Er³⁺-doped fluorotellurite thin film glasses with improved photoluminescence emission at 1.53 μm

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Abstract

Transparent oxyfluoride tellurite thin film glasses have been produced at room temperature by pulsed laser deposition in O₂ atmosphere from an Er-doped TeO₂-ZnO-ZnF₂ bulk glass. Thin film glasses present high refractive index ($n \geq 1.95$) and good transparency ($T \geq 80\%$) in the visible ($\lambda > 400\text{nm}$) and near infrared range. However, their photoluminescence (PL) performance at 1.5 μm is poor. Thermal annealing at moderate temperatures ($T \leq 315\text{ }^\circ\text{C}$), well below glass crystallization, increases the PL

intensity by more than one order of magnitude as well as the PL lifetime up to $\tau \approx 3.3$ ms. Film glasses present a larger fraction of TeO_3 trigonal pyramids than the bulk glass and a very large OH^- content. The structure and composition of film glasses does not change upon annealing and thus the activation of the PL response is related to the improvement of the surface morphology and the significant decrease of their OH^- content.

Keywords: Rare-earth-doped glasses, oxyfluorides, tellurite glasses, erbium, thin films,

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1. Introduction

The age of all-optical metropolitan and local area networks has finally come. The deployment of cost-effective and compact integrated optical devices will allow high-density wavelength division multiplexing (WDM) schemes if functional integrated optical circuits allowing operation in the whole telecommunication window range (1.2-1.7 μm) are developed [1, 2]. However, current optical communication systems rely on the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ emission at 1.5 μm , of Er-doped waveguide amplifiers (EDWA)] that are mostly based on silica glasses deposited on Silicon substrates [3, 4, 5].

The glass host in which rare earth (RE) ions are embedded affects their photoluminescence emission characteristics through the modification of the rare earth environment [6, 7]. Thus, a large effort has been devoted to find alternative hosts to silica glass to achieve better device performances. Among them, rare earth doped tellurite glasses combine good mechanical, chemical and thermal properties, such as chemical durability, glass stability or strength with excellent optical properties (broad transparency range, large refractive index) and a reduced phonon energy ($\sim 800 \text{ cm}^{-1}$) compared to other oxide glasses [6, 8, 9, 10]. These characteristics contribute to increase the radiative transition rates when doped with RE ions, whereas their high RE ion solubility makes possible to co-dope them with more than a single RE ion, such as Er^{3+} and Tm^{3+} , to achieve broad PL emission [11]. However, one of the main drawbacks of tellurite glasses is the presence of hydroxyl (OH^-) groups that quenches radiative emission of RE ions [12]. The addition of fluorine reduces the OH^- concentration in fluorotellurite glasses [13, 14, 15] and leads to a reduction of electron-phonon coupling [13]. The decrease of the multiphonon relaxation rate increases the quantum efficiency from excited states of RE ions, thus increasing their emission lifetime [16, 17]. In addition, fluorotellurite glasses show an enhancement of RE radiative transition rates

and a spectral broadening of their photoluminescence (PL) emission bands due to their high refractive index and the variety of sites for the RE ions [7, 16]. In particular, fluorotellurite glasses belonging to the $\text{TeO}_2\text{-ZnO-ZnF}_2$ system are promising RE hosts to be used in active optical applications, since they present high absorption cross-section [13, 17], broad emission (≈ 150 nm) that covers S, C+L and U telecommunication bands when codoped with Er^{3+} and Tm^{3+} [18], and laser emission has been demonstrated in the case of Nd^{3+} doped fluorotellurites [19]. Finally, we have recently reported the synthesis of fluorotellurite glass-ceramics, which opens a new range of applications [20].

The practical application of RE doped glasses in integrated devices requires first the fabrication of high quality thin films a few microns thick with good PL performance. Different chemical and physical methods have been attempted to produce RE doped thin film glasses such as sol-gel, chemical vapor deposition, sputtering or pulsed laser deposition (PLD) [21, 22, 23, 24, 25]. In particular, PLD has demonstrated to be a very versatile technique to produce thin films and it has been successfully applied to the synthesis of good quality tellurite, oxyfluoride silicate or phospho-tellurite glasses having a complex stoichiometry [24, 26, 27, 28].

The aim of this work is to transfer the excellent performance of RE-doped bulk $\text{TeO}_2\text{-ZnO-ZnF}_2$ glasses to the thin film configuration. We demonstrate that Er^{3+} -doped oxyfluoride $\text{TeO}_2\text{-ZnO-ZnF}_2$ thin films with good optical properties can be produced at room temperature using reactive PLD in O_2 atmosphere. However, the optimization of their PL performance at $1.5\ \mu\text{m}$ requires a post-deposition annealing of the films, which leads to a large increase of the emission intensity and lifetime of the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition. This behavior is related to the improvement of the film surface morphology and the reduction of the OH^- concentration in the films upon annealing.

