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Upconversion in low rare-earth concentrated phosphate glasses using direct $NaYF_4:Er^{3+}$, Yb^{3+} nanoparticles doping

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ABSTRACT

Upconversion (UC) was obtained from phosphate glasses which contain only 0.01 at.% of Er^{3+} and 0.06 at.% of Yb^{3+}. The glasses were prepared using direct doping method by adding $NaYF_4:Er^{3+}$, Yb^{3+} nanoparticles (NPs) into the glass at a doping temperature of 575 °C and 3 minute dwell time. The fraction of NP's survival during glass preparation can be augmented from 5 to 20% when replacing Na_2O by NaF in the glass. Our study suggests that the corrosion behavior of the glass melt is an important parameter to consider in order to engineer new NPs-containing glasses with high UC efficiency.

Er^{3+} and Yb^{3+} codoped glasses have attracted great interest in recent years because of their numerous applications as optical fibers, waveguide lasers and also as upconversion (UC) lasers which allow the conversion of NIR radiation usually to shorter wavelengths due to the absorption of two or more photons [1]. These types of lasers with strong UC can provide practical solutions for applications as diverse as solar cells, medical imaging, underwater surveillance and full colour all-solid state displays just to cite a few [2–4]. In Er^{3+}, Yb^{3+} codoped glasses, UC energy transfer involving the two distinct ions occurs leading to green and red emission.

The host matrix and the amount of rare-earth ions have a significant impact on the UC efficiency as UC depends largely on the energy level structure of RE ions and local environment [5]. Therefore, the choice of appropriate host matrix is crucial for efficient UC luminescence [6]. Silica glass, as a host material for fibers, has proven to be very attractive because it has a number of very favourable properties such as wide wavelength range with good optical transparency, high mechanical strength against pulling and bending as well as chemically stability. However, some potential applications of these glasses suffer from high melting temperature. Tellurite glasses are preferable due to their low phonon energy and excellent mechanical strength [7–8]. New tellurite glasses were successfully prepared with upconversion $LiYF_4$ nanocrystals via direct doping method with high UC luminescence efficiency [9]. However, as explained in [10], tellurium is potentially disruptive to the tellurite glass network in a corrosive environment and poses safety concerns for wide use of tellurite-based glass. The tellurium toxicity due to such possible leakage could then be an issue. Phosphate glasses could be alternative materials due to their *eco-friendly* compatibility [11]. However, these glasses have a large phonon energy, which is disadvantageous to the UC emission [12]. As phosphate glasses exhibit a very high solubility for rare earth ions, upconversion can be achieved in those glasses using high rare-earth concentrations (up to 4 mol% of Er_2O_3 and 20 mol% of Yb_2O_3 as reported in [13]).

Therefore, we investigate the possibility of integrating synthetized $NaYF_4:Er^{3+}$, Yb^{3+} nanocrystals into phosphate glasses to develop new soft upconverter glasses. In this letter, we demonstrate that upconversion can be obtained in phosphate glasses which contain a low doping level of Er^{3+} (0.01 at.%) and Yb^{3+}(0.06 at.%).

The glasses with the composition $(90NaPO_3 - (10 - x)Na_2O - xNaF)$ (mol%) with $x = 0$ and 10 were prepared using a standard melting process in a quartz crucible using $Na_6O_{18}P_6$ (Alfa-Aesar, technical grade), Na_2CO_3 (Sigma-Aldrich, >99.5%) and NaF (Sigma-Aldrich, 99.99%). Prior to the melting, the glass with $x = 0$ was treated at 400 °C for 30 min to decompose Na_2CO_3 and evaporate CO_2. After melting the glasses at 750 °C, 3.75 wt% of $NaYF_4:Er^{3+}$, Yb^{3+} was added at lower temperature and then the glass was poured onto a brass mold. Finally, the resulting glasses were annealed at 40 °C below the glass transition temperature for 8 h in air. The nanoparticles (NPs) under

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Table 1
Thermal properties of the investigated glasses.

x	T_g (°C) (±3 °C)	T_x (°C) (±3 °C)	$\Delta T = T_x - T_g$ (±6 °C)
0	284	374	90
10	246	356	110

investigation were $NaYF_4:Er^{3+}$, Yb^{3+}, the synthesis of which can be found in [14]. The nanoparticles were synthetized with 3 at.% Er^{3+} and 17 at.% Yb^{3+}.

Differential Thermal Analysis of the glasses was done using DTA, Netzch Jupiter F1 at a heating rate of 10 °C/min. The analysis was carried out in Pt crucibles. The glass transition temperature T_g was calculated as the inflection point of the endotherm obtained as the first derivative of the DTA curve. The onset of crystallization temperature T_x was ascertained from the beginning of the crystallization feature, and peak of the exotherm respectively. All the temperatures were obtained with an accuracy of ±3 °C.

The transmission spectra were recorded from polished glasses with a thickness of 3 mm in the range of 200–700 nm at room temperature, using an UV-3600 Plus UV–VIS-NIR Spectrophotometer Shimadzu.

A scanning electron microscope (Carl Zeiss Crossbeam 540) equipped with Oxford Instruments X-Max^N 80 EDS detector was used to image and analyze the composition of the samples. The polished glasses were coated with a thin carbon layer before EDS mapping. The accuracy of the elemental analysis was ±1.5 mol%.

