal, T. Oxyfluoride tellurite glasses doped with erbium: Thermal analysis, structural organization and spectral properties. *J. Non Cryst. Solids* 2003, 325, 85–102. [CrossRef]
- 34. Shyu, J.-J.; Chiang, C.-C. Effects of Er₂O₃ Doping on the Structure, Thermal Properties, and Crystallization Behavior of SnO–P₂O₅ Glass. *J. Am. Ceram. Soc.* **2010**, *93*, 2720–2725. [CrossRef]
- 35. Nommeots-Nomm, A.; Boetti, N.G.; Salminen, T.; Massera, J.; Hokka, M.; Petit, L. Luminescence of Er³⁺ doped oxyfluoride phosphate glasses and glass-ceramics. *J. Alloys Compd.* **2018**, *751*, 224–230. [CrossRef]
- Chen, D.; Wang, Y.; Yu, Y.; Ma, E.; Bao, F.; Hu, Z.; Cheng, Y. Influences of Er³⁺ content on structure and upconversion emission of oxyfluoride glass ceramics containing CaF₂ nanocrystals. *Mater. Chem. Phys.* 2006, 95, 264–269. [CrossRef]