2. Experimental procedure

Fluorotellurite thin film glasses were produced by PLD using an ArF excimer laser (LPX-Pro, Lambda Physik: $\lambda = 193$ nm, $\tau = 20$ ns FWHM, repetition rate = 10 Hz) focused on a bulk fluorotellurite glass with nominal composition 74.6 TeO₂–8.8 ZnO–16.6 ZnF₂:0.7 ErF₃ (mol%). The target was prepared by the conventional melt-quenching technique as described elsewhere [20]. Film deposition was carried out in a vacuum chamber evacuated to 10⁻⁵ Pa and then filled with a dynamic oxygen flow of 10 Pa. [28]. The target-substrate distance was 40 mm and the laser beam was focused on the glass surface at 45° with an energy density of 2 J/cm².

Thin film glasses were deposited at room temperature on silicon and fused silica substrates that were previously ultrasonically cleaned with acetone and ethanol. Both target and substrate were rotated during film deposition to prevent fast target surface damage and to ensure film homogeneity. As-grown film (RT-film) glasses underwent thermal treatments in air at temperatures $\leq 320^\circ\text{C}$ to activate the photoluminescence of Er³⁺ ions.

Bulk and film composition was determined using ion-beam techniques. Te, Er, Zn, and O contents were determined by Rutherford backscattering spectrometry (RBS) using two different incident beams (H⁺ at 1.5 MeV and ⁶Li⁺ at 3 MeV) and the SIMNRA code to analyze the experimental spectra [29], while Proton induced Gamma-ray emission (PIGE) was used to determine the fluorine content in the samples by using an incident proton beam at 2.3 MeV and looking at the Gamma ray peaks at 110 y 197 keV coming from the ¹⁹F(p,p' γ) ¹⁹F reaction [30]. The oxidation state of the cations was measured by X-ray photoelectron spectroscopy (XPS). XPS measurements were performed with a Perkin-Elmer PHI 5400 spectrometer equipped with an Al K α X-ray source ($h\nu = 1486.6$ eV). The area of analysis was 1 mm². In order to take into account the charging

effects on the measured binding energies, they have been determined by referencing to the adventitious C 1s peak at 284.8 eV. The intensities were estimated by calculating the area under each peak after smoothing and removing the background using the modified method of Shirley and adjusting the experimental curve to a Gaussian-Lorentzian ratio variable curve using an iterative algorithm.

The glass network structure was analyzed by Raman spectroscopy using a confocal Raman microscope (Renishaw inVia) equipped with a He-Cd laser emitting at $\lambda_{\text{exc}} = 442$ nm that was focused on the samples using a $\times 100$ magnification objective (spectral resolution: 2 cm^{-1}). The output laser power was 30 mW. Rayleigh and anti-Stokes scattering were removed using an edge filter and the signal was detected by means of an electrically refrigerated CCD camera [28]. Acquisition time was 10 min for each spectrum. Substrate contribution was carefully subtracted in the case of thin films samples. The surface morphology of thin films was characterized using a HITACHI Scanning Electron Microscope SU8000 operating at 1 kV, whereas surface roughness was analysed using a multimode AFM (Veeco Metrology).

Spectroscopic ellipsometry has been carried out to determine the parameters $\tan\Psi$ and $\cos\Delta$ of thin films using a VASE ellipsometer (J.A. Woolam Co.) at three angles of incidence (60° , 65° , and 70°) in the wavelength range from 400 to 1600 nm. Real (n) and imaginary (k) parts of the refractive index, and film thickness were obtained by fitting the ellipsometric data using a Cauchy-type dispersion for n , an exponential decay for k and the Marquardt–Levenberg iterative algorithm [31]. The experimental error for n is ± 0.01 , while in the case of k is 1% for values above our experimental resolution limit (10^{-4}). Transmission spectra of bulk and thin films were recorded using a Cary 5000 spectrophotometer in the 200–2000 nm wavelength range, while the presence of OH^-

groups has been investigated using a FTIR spectrometer (Bruker IFS 66) with a resolution of 4 cm⁻¹.

Steady-state PL emission measurements were made at room temperature using a diode laser emitting at 980 nm as excitation source. The fluorescence emission at 1.5 μm was analyzed with a 0.25 m monochromator, detected with an extended IR Hamamatsu R5509-72 photomultiplier and finally amplified by a standard lock-in technique. The room temperature lifetime of the ⁴I_{13/2} level was obtained by exciting the samples at 980 nm. Luminescence decay curves at the peak of the emission spectrum were processed by a Tektronix digital oscilloscope.

