Effect of heat-treatment on the upconversion of $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals containing silver phosphate glass

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Abstract

Novel $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals containing phosphate glasses with composition 83.25$NaPO_3$-9.25NaF-5ZnO-2.5Ag_2O (in mol%) were prepared by adding the $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals in the glass using the direct doping method. The optical and luminescence properties of this new glass are presented and discussed. The newly developed glass exhibit visible emission under 980nm pumping with high intensity confirming the presence of the $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals in the glass. From the absorption spectrum of the as-prepared glass, we showed that the as-prepared glasses contained already Ag nanoparticles which are thought to precipitate due to the decomposition of some of the $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals occurring during the glass preparation. A heat treatment of the glass was found to lead to the migration of Ag species at the surface of the glass as evidenced using SEM and to a decrease of the intensity of the upconversion mostly due to an increase of the inter defects in the $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals due to the heat treatment. '

Keywords: $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals, silver nanoparticles, phosphate glass, absorption, luminescence

Introduction

There has been significant research in the development of rare-earth (RE) doped glasses as these glasses can find potential applications in solar cells, color displays, high resolution sensing, biomedical imaging and bio-label to name few examples [1–6]. Unlike silica glass which possesses a 3D network, phosphate glasses can dissolve considerable amounts of alkaline earth, transition metal and rare earth ions due to their 2D network [7]. Additionally, phosphate glasses can be engineered with excellent transparency, low viscosity, high ultraviolet(UV) transmission and thermal stability [8]. However, some phosphate glasses possess low chemical durability and thermal stability which can be improved by adding elements such as MgO or ZnO [9,10].

Among the RE ions, Er^{3+} ions are one of the most studied RE ions since Er^{3+} ions can provide infrared-to-visible upconversion emissions as well as a C-broadband in the telecommunication range, supreme importance to fabricate optical fibers and amplifiers[11]. An enhancement of the emission properties due to Ag nanoparticles (NPs) was reported in Er^{3+} doped glasses and was related to an increase in the local incident field close to the optical center, an increase of intrinsic radiative decay rate and/or to fluorophore-metal resonance energy transfer[12]. Therefore, RE-doped glasses containing metallic NPs have gained attraction for the few past decades. Several methods to grow metallic NPs inside glass matrices have been intensively investigated, such as sol-gel[13], heat treatment [14–16], direct metal-ion implantation[17], sonochemical method[18], SILAR (successive ionic layer adsorption and reaction) technique[19] just to cite a few, the heat treatment method being the most used due to its simplicity and cost effectiveness. Basically, in the heat treatment method, the formation of Ag NPs consists of two-steps: first the metal ions are added inside the glass matrix and secondly post heat treatment is performed to form metal clusters aided by nucleation and growth.

Recently, Ag nanoparticles were successfully formed in glasses with the composition (87.3-x)NaPO$_3$-(9.7-x)NaF-xZnO-2.5Ag$_2$O-0.5Er$_2$O$_3$ with x = 0, 1.25, 2.5, and 5 (in mol%)[20] . The addition of ZnO was found to enhance the intensity of the emission at 1.5 µm and to promote the silver ions clustering ability when heat treating the glass leading to an increase in the intensity of the emission at 1.5 µm. However, we showed that the temperature of the heat treatment should be optimized to avoid the formation of an excessive amount of the Ag aggregates to avoid a decrease in the intensity of the emission at 1.5µm due to the energy transfer from the exited states of Er^{3+} to the silver NPs, as suggested in [21]

NaYF$_4$ crystal is considered to be one of the most efficient host lattices with low phonon energies (<350 cm^{-1}) to minimize energy losses at the intermediate states of lanthanide ions [22]. NaYF$_4$:Yb^{3+}, Er^{3+} nanocrystals containing phosphate glasses with the composition 90NaPO$_3$-xNaF-(10-x)Na$_2$O with x=0 and 10 (in mol%) were successfully prepared using the direct particles doping method [23]. The direct doping parameters such as the doping temperature (T$_{doping}$) and dwell time were optimized to balance the survival and dispersion of the nanocrystals in the glass. The strongest upconversion was obtained from the glass with x=10 prepared using a T$_{doping}$ of 550°C and a 3 min dwell time[24] .

