A highly efficient method of dehydroxylation and fining of Nd phosphate laser glasses

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Abstract

We describe herein a method that shows to be highly efficient in the dehydroxylation and fining process of phosphate glasses and that has been tested on the Nd-doped 15Na₂O-15K₂O-20BaO-50P₂O₅ metaphosphate composition. The method consists of a two-steps procedure: first, the batch is melted in a ceramic crucible; then, the obtained glass is remelted under a constant N₂ flow, while being placed inside a graphite crucible with a much bigger surface area as compared to its depth. This allows the melt to be spread over the crucible area resulting in a relatively thin layer with a high area in contact with the atmosphere at the temperature of remelting. It has been demonstrated that the water content decreases with both temperature and time length and that the glass samples obtained are completely free of bubbles and stria showing very high chemical and optical homogeneity. This method employed, has been proven to be very effective, as evidenced by the great increase in the lifetime of Nd³⁺ luminescence - reaching a maximum of 380 μs - which is much higher than the one measured in the untreated glass.

1. Introduction

The production of optical phosphate glasses and Nd-doped phosphate glasses for high energy lasers in particular, possesses several aspects that are of extreme importance in achieving high efficiency and reliability. As such, a strict control of the impurities, platinum inclusions and content of OH must be considered during the processing of the glasses. The presence of water is perhaps one of the most critical issues but less easy to deal with. Water may result in high rates of quenching of the neodymium luminescence [1] and may decrease the laser efficiency [2]. Despite their good optical characteristics, the fact that phosphate based glasses are very prone to hydration and to retain high amounts of water after melting, forces the implementation of appropriate dehydroxylation methods within the melting lines. As it was shown by Ebendorff-Heidepriem *et al.* a number of factors may influence on the final water content of the glasses, that is, the raw materials and preparation conditions (melting temperature and time) as well as the use of dehydration agents such as fluorinated compounds [3]. Nowadays, the most effective methods developed so far consist of bubbling of the melt with a carrier gas, commonly O₂ although compounds such as CCl₄, Cl₂ or POCl₃, SOCl₂ or their mixtures have also been employed [4,5]. These gases, not only help to significantly reduce the water content to the acceptable limits, but oxidizing gases impede the formation of metallic platinum inclusions, that also represent a serious source of damage under laser operation [6,7]. Thus, gas bubbling helps in reducing the content of water and simultaneously homogenizes the melt by providing additional fining. Other more simple methods, though not much used for the production of laser glasses, have been studied, such as the melting of the phosphate batch under inert or reducing atmosphere, using an induction furnace vitreous carbon or alumina crucibles [8]. In addition to the higher coefficients of expansion and lower fracture toughness of phosphate glasses, the reduction of water from the glasses has become a

critical issue for mechanical strength and control over the crack growth [9]. Most of the studies so far about the influence of OH ions on the luminescence properties of phosphate glasses have dealt with Nd-doped compositions designed for the production of laser glasses. However, some other works explored the effects of water regarding the optical activity of Er and Yb containing aluminophosphate glasses [10,11], in Er-doped tellurite glasses [12] and also on the glass transition temperature [13].

In a previous work we studied the synthesis of oxynitride Nd-doped phosphate glasses from the composition $15\text{Na}_2\text{O}-15\text{K}_2\text{O}-20\text{BaO}-50\text{P}_2\text{O}_5$, and observed that it is possible to further improve their optical characteristics after nitridation of the base glass by reducing the water content in a subsequent remelting under a N_2 flow [14]. Therein, we did not reduce the water content in a very large extent but it was enough to result in a significant increase in the Nd^{3+} lifetime. During the nitridation of phosphate melts, once the NH_3 flow is removed and changed to N_2 , the cooling rate of the melt down to room temperature is actually very low, no quenching occurs, and the final glass is obtained free of internal tensions and does not need to be submitted to additional annealing. These results, made us realize the possibility that by applying the same method directly to the original, not nitrated glass composition. Initial trials demonstrated to be successful after a remelting under N_2 at 800°C for 3 h. Moreover, the glass did not spontaneously crystallize upon cooling, a possible scenario feared to result from the low cooling rates employed. In this contribution we are showing the results of a strong reduction of the water content obtained after a series of remelting treatments under a constant N_2 flow, using the same graphite crucible. The effectiveness of this method could be demonstrated through the significant increase of the Nd^{3+} luminescence lifetime.