3. Results

3.1 Optical characterization

Figure 1 compares the transmittance of bulk glass and a representative RT-film glass deposited on fused silica. We observe in both cases a large transmittance and a sharp edge. If we define the optical cutoff as the wavelength at which $T = 0.5 T_{MAX}$ [32], this occurs at $\lambda_B \approx 390$ nm and at $\lambda_F \approx 330$ nm for the bulk and the thin film glasses, respectively. This apparent blue shift of the absorption edge for the thin film is a consequence of its reduced thickness, which was confirmed by measuring films with different thickness: the thicker the film, the longer its optical cutoff. The transmittance of the bulk glass is about 80 % for wavelengths larger than 450 nm and shows the characteristic absorption bands due to Er³⁺ transitions from the fundamental to higher energy levels, whereas the thin film presents a slightly higher transmission (> 85 % for $\lambda > 360$ nm). In addition, we clearly observe interference fringes in the case of the RT-film, whose number and intensity are related to its refractive index and thickness, which reflects the good optical quality of the as-grown films. The absorption bands related to Er³⁺ are not observed for thin film glasses due to their reduced thickness and the

masking effect of the interference fringes. The inset in Fig. 1 shows the dispersion of the real part of the refractive index (n) in the 400-1600 nm spectral range obtained from the ellipsometric data both for bulk and RT-film glasses. In both cases n presents a strong decay for wavelengths up to 700 nm and a slow decrease at longer wavelengths. The bulk glass shows a value in the infrared region ($n > 2$) that is slightly higher than that of the RT-film ($n > 1.94$). The thickness of the film glass was found to be $\approx 1 \mu\text{m}$ from the ellipsometric data. Finally, the imaginary part of the refractive index (k) of RT-films, not shown here, has a high value in the vicinity of the absorption edge ($k \approx 10^{-1}$ at λ_F) and it diminishes below our experimental resolution limit ($k < 10^{-4}$) in the transparency spectral range ($\lambda > 400 \text{ nm}$).

Figure 1. Transmittance spectra of (---) bulk glass and (—) a RT-film glass deposited on fused silica. The transmittance of (- · - · -) a bare fused silica substrate is included for comparison. The inset shows the dispersion of n for bulk and RT-film glasses.

3.2 PL emission

PL intensity is very low in the case of RT-film glasses. Thus, RT-films were annealed in air in consecutive steps at increasing temperatures (T_{ann}) in the range 270-320 °C for 2-3 hours at each temperature, in order to improve the PL response. Figure

2a shows the evolution of the PL intensity at 1.53 μm for a film that underwent successive annealings at increasing temperatures. The increase of PL emission intensity is small for $T_{\text{ann}} \leq 300$ $^{\circ}\text{C}$, while it increases significantly for $T_{\text{ann}} = 310\text{-}315$ $^{\circ}\text{C}$, reaching a 20 fold increase with respect to the RT-film after annealing at 315 $^{\circ}\text{C}$. A further annealing at 320 $^{\circ}\text{C}$ led to a decrease of PL intensity due to the degradation of the adherence of the film to the substrate, thus annealing at higher temperatures was not attempted. This suggests that the optimal annealing temperature is in the range 300-315 $^{\circ}\text{C}$. The inset in Fig. 2a compares the PL spectrum in the 1.4-1.7 μm range obtained for a film that was step annealed at 300 $^{\circ}\text{C}$ for 3 hours, then at 310 $^{\circ}\text{C}$ for 3 hours and finally, at 315 $^{\circ}\text{C}$ during 2 hours (AN-film) with that of the bulk glass. Both spectra present a similar shape and they peak at 1.53 μm , whereas the FWHM is slightly narrower in the case of the film (57 ± 1 nm) than that of the bulk (65 ± 1 nm).

Figure 2. (a) Evolution of the PL emission intensity at 1.53 μm with the annealing temperature for thin film glasses. (b) Relation between τ_{PL} and annealing temperature (T_{ann}) for a fluorotellurite film (AN-film) annealed in three consecutive steps. Insets in (a) and (b) compare: (a) the room temperature normalized photoluminescence emission spectrum of the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ emission and (b) the fluorescence decay of the $^4\text{I}_{13/2}$ level for (---) the bulk glass and (—) an AN-film. The horizontal dashed line in (b) indicates the lifetime of the bulk glass.

Figure 2b shows the evolution of the lifetime of the $^4I_{13/2}$ level (τ_{PL}) measured for the fluorotellurite film after each step annealing in the temperature range 300-315°C. As it is illustrated in the inset of Fig. 2b for the case of an AN-film, the decay curve of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition can be fitted by a single exponential function, similarly to what was observed for the bulk glass [17]. τ_{PL} increases from 2.3 ms up to 3.3 ms by increasing the annealing temperature from 300 to 315 °C (Fig. 2b). However, this value is still shorter than the τ_{PL} of the bulk glass (3.8 ms).

3.3 Structure and morphology of thin film glasses

There are different factors such as Er clustering, the presence of structural defects or a high OH⁻ concentration in the glass matrix [8, 33, 34] that may lead to PL quenching in the case of RT-thin film glasses, which otherwise present excellent optical properties as shown in Fig. 1. Thus, we have investigated their composition, structure and morphology. Table I compares the atomic composition for bulk, RT-film and AN-film glasses in at. % ([X], with X= Te, Zn, Er, O and F) determined from RBS and PIGE analysis.

Table I: Measured atomic composition (in at. %) for bulk and both