The upconversion luminescence spectra were measured with an Avantes AvaSpec-2048 × 14 CCD spectrometer at room temperature. The materials were excited with an Optical Fiber Systems IFC-975-008 NIR laser (6 W; $\lambda_{exc} = 974$ nm). Emission was collected at a 90° angle to the excitation and directed to the detector with an optical fiber (diameter: 600 μm). In the excitation path, a long-pass filter with a cutoff at 900 nm (Edmund Optics) was used to ensure a pure NIR excitation. In the emission light path, 900 nm filter (Newport, 10SWF-900-B) was used to exclude the scattered excitation radiation.

As explained in [9], it is crucial to identify a suitable temperature for doping and dispersing the particles in the glass melt to succeed in doping the glasses homogenously with particles. The particles need to be, of course, thermally stable at this doping temperature to ensure the survival of the particles within the glass during the glass preparation. The nanoparticles of investigation were $NaYF_4:Er^{3+}$, Yb^{3+}, synthetized with 3 at.% Er^{3+} and 17 at.% Yb^{3+} as the evaporation of these particles and melting of NaF were reported in [14] to occur at 750 °C which appears to be the upper limit for the doping temperature.

Our first step was to identify a glass composition, the doping temperature of which could be lower than the particles upper limit of the doping temperature. Glasses with the composition $(90NaPO_3 - (10 - x)Na_2O - xNaF)$ (mol%) with x = 0 and 10 were chosen as the glass hosts for the particles addition because of their low melting temperature (750 °C) and their relative good thermal stability against crystallization as suspected from their value of ΔT ($\Delta T = T_x - T_g$) which is a gauge of the glass' resistance to crystallization (Table 1). Typically a ΔT value larger than 100 °C suggests reasonable

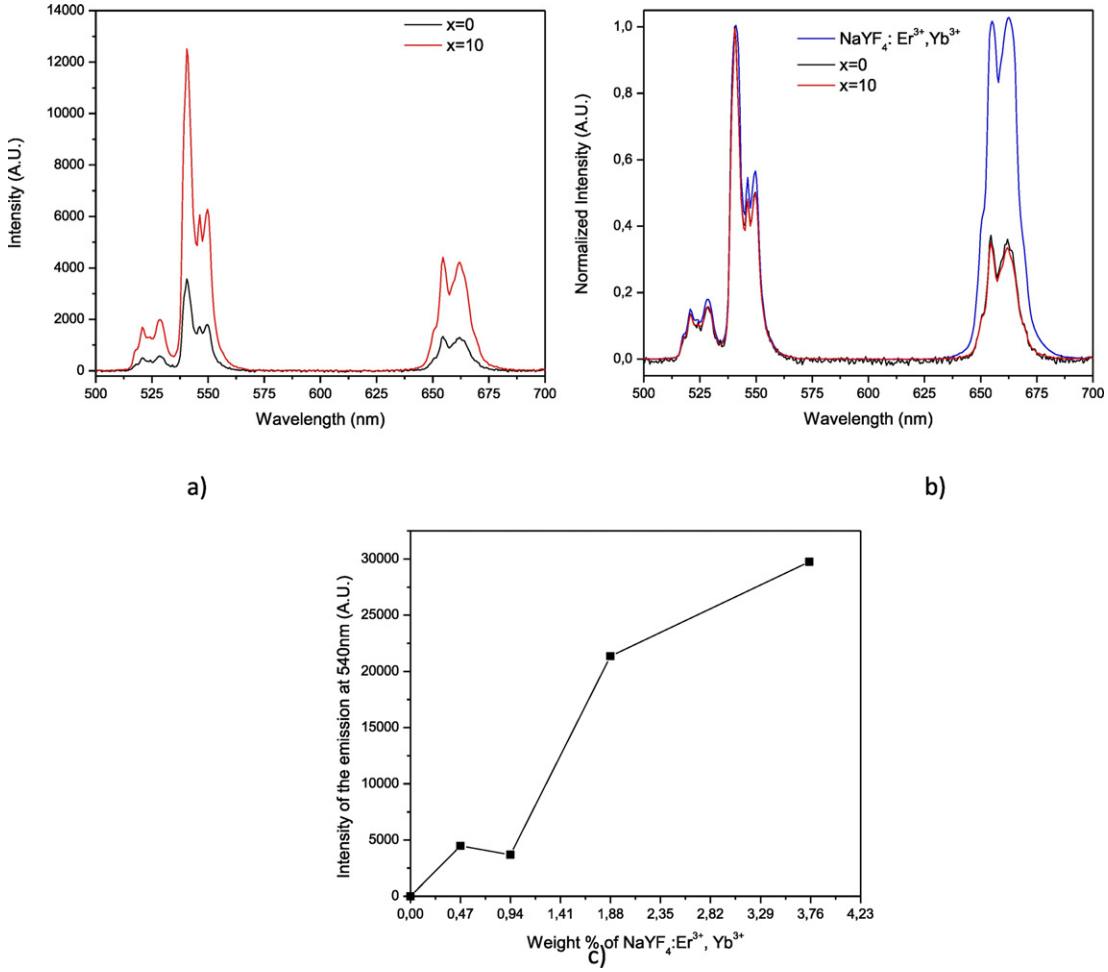

Fig. 1. Upconversion spectra of the NPs-containing glasses ($\lambda_{exc} = 974$ nm) (a), (b) normalized upconversion spectra of the NPs-containing glasses and of the $NaYF_4:Er^{3+}$, Yb^{3+} alone and (c) Intensity of the emission at 550 nm of samples with known amount of $NaYF_4:Er^{3+}$, Yb^{3+}.