In this paper, new NaYF$_4$:Yb^{3+}, Er^{3+} nanocrystals containing glass with the 83.25NaPO$_3$-9.25NaF-5ZnO-2.5Ag$_2$O (in mol%) were prepared using the direct doping method and heat treated in order to precipitate Ag nanoparticles in the glass in order to prepare new glasses with strong upconversion under 980nm pumping. At first, we present the optical and luminescence properties of the newly developed glass and discuss the impact of the direct doping process on the survival of NaYF$_4$:Yb^{3+}, Er^{3+} nanocrystals and on the formation of Ag nanoparticles in the as-prepared

glass. Then, we present results related to the impact of the heat treatment on the precipitation of Ag nanoparticles in the glass and on the intensity of the upconversion of the glass.

Experimental

Glasses with the composition $90NaPO_3$-$10NaF$ (in mol%) (label as 0Ag) and $83.25NaPO_3$-$9.25NaF$-$5ZnO$-$2.5Ag_2O$ (in mol%) (labeled as 2.5Ag) were prepared with $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals using the direct doping method. The raw materials were $Na_6O_{18}P_6$ (Alfa-Aesar, technical grade), NaF (Sigma-Aldrich, 99.99%), ZnO (Sigma-Aldrich, 99.50%) and Ag_2SO_4 (Sigma Aldrich, 99.99%). The preparation of the Ag0 glass can be found in [24]. The Ag2.5 glass was melted at 875°C for 5 minutes in a quartz crucible and the temperature of the glass melt was reduced to 550ºC prior to adding the $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals. The glass was quenched 3 min after adding the $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals and finally annealed at 40°C below its glass transition temperature in air for 8 hours. The $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystal were prepared by using the method described by Hyppänen *et al* [25].

The glass transition temperature (T_g) was determined by differential thermal analysis (DTA) (TA instruments SDT Q600) using heating rate of 10°C/min and platinum pans in N_2 atmosphere. The glass transition temperature was taken at the inflection point of the endotherm, as obtained by taking the minima of first derivative of the DTA curve. The accuracy of measurement was ± 3 °C.

The absorption spectra were measured in a polished sample of thickness 2mm using a UV-Vis-NIR spectrophotometer (UV-3600 Plus, Shimadzu) from 200 to 1800 nm with 0.5 nm interval.

The upconversion spectra were measured using a Spectro 320 optical spectrum analyzer (Instrument Systems Optische Messtechnik GmbH, Germany) at room temperature. The center

emission wavelength (λ_{exc}) of the laser was ~975 nm and its incident power at the sample surface was ~23.5 mW. The upconversion spectra of the investigated samples were collected from polished glasses with the same thickness (2mm) to allow the comparison of the emission intensity.

A FLS1000 Photoluminescence Spectrometer equipped with a xenon arc lamp and a PMT-900 detector was also used for the measurement of the emission spectra obtained using an excitation at 320nm.

A scanning electron microscope (Crossbeam 540, Carl Zeiss, Oberkochen, Germany) and an EDS detector (X-MaxN 80, Oxford Instruments, Abingdon-on-Thames, UK) was used to image and analyze the composition of the samples.

Results and discussion

The glass with the composition $90NaPO_3$-$10NaF$ (in mol%) (labeled 0Ag) was successfully prepared with $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals using the direct doping method [23,26]. Due to the presence of the $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals in the glass matrix, the glass exhibits upconversion with high intensity under 980nm excitation. In order to increase the intensity of the upconversion, Ag_2O was added in the glass as in[12]. ZnO was also added in the glass to promote the formation of Ag nanoparticles as in our previous study[20]. Therefore, the glass with the composition $83.25NaPO_3$-$9.25NaF$-$5ZnO$-$2.5Ag_2O$ (in mol%) (labeled 2.5Ag) was prepared with $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals using the direct doping method as in[23,24]. Although the melting temperature was increased from 750 to 875°C due to the change in the glass composition, the 2.5Ag glass could be prepared using the same doping parameters than the ones used to prepare the 0Ag glass: T_{doping} at 550°C and dwell time of 3min. No visible agglomerates of the $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals could be seen in the 2.5Ag glass with naked eyes indicating the good dispersion of the $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals. However, the 2.5Ag glass exhibits a yellowish color after quenching. As