2. Experimental

Glass batches of 80 g with composition 15Na₂O-15K₂O-20BaO-50P₂O₅ (mol. %), doped with a reference Nd₂O₃ content of 0.5 wt. %, that corresponds to a ca. 0.2 mol %, were obtained by the mixture of reagent grade chemicals, Na₂CO₃, K₂CO₃, BaCO₃, (NH₄)₂HPO₄ (Scharlau) and Nd₂O₃ (Sigma-Aldrich) in porcelain crucibles (Haldenwanger 79MF 1a). The batches were slowly calcined overnight up to 400°C, and then melted at 900°C for 2 h in air. The dehydroxylation reactions are performed inside a tube furnace by remelting 6 to 8 g of the original glass under constant N₂ flow at variable temperatures and time lengths, between 800°C and 1000°C and 1 to 9 h. These re-melts were conducted using a square-like crucible or mold, made of graphite of the CB1 grade from CARBOSYSTEM S.L.L., which is isostatic-type graphite with apparent density of 1.85 g.cm⁻³ and a porosity of 13%. The cavity to contain the glass is 6 cm long, 4 cm width and ca. 1 cm in depth. Nitrogen is constantly flowing through the furnace between heating and cooling and, as said above, the final cooling step proceeds at a free rate, which is higher at the beginning of the cooling step and continually decreases to very small rates. The real cooling rate in the furnace was of 7.5 °C/min for the first 20 minutes, below 4°C/min at 60 minutes and about 2.5 °C/min at the first 100 minutes, reaching a temperature of 380°C. This means that for the glass studied, for which the T_g is 300°C as said in reference [14], the undercooled melt reaches the transition region at a rate of below 2°C/min, which in turn means that the obtained glass will be completely annealed after the process. The glass can also be taken out the crucible easily as it does not stick to it. The results presented here are from experiments carried out under N₂; however, some of the treatments were also done under Ar flow showing the same effect on the glasses.

The composition of some of the glass samples was checked by means of X-ray Fluorescence Spectroscopy in a PANalytical MagicX 2400 spectrometer using the pearl method by mixing

0.3 g of glass with 5.5 g of $\text{Li}_2\text{B}_4\text{O}_7$. The analyses confirmed the batched composition as well as the constant content of all oxide components for up to 12 h remelting at 800°C.

As it was done in the previous work [14], the coefficient of absorption of OH (α_{OH}) was calculated using equation (1), according to the method described in reference [3,15], from the Fourier-Transformed Infrared spectra (FTIR) that were performed with a Perkin-Elmer Spectrum 100 spectrometer on plane-parallel square samples of about 1 cm², between 1 and 2 mm thickness, and polished with SiC grinding paper up to the P4000.

$$\alpha_{\text{OH}} = -\log(T_{3000}/T_{5000})/t \quad (1)$$

T_{3000} and T_{5000} are the transmission at 3000 and 5000 cm⁻¹, respectively, and t the sample thickness in cm.

The Nd^{3+} lifetime measurements were performed by exciting the samples with a Ti-sapphire laser pumped by a pulsed frequency-doubled Nd:YAG laser (9 ns pulse width). The fluorescence was analyzed with a 0.25 m monochromator and the signal was detected by an extended IR Hamamatsu H10330A-75 photomultiplier. Data were processed by a Tektronix oscilloscope.

3. Results and discussion

The temperature initially selected was 800°C in order to reproduce the conditions in reference [14]. Then, progressive increases in temperature and time were studied to follow their effect onto the dehydroxylation of the glasses. However, remelting the glasses at temperatures above 900°C for 3 h or for long remelting times of 12 h at 900°C, gave rise to samples showing orange-brownish coloration, and a loss of transparency, much more important at the highest temperature or durations. This is thought to be due to the partial reduction of phosphorus, as it may happen when treating phosphate glasses under NH_3 flow above 800°C. Additionally we performed the chemical analysis on several of the samples obtained (800°C

between 3 and 12 h melting time) to detect any important changes in composition, but found that the contents of the oxide components are in all cases within ± 1 mol. % of the formulated batch composition for all tests.

After normalization of the transmittance spectra, the absorbance was calculated and represented in Figures 1 and 2 for the remelting treatments performed at a fixed temperature of 800°C, between 1 and 9 h, and for 3 h between 800°C and 900°C, respectively. The FTIR spectrum of the original glass (PG) is also shown in both Figures as a reference. As it may be clearly observed, the absorbance above 2500 cm^{-1} suffers a strong decrease as a result of the important reduction of the water content in the glasses with the increase of temperature and time. In Figure 3 and inset, the coefficient of absorption of OH ions is represented against the variable melting times and temperatures, respectively. It is noteworthy to mention that the effect of dehydroxylation manifests most strongly within the first 3 h of melting time under N_2 at either 800°C or 900°C of temperature. This may also be thought to arise from the fact that the removal of water from the melt is based on a diffusion controlled process that is much facilitated by the larger melt surface exposed to the atmosphere, especially when taking into account the depth of the melt within the graphite crucible employed. Furthermore, as it is inferred from the results, the mechanism of dehydroxylation is also a thermally activated process which is also reflected by the regular decrease of OH absorption along with the melting temperature and fixed time of 3 h.

