Contents lists available at ScienceDirect

Materials Letters

Optical characterisation of Er^{3+}-doped oxyfluoride glasses and nano-glass-ceramics

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A B S T R A C T

We present the optical properties such as the linear refractive index (n), the absorption coefficient (α), the energy band gap (E_g) and the nonlinear refractive index (n_2) measured by spectroscopy and degenerate four wave mixing methods for Er^{3+}-doped oxyfluoride glasses and nano-glass-ceramics.

The n_2 of the Er^{3+}-doped oxyfluoride nano-glass-ceramic is almost twice that of the Er^{3+}-doped parent oxyfluoride glass and undoped oxyfluoride glass. The n_2 values of the Er^{3+}-doped oxyfluoride glass and non-Er^{3+}-doped oxyfluoride glass are almost the same.

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1. Introduction

Nonlinear optical materials continue to attract attention because of their potential application in novel photonic, electronic and optoelectronic devices [1,2]. Materials that show a nonlinear intensity-dependent refractive index are of great importance for all-optical switching in integrated-optic circuits [3]. Potential candidates to fabricate all optical switching device are Er^{3+}-doped fibre gratings [4].

Rare-earth (RE)-doped optical waveguides are well known for their amplifying and lasing characteristics but may also be of interest for their intensity-dependent refractive index. These materials show sharp absorption peaks and therefore exhibit a relatively broad dispersive refractive-index change. Measurements of the nonlinear refractive index of erbium-doped polycrystalline Y_2O_3 optical waveguide and optical fibres have previously been reported, and attractive nonlinear optical properties were observed [3,5].

RE-doped, transparent, nano-glass-ceramics are prepared by heat-treating the parent glass [6–8]. We have found that during the crystallisation, the active RE ions tend to partition into a lower phonon energy nano-crystalline phase. For the composition studied here, the nano-crystalline phase was originally thought to be cubic fluorite-structured βPbF_2 with ErF_3 in solid solution, but is now considered to be based on a distorted trigonal unit cell

$Pb_8Er_6F_{32}O(F_2)$ which exhibits a pseudo-fluorite (cubic) cation sublattice [9]. After nano-ceramming, the modified surrounding crystal field influences the absorption and emission spectra of the active RE ions.

2. Experimental

Absorption spectra in the spectral region 300–1100 nm were measured using a double beam Perkin-Elmer UV–VIS Lambda 2 spectrometer. The refractive indices (n) as a function of light wavelength were measured using spectroscopic ellipsometry (SE HORIBA Jobin Yvon) in the range 300–900 nm.

The third order nonlinear optical susceptibility ($\chi^{<3>}$) of the materials studied was measured by the standard backward degenerate four wave mixing (DFWM) geometry described elsewhere [10] using a Nd:YAG laser working at 532 nm (30 ps, 1 Hz). The DFWM method is sensitive only to the absolute value of $\chi^{<3>}$ ($\chi^{<3>} = \chi_R^{<3>} + i\chi_I^{<3>}$). The real part ($\chi_R^{<3>}$) of $\chi^{<3>}$ is related to the nonlinear refractive index changes, which may be extracted from the DFWM measurement. The imaginary part ($\chi_I^{<3>}$) of $\chi^{<3>}$ is related to the two-photon absorption coefficient (β) determined from the nonlinear transmission measurement [11].

In the DFWM method, three laser beams of the same frequency (ω) were temporally and spatially overlapped into the material and generated a fourth beam (a phase-conjugated beam designated by E_4) of the same frequency (ω), whose intensity was proportional to the product of the intensities of the interacting beams. The intensity of the phase-conjugated signal (I_4) was

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measured by means of a photo-multiplier tube (Model Hamamatsu R1828) and fed into a digital storage oscilloscope (Tektronix TDS 3054). A part of the input laser beam was split off and measured using a sensitive photodiode, to monitor the input laser energies as well as the fluctuations in them $I_3 = 6 \times 10^{-2} I_1$.

3. Materials' preparation

The oxyfluoride glass $32(SiO_2):9(AlO_{1.5}):31.5(CdF_2):18.5(PbF_2):5.5(ZnF_2):3.5(Er^{3+}–F_3)$ mol% [8] was prepared by melting the batch consisting of the respective oxides and fluorides. Glass batching was carried out in an MBraun 150B-G glovebox under N_2 (≤ 0.1 ppm) H_2O and (≤ 0.1 ppm O_2) and weighing of the batch was carried out to an accuracy of ± 0.5 mg. Thus, the trivalent Er^{3+} ions were added as erbium trifluoride, which was weighed during batching in order to control the Er^{3+} concentration added to the doped parent glass. In previous work, it has been estimated that the 3.5% of the totally added Er^{3+} ions partition to the nano-crystalline phase after the nano-glass-ceramming processing. Note, that the composition of the zero mol% $Er^{3+}–F_3$ doped oxyfluoride glass was calculated by keeping the remaining batch components in an identical molar ratio to that of the doped glasses. Chemical precursors were Alfa Aesar (except ErF_3 from BDH). Precursor chemicals were stored in the glovebox and batched into a cleaned, 95% Pt/5% Au lidded crucible. As-received ZnF_2 was purified [12]. For glass melting the melt crucible was held inside an alumina cradle, within a silica glass lidded liner (MultiLab) through which was passed air flowing at 0.16 dm³/s, pre-dried by passage through a molecular sieve column. The melting furnace was preheated to 800 °C. The batch was held for 20 min at 800 °C, then ramped to 1050 °C at 300 °C/h, held isothermally for 1 h then cast in the ambient atmosphere into an Al mould, preheated to 350 °C and then annealed at 350 °C for 1 h before ramping down to room temperature at 20 °C/h.