depicted in Figure 1a, the color of the glass can be related to the presence of an absorption band at ~430nm. One should point out the presence of other bands with small intensity which can be related to the 4f-4f transition of Er^{3+} ions. The band at 430nm can be associated to the surface plasmon resonance (SPR) band of Ag nanoparticles (NPs) according to [15]. This SPR band is asymmetric indicating that the average distance between Ag particles may be larger than their sizes as suggested in[27]. From the position of this SPR absorption band, the size of the Ag NPs is suspected to be larger than 40nm. The emission spectrum of the 2.5Ag is presented in Figures 1b. Upon 320nm excitation, the emission band is a broad which can be formed by bands located at ~480nm, ~540nm and ~620nm. These bands can be related to Ag^+ species, Ag^+ - Ag^+ species and Ag_3^{2+} species, respectively according to [28,29]. An absorption band relative to Er^{3+} ions can be seen in superposition of the broad emission band of Ag species.

Silver NPs are typically formed in the glass using a 2 step process: (i) the inclusion of metal ions into the glass matrix and (ii) the formation of clusters upon a post-treatment[14–16]. Here, we showed that our as-prepared glass can be processed with Ag NPs without additional heat treatment. Similar generation of Au nanoparticles without heat treatment was reported in silicate glass in which selenium oxide and carbon were used as additives [30].

In order to understand the formation of the Ag NPs in the 2.5Ag glass, nanocrystals free 2.5Ag glasses were prepared using standard melting process (melting and quenching at 875°C) and also using the melting process used for the preparation of the nanocrystals containing glass (melting at 875°C and quenching at 550°C). After quenching, both glasses were colorless with low or few Ag NPs based on their absorption spectra (see Figure 2a) indicating that the precipitation of the Ag NPs does not occur due to the low quenching temperature. Therefore, it is the presence of the NaYF₄:Yb^{3+}, Er^{3+} nanocrystals in the glass which is thought to lead to the precipitation of the Ag

NPs. Glasses were prepared with different amount of $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals and as shown in Figure 2b, the intensity of the absorption band at 430nm increases as the wt% of the $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals increases. As explained in [26,31], although the direct doping method is optimized to balance the survival and dispersion of the particles, decomposition of some of the $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals is expected to occur during the glass preparation. The decomposition of the nanocrystals leads to the diffusion of the elements from the nanocrystals (Na, Y, F, Er and Yb) to the glass. One should point out that fluorine component is usually added in the glass to promote the precipitation of Ag nanoclusters[32] and RE ions were also reported to have also a catalyst role on the formation of Ag nanoparticles glass [33] [34]. Therefore, Na, Y, F, Er and Yb from the $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals might act as reducing agents leading to the precipitation of Ag NPs from the decomposition of the $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals. It is also possible that the Ag NPs form due to the presence of negative charges in the glass network. Indeed, the absorption band at 430nm can also be related to phosphorus oxygen hole center (POHC) which has an unpaired electron shared by two nonbridging oxygen atoms bonded to the same phosphorus[35]. As reported in[20], the addition of ZnO and Ag_2O in the $90NaPO_3$-$10NaF$ glass leads to an increase in the Q_1 units at the expense of Q_2 units and so to a greater number of non-bridging oxygens (NBOs). Therefore, it is also possible that the other source of the negative charges available to the matrix assisted reduction of the Ag^+ ions in this system is provided by the NBOs in agreement with[36].

The survival of the $NaYF_4$:Yb^{3+}, Er^{3+} in the 2.5Ag was confirmed by observing upconversion when pumping the glass at 975nm (see Figure 3). The upconversion spectrum exhibits the typical green ($^2H_{11/2}$–$^4I_{15/2}$ and $^4S_{3/2}$–$^4I_{15/2}$) and red ($^4F_{9/2}$–$^4I_{15/2}$) typical emissions of Er^{3+}[37]. Also shown in Figure 3 is the upconversion spectrum of the 0Ag glass. Although the glasses were prepared

7

with the same amount of $NaYF_4:Yb^{3+}$, Er^{3+} nanocrystals (5 wt%), the intensity of the upconversion from the 2.5Ag glass is lower than from the 0Ag glass. The low intensity of the upconversion of the 2.5Ag glass as compared to the 0Ag glass might be related to a lower amount of the $NaYF_4:Yb^{3+}$, Er^{3+} nanocrystals surviving the melting process of the 2.5Ag glass due to the stronger corrosive behavior of the 2.5Ag glass melt as compared to that of 0Ag glass melt as explained in[31]. The low intensity of the upconversion from the 2.5Ag glass can also be related to the energy transfer from the exited states of Er^{3+} to the silver NPs as seen in [20].

