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Influence of the preparation conditions of erbium-doped bismuth germanate glasses on its optical response

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ABSTRACT

The influence of the glass preparation conditions (melting temperature and crucible material) and of post-preparation heat treatments on the refractive index, optical absorption and near infrared luminescence of an Erbium-doped Bi_2O_3-GeO_2 glass has been studied. The optical absorption and emission are strongly dependent on these conditions and Bi to Er energy transfer is observed to occur. In some cases, a high absorption due to the formation of Bi nanoparticles is obtained. Consequently transmission-temperature hysteresis loops during heating-cooling cycles are observed due to the reversible melting and solidification of nanoparticles. Our results indicate that, with adequate composition and preparation conditions, bismuth germanate glasses can be very useful for a large variety of optical devices, such as amplifiers and thermo-optical modulators and filters.

1. Introduction

Rare earth-doped materials have been essential for many years for the development of photonic applications, such as lasers and amplifiers [1–2]. In this sense, Er^{3+} ions have played a key role in the development of fiber and planar amplifiers as they emit at the standard telecommunications wavelength around 1.54 μm. Due to their wide transparency range, low propagation losses and isotropic refractive index, glasses are very promising as host materials. Germanate glasses are good candidates since, besides their high mechanical strength, chemical durability, thermal stability and excellent transmission in the infrared region, they have maximum vibrational frequencies smaller than those of many other types of glasses, such as silicate, phosphate and borate glasses [3–4]. They are also important for other applications, such as directly ultra-short-pulsed-laser-written optical waveguides with nonlinear optical properties and infrared transmitting windows.

Among germanates, bismuth germanate glasses have advantages for rare-earth emission because of their high refractive index (that favors high rare-earth absorption and emission cross sections), good mid-infrared transmission and significantly low phonon energy (which reduces the non-radiative multiphonon relaxation) [5], so rare-earth doping of these glasses has been widely studied [5–14]. On the other hand, many glasses in which Bi_2O_3 is one of their main components as well as Bi-doped glasses exhibit a very broad emission band in the near infrared (NIR) wavelength region when excited in the visible range due to Bi ions-related centers (see refs. [15–19] and references therein). This opens the possibility of developing a broadband optical fiber amplifier based on Bi-containing glasses for use in fiber optics communications [20]. In fact, optical amplification and laser action have been demonstrated in Bi-doped glasses [21–23]. Co-doping bismuth glasses with rare earth ions emitting in the NIR range can further broaden the emission bandwidth.

Nevertheless, the way in which bismuth-containing glasses are prepared has a strong influence on the Bi-related optical absorption and luminescence. Darkening of the glass may occur when melting the component mixture at high temperature because of the reduction of Bi species until Bi nanoparticle formation is achieved [24–26], which is detrimental for the luminescent response [19]. Also, contamination from crucibles during melting may alter the glass composition with possible influence on the glass optical properties: for example, it is known that Al_2O_3 enters the melted component mixture when using alumina crucibles and it has been shown that the presence of Al_2O_3 affects the Bi luminescence response [18,27–28]. Furthermore, the Bi-related NIR luminescence is very sensitive to thermal annealing treatments of as-prepared glasses [29–30] and, even more, these thermal treatments could lead to Bi nanoparticle formation [31–32]. This should be considered during the fiber drawing process to avoid performance degradation [29].

The purpose of this paper is then to study the effect on the luminescence response of an Er-doped pure bismuth germanate glass (that is, with a composition as simple as possible) of preparation conditions

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such as the melting temperature, the crucible material (platinum or alumina), and several post-preparation thermal annealing treatments, as well as the Er content of glasses. Bulk glasses in the system GeO_2-Bi_2O_3 can be obtained for compositions containing up to 90 mol% Bi_2O_3 [33–36]. The nominal molar composition chosen for our glasses has been $86GeO_2$-$14Bi_2O_3$, since, on one hand, deviations from ideal mixing occurs at lower GeO_2 contents [37] and, on the other, it has been found that Al ions have only a little effect on the Bi-related luminescence emission when the Bi_2O_3 content is low [18]. Moreover, for such a low Bi_2O_3 content, only low Bi_2O_3-induced depolymerization of tetrahedral GeO_4 chains is expected [34]. Although the Bi emission intensities observed in our samples are low, our results indicate that the preparation conditions and the heat treatments of glasses are determinant in achieving a good optical response. Indeed, under certain conditions, Bi nanoparticles precipitate allowing these glasses to be used for thermo-optical devices [38]. These results can be extrapolated to more complex bismuth germanate glasses and show that much care has to be taken when fabricating and processing them in order to get a good optical performance.

2. Experimental

10 g batches were prepared from GeO_2 (Aldrich 99.998%), Bi_2O_3 (Aldrich 99.9%), and Er_2O_3 (Aldrich 99.99%) raw materials. They were melted for 1 h in platinum or alumina crucibles at different temperatures in an electrical vertical Thermostar furnace and stirred to ensure homogenization. The melt was poured onto a preheated brass mould, followed by annealing and slow cooling down to room temperature. The glasses showed no visible sign of phase separation or bubbles. The samples were cut into around 1 mm thick slices and polished for optical measurements. Thermal annealing treatments of samples were performed in air atmosphere.