The doped oxyfluoride glasses were heat treated under flowing He inside the small furnace of a thermomechanical analyser (Perkin Elmer TMA 7). Samples were loaded into the TMA7 at room temperature. The TMA7 was purged with He gas at 30 cm³/min, then ramped up to the heat treatment temperature at 40 °C/min, held isothermally at that temperature for the desired time, then cooled at 40 °C/min to room temperature. The Er^{3+} doped oxyfluoride glass was heat treated at 430 °C for 1 h (ErF_3 3.5 mol%).

4. Results and discussion

The linear absorption spectra of non-Er^{3+}-doped oxyfluoride glass (No Er% unceramed), the Er^{3+} doped oxyfluoride glass (ErF_3 3.5 mol% uncerammed) and nano-glass-ceramics (ErF_3 3.5 mol% cerammed at 430 °C for 1 h) are illustrated in Fig. 1. It is observed that, in the case of the Er^{3+}-doped oxyfluoride glass and nano-glass-ceramic, there are 11 absorption bands in the spectral region 300–1100 nm, which correspond to the transitions from the Er^{3+} ground state, $^4I_{15/2}$, to various excited states [13].

The refractive indices (n) of the materials studied as a function of wavelength are shown in Fig. 2. As can be seen, far from the absorption bands and beyond the optical band gap, the n decrease continuously as the wavelength increases thus displaying normal dispersion. This behaviour can be described using a well-known first order Sellmeier relation [14]. From Table 1 we can see that the n of the oxyfluoride glass decreases with increase of Er^{3+}-doping and on nano-ceramming the glasses at 532 nm. The opposite behaviour was obtained for the absorption coefficient (α) obtained at 532 nm, which was calculated from Lambert–Beer law. This may be due to that Er^{3+} absorption peaks for nano-glass-ceramic have
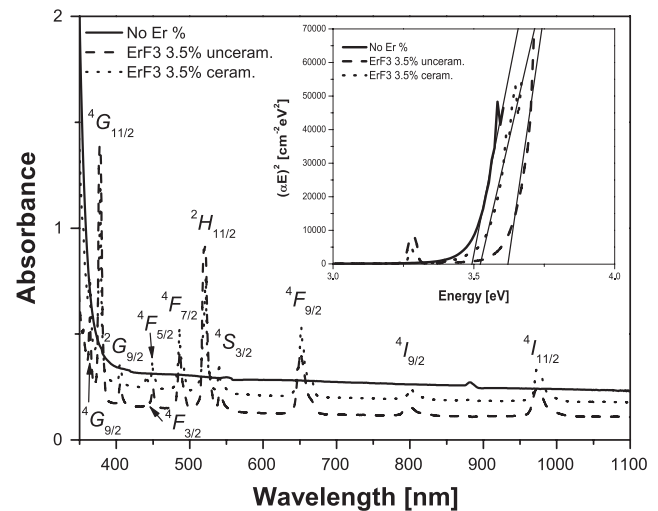

Fig. 1. The linear absorption spectra of the materials studied. Inset: determination of optical energy band gap of the materials studied.
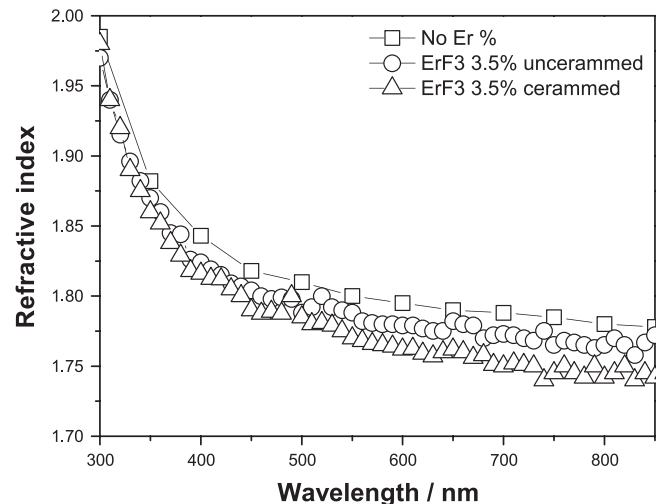

Fig. 2. Refractive indices of the materials studied as a function of wavelength.

narrowed compared with unceramed Er^{3+} doped glass at around 532 nm.

The most important factor governing the optical properties is the energy band gap (E_g). From the absorption or transmission data, the E_g could be determined using the Tauc method [15] using the following equation:

$$(\alpha \, h\nu) = B(h\nu - E_g)^n \tag{1}$$

where $h\nu$ is the photon energy, B is the band tailing parameter, and n is equal 1/2 for a direct allowed transition, 3/2 for a direct forbidden transition, 2 for an indirect allowed transition and 3 for an indirect forbidden transition.

This relationship assumes that the densities of the electron states in the valence and conduction bands, near the band gap, have a parabolic distribution and, also, that the matrix elements for the interband transitions associated with the photon absorption are equal for all the transitions [16].

The inset of Fig. 1 shows the Tauc plots used to determine the E_g of the materials studied. From Table 1, we can see that the E_g decreases with increases of Er^{3+}-doping and nano-ceramming glasses.

The nonlinear optical properties of the materials studied were investigated using the nonlinear transmission (NLT) and the degenerate four wave mixing (DFWM) methods at 532 nm. We