The 2.5Ag glass was heat treated for 4h at (T_g+10°C) in order to grow Ag NPs as performed in [20,38]. T_g was measured at (276 ± 3)°C. The absorption spectrum of the heat treated 2.5Ag glass is presented in Figure 4. The heat treatment leads to an increase in the intensity and in the bandwidth of the absorption band at 430nm which also shifts to longer wavelength. These changes indicate that the heat treatment increases the number of the Ag NPs, which are also suspected to increase in size [39]. Indeed, as shown in Figure 1b, the emission band shifts to longer wavelength confirming the formation of molecule-like Ag nanoclusters (ML-Ag NCs) with large sizes after heat treatment. As depicted in the SEM image of the cross-section of the 2.5Ag glass prior to and after heat treatment (Figures 5a and b), the heat treatment leads to the migration of the Ag species to the surface forming a layer of Ag species of ~2µm at the surface of the glass (see Figure 5c). Similar results were reported by Ennouri *et al* [38].

As shown in Figure 6a, the intensity of the upconversion is reduced by 40% after heat treatment, probably due to the energy transfer from the exited states of Er^{3+} to the silver NPs as discussed earlier. As shown in Figure 6b, a heat treatment of the as-prepared $NaYF_4:Yb^{3+}$, Er^{3+} nanocrystals at the same temperature (285°C) for 4h also leads to a similar decrease in the intensity of the upconversion. An increase in the heat treatment temperature and duration further reduces

the intensity of the upconversion. Similar decrease in the intensity of the upconversion upon heat treatment was reported recently in[40] and was related to the thermal activation of the deleterious thermal phonons from host lattice, internal/surface crystalline defects and surface chemical bonds. Therefore, it is the increase of the inter defects in the $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals which is thought to cause the intensity of the upconversion to decrease after heat treatment of the 2.5Ag glass.

Conclusion

Fluorophosphate glass with the composition $83.25NaPO_3$-$9.25NaF$-$5ZnO$-$2.5Ag_2O$ (in mol%) was prepared by adding $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals in the glass melt using the direct doping method. This glass exhibits upconversion confirming the survival of the nanocrystals during the glass preparation. However, compared to the glass with the composition $90NaPO_3$-$10NaF$ (in mol%) prepared with the same amount of nanocrystals and same method, the intensity of upconversion from the newly developed glass is lower indicating that the amount of the $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals surviving the melting process is probably lower in the newly developed glass than in the glass with the composition $90NaPO_3$-$10NaF$. The low upconversion intensity of the newly developed glass could be also related to energy transfer from the exited states of Er^{3+} to the Ag nanoparticles already present in the as-prepared glasses, as evidenced from the optical and spectroscopic properties of the glass. The precipitation of the Ag nanoparticles in the as-prepared glass is thought to be due mainly to the decomposition of some $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals during the glass preparation. A heat treatment of the glass near its glass transition temperature leads to the formation of a large number of Ag nanoparticles which migrate to the surface as evidenced using SEM and to a decrease in the intensity of the upconversion due to an

increase in the inter defects in the $NaYF_4:Yb^{3+}$, Er^{3+} nanocrystals.