Density was measured 5 times for each sample by the Archimedes method with bromonaphtalene as the immersing liquid and then averaged. The standard deviation was taken as the error. The microanalysis of major components was performed by energy dispersive X-ray spectrometry (EDX) with an Oxford Inca analyzer attached to a Hitachi S-4800 scanning electron microscope. A differential thermal analyzer from T. A. Instruments, Q600 model, was used to obtain the glass transition temperature. The measurement was repeated several times to estimate the error. The refractive index and the extinction coefficient were measured in the range from 300 to 1700 nm using a J. A. Woollam VASE spectroscopic ellipsometer. Absorption spectra were measured in the wavelength range from 190 to 3300 nm using a Varian Cary 5000 UV–VIS-NIR spectrophotometer. Raman spectra were recorded with a Renishaw Raman Invia spectrometer under excitation at 532 nm with an unpolarised Nd:YAG laser. Spectra were obtained at 5% of the maximum laser power (500 mW) for an exposure time of 10 s at 2 cm^{-1} resolution. Photoluminescence (PL) was excited at 514.5 nm with an Ar^+ laser and at 980 nm with a T-sapphire laser at a pump power of 120 mW focused on the sample surface with a spot of about 1 mm diameter, the laser beam being modulated with a mechanical chopper. PL spectra in the NIR wavelength range from 1000 to 1700 nm were performed at room temperature through a single grating monochromator (focal length 300 mm) using a Peltier-cooled Hamamatsu photomultiplier and standard lock-in techniques. These spectra were normalized to the sample thickness. Decay curves at the peak of the emission spectrum were recorded 5 times for each sample using a 50 MHz digital storage oscilloscope. The obtained lifetimes were averaged and the standard deviation was taken as the error. The evolution of the optical transmission as a function of temperature was studied in the range 20–430 °C in a home-made oven set inside a vacuum chamber with a base pressure of 0.1 Pa. The heating- cooling cycles were performed at 10 °C min^{-1}. The illumination source was an incandescent lamp at normal incidence and the light transmitted by the sample was collected by an Acton Research Spectra-Pro 275 monochromator and a Hamamatsu R562 photomultiplier.

3. Results and discussion

3.1. Effect of the temperature of melting

When using Pt crucibles, the melt is very viscous, so pouring can not be achieved below 1250 °C. The glass color is very dark, most likely due to the formation of Bi nanoparticles [24,31]. Optical absorption is very high and thus the PL response of samples is very low. Therefore the PL of glasses prepared in these crucibles has not been studied in detail. Instead, using alumina crucibles allows melting at temperatures as low as 1000 °C. Glasses obtained by melting batches at 1000 °C in these crucibles are transparent, only slightly pink colored due to Er doping. Those obtained by melting at 1200, 1300 and 1400 °C show a brownish color which darkens as the melting temperature (T_M) is increased.

EDX results are shown in Table 1. The composition of the glass prepared in a Pt crucible is very close to the nominal one (26.2 at% Ge + 8.6 at% Bi + 65.2 at% O), the small difference being attributed to errors in the weighing of the raw materials. Melting in alumina crucibles leads to alumina incorporation to the melt, the Al_2O_3 content of the obtained glass increasing with increasing T_M. Therefore the relative content of both GeO_2 and Bi_2O_3 decreases. As a result of these changes in composition, the glass density decreases and the glass transition temperature increases when increasing T_M, as shown in Fig. 1. The values for the glass prepared by melting at 1250 °C in a Pt crucible match the general trend of this dependence on the Al_2O_3 content.

The refractive index of the Er-doped glasses prepared in alumina and platinum crucibles as a function of wavelength is plotted in Fig. 2. It has been found that the change of refractive index upon Er doping within the range of concentrations studied in this work (from 0 to 2 wt% of Er_2O_3, that is, from 0 to 0.8 mol%) is negligible. As seen in this figure, for glasses obtained in alumina crucibles the refractive index in the 300 to 1700 nm wavelength range decreases with growing T_M. This is consistent with the increasing Al_2O_3 content and the decreasing glass density with T_M. It is worthwhile to note that the refractive index values in the visible region, as well as the density value of our glasses obtained by melting at 1200 °C, agree with those obtained by Riebling [37] for a glass with a similar composition.

Fig. 3 shows the Raman spectra of the sample obtained by melting at 1000 °C in an alumina crucible. Every sample shows the same spectrum which can be deconvoluted into 4 Gaussian components peaked at around 370, 495, 533 and 740 cm^{-1}. Due to the strongly changing absorption values at the excitation wavelength (see below), an accurate study of the intensity evolution of the Raman spectra as a function of T_M cannot be made. These Gaussian bands arise from stretching vibration modes of Bi—O—Bi and Ge—O—Ge bridges and from Ge—O bond stretching vibrations of interconnected tetrahedra with non-bridging oxygen atoms [10,33,39–43]. None of them seems to be related to Al ions because in Pt-crucible-prepared glasses (in which Al_2O_3 is not present) the same Raman bands as in alumina-crucible-prepared ones appear.

The optical absorption spectra (normalized to the sample thickness) of glasses doped with 0.5 wt% Er_2O_3 are depicted in Fig. 4a. For the glass prepared by melting at 1000 °C in an alumina crucible, absorption bands at 378, 489, 521, 653, 799, 977, and 1531 nm, which correspond to the transition from the Er^{3+} ground state ($^4I_{15/2}$) to the $^4G_{11/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ excited states, respectively, are observed. As T_M is increased, absorption increases in the 350 to 1400 nm range and a wide band at around 500 nm and a slight shoulder at around 850 nm develop. The 500 nm band amplitude is seen to increase when increasing T_M while the amplitudes of the Er^{3+} bands do not change. The glass prepared in a Pt crucible shows a very strong absorption in the whole range.