As it was stated before, the glasses do not require further annealing once the remelting is finished because of the very slow cooling rate to which they are submitted. In the case under study, the composition entails a 20 mol % BaO which is thought to stabilize enough the glass network and thus prevents crystallization upon cooling. Actually, a glass of the same system with composition $22.5\text{Na}_2\text{O}-22.5\text{K}_2\text{O}-5\text{BaO}-50\text{P}_2\text{O}_5$ (mol. %) was similarly re-melted at 800°C for 9 h but produced a completely crystallized sample.

All glass samples were visually inspected through a polarized light beam and did not show birefringence. What may be even more important is the complete elimination of stria and bubbles for even the shortest times at either temperature, which points to a quite good optical homogeneity.

The reduction of the water content was confirmed by the increase of the fluorescence lifetime of the $^4F_{3/2}$ state of Nd^{3+} . The experimental decays were obtained by exciting the $^4F_{5/2}$ state at 800 nm collecting the luminescence at 1054 nm for the glass samples treated at 800°C for 1, 3, and 9 h and at 900°C for 1, 3, and 6 h. In all cases the decays can be described by a single exponential function. As an example, Fig. 4 shows the decays for the original glass (PG) and the treated samples at 800°C-9h and 900°C-3h. As can be seen in this figure, the treated samples exhibit longer lifetimes than the base glass. The lifetime values of the measured samples are displayed in Table 1. The lifetime increases from 300 μs for the base glass to 380 μs for the sample treated at 900°C-6h. The increase of the lifetime after the thermal treatment indicates a suppression of non-radiative relaxation due to the significant reduction of OH groups. The high vibration frequency of these groups increases the probability of multi-phonon energy transfer processes from Nd^{3+} to OH vibrations which leads to non-radiative quenching of the Nd^{3+} fluorescence [1]. While the composition tested in this study is different from those of laser glasses such as LHG-8 and LG-770, from Hoya Corporation and Schott Glass Technologies, respectively, the Nd lifetimes obtained after removal of OH in the present glass are comparable to the ones in the above commercial glasses [7]. However, the properties of glasses with variable contents of Nd_2O_3 need to be tested as well in order to get insights from the fluorescence quenching from hydroxyl ions.

On the other hand, this methodology is currently under further investigation for a wider range of compositions, including different alkali modifiers, glass stabilizers as well as Al_2O_3 -containing compositions, which might be better suited to work as laser hosts due to their

superior mechanical properties. As it was pointed out above, the fact that the studied melt composition does not crystallize during the cooling step of the re-melting is thought to be another advantage of the employed method, as the obtained glasses do not need further annealing treatment. Thus, in the search for new compositions suitable of being submitted to the same procedure, one should manage the choice of glass modifiers and stabilizers under the prerequisite that it does not crystallize after the re-melting under N_2 . Additionally, a thorough exploration concerning the usefulness of the methodology and the possibility of implementation at bigger scales for the production of laser phosphate glasses should also be performed.

4. Conclusions

We presented in this work an alternative method for an effective dehydroxylation of phosphate laser glasses that has been tested on the composition $15Na_2O-15K_2O-20BaO-50P_2O_5$ (mol %) doped with a 0.5 wt. % Nd_2O_3 . The remelting of the glass in a graphite crucible under a N_2 flow facilitates the release of water due to the large melt surface area in contact with the atmosphere. Moreover, the suggested method provides at the same time an optimum fining. Dehydroxylation has been demonstrated to be very effective, and as a consequence, we were able to observe an increase in the lifetimes of the $^4F_{3/2}$ state of Nd^{3+} due to a strong reduction of non-radiative relaxation processes involving OH groups. Even though this method of dehydroxylation has shown to be very effective in small glass samples at the laboratory scale, further studies should be conducted to address the issues associated to appropriate scaling of the method, such as those concerning necessary means to allow melting of much bigger quantities and suitable for having an accurate control of the cooling step that will be depending on the chosen composition.

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Table captions

Table 1: Luminescence lifetimes of Nd^{3+} ions in the original glass PG and samples obtained by remelting at 800°C and 900°C and variable times.

Glass sample	Nd^{3+} lifetime, τ (μs)	OH absorption coefficient, α_{OH} (cm^{-1})
PG	300	8.76
PG-800-1	339	3.59
PG-800-3	370	1.41
PG-800-9	370	0.46
PG-900-1	355	0.92
PG-900-3	376	0.38
PG-900-6	380	0.30

Figure captions

Figure 1: Absorbance of glass samples obtained at 800°C for between 1 and 9 h.

Figure 2: Absorbance of glasses after remelting between 800°C and 900°C for 3 h.

Figure 3: Coefficient of absorption of OH (α_{OH}) as a function of melting time at 800°C and 900°C temperatures. The inset shows the coefficient of absorption for a fixed melting time of 3 h between 800°C and 900°C.

Figure 4: Semi-logarithmic plot of the experimental decays from the $^4\text{F}_{3/2}$ state for the base glass (black line) and the re-melted samples at 800°C-9h (red line) and 900°C-3h (blue line) doped with 0.5 wt. % Nd_2O_3 .

Figure 1

Figure 2

Figure 3

Figure 4