Acknowledgement

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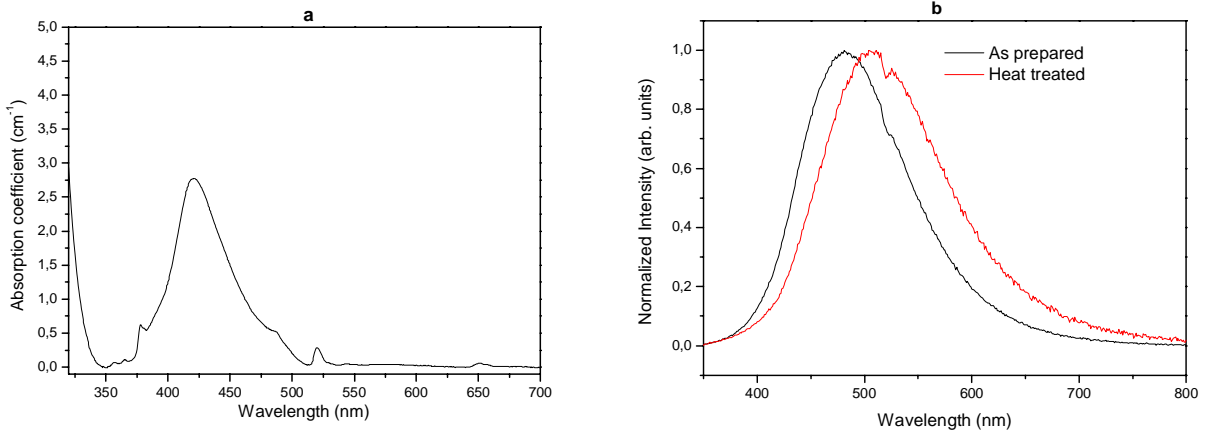
Figure Caption

Figure 1: Absorption spectra of the as-prepared 2.5Ag glass a) and emission spectra of the 2.5Ag glass prior to and after heat treatment at (T_g+10°C) for 4hours (λ_{exc}=320nm) b)

Figure 2: Absorption spectra of the nanocrystals free 2.5AgO glasses melted at 875°C and quenched at 875 and 550°C a) and of the nanocrystals containing 2.5Ag glasses prepared with different wt% of $NaYF_4$:Yb^{3+}, Er^{3+} nanocrystals b)

Figure 3: Upconversion spectra of the investigated glasses (λ_{exc}=975nm)

Figure 4: Absorption spectra of the 2.5Ag glass prior to and after heat treatment at (T_g+10°C) for 4hours

Figure 5: Ag color mapping measured at the cross-section of the 2.5Ag glass prior to a) and after heat treatment at (T_g+10°C) for 4hours b) (the gradient of the blue color being related to an increase in the Ag content) and Ag concentration profile measured from the surface of the heat-treated glasses c)

Figure 6: Upconversion spectra of the 2.5Ag glass prior to and after heat treatment at (T_g+10°C) for 4hours.a) and upconversion spectra of the NCs prior to and after heat treatment at different temperatures and durations b) (λ_{exc}=975nm)

Figure 1: Absorption spectra of the as-prepared 2.5Ag glass a) and emission spectra of the 2.5Ag glass prior to and after heat treatment at (T_g+10^oC) for 4hours ($\lambda_{exc}=320nm$) b)
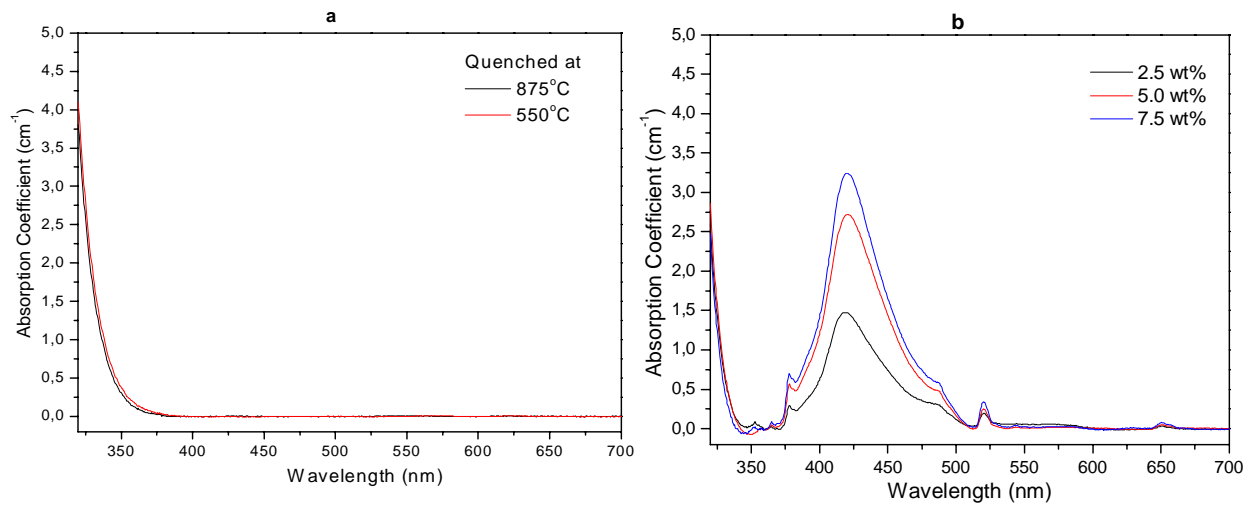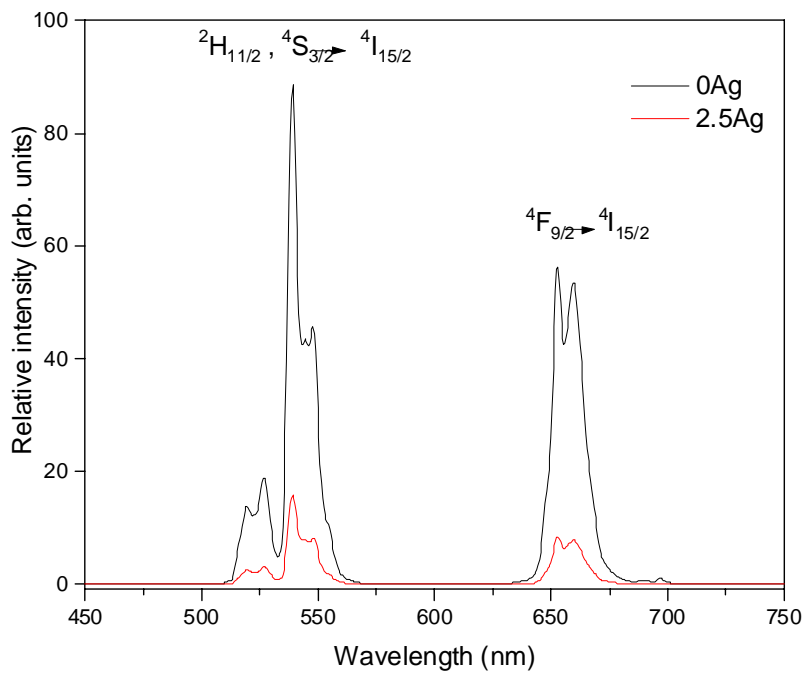
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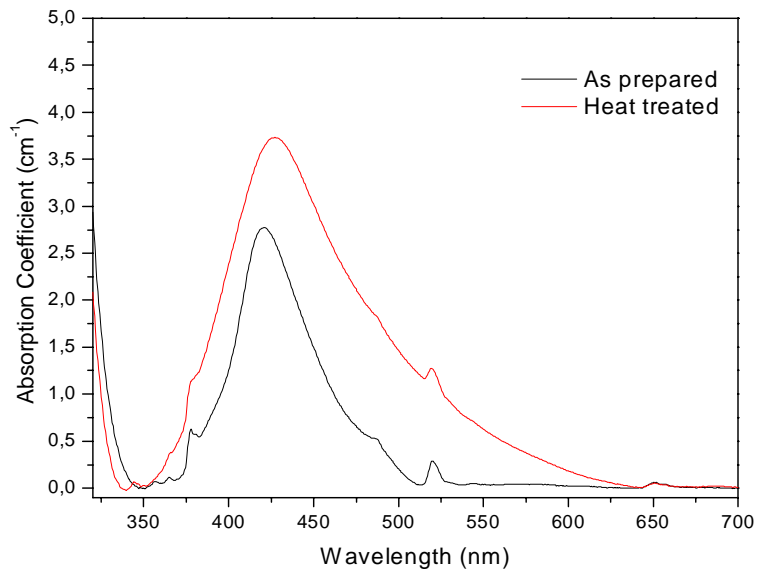*Figure 3: Upconversion spectra of the investigated glasses (λ_{exc}=975nm)*

Figure 4: Absorption spectra of the 2.5Ag glass prior to and after heat treatment at (T_g+10ºC) for 4hours

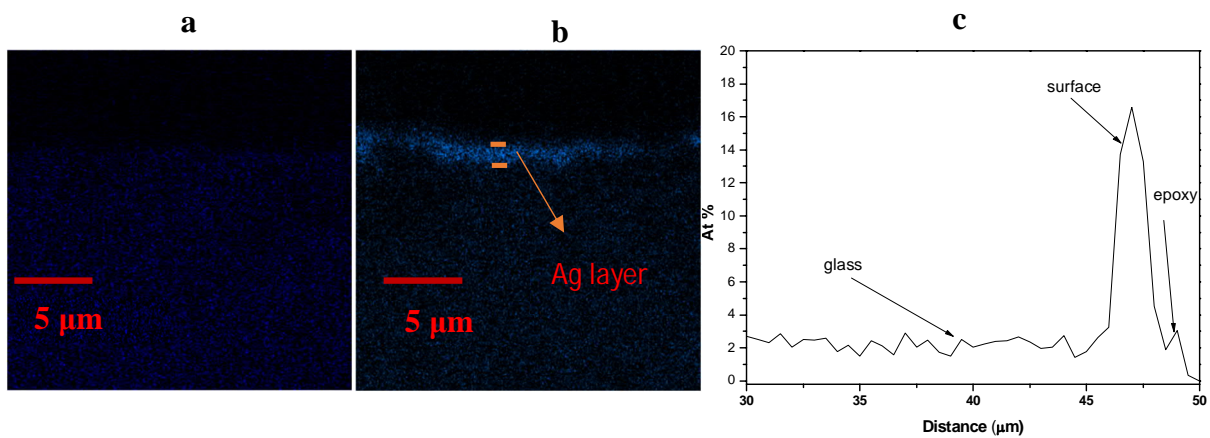*Figure 5: Ag color mapping measured at the cross-section of the 2.5Ag glass prior to a) and after heat treatment at (T_g+10ºC) for 4hours b) (the gradient of the blue color being related to an increase in the Ag content) and Ag concentration profile measured from the surface of the heat-treated glasses c).*
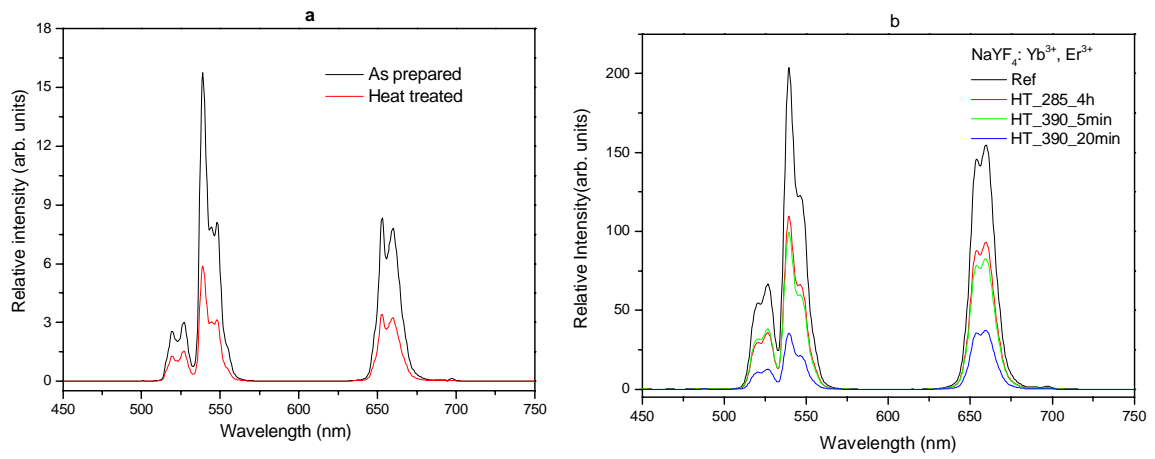
Figure 6: Upconversion spectra of the 2.5Ag glass prior to and after heat treatment at (T_g+10^oC) for 4hours.a) and upconversion spectra of the NCs prior to and after heat treatment at different temperatures and durations b) (λ_{exc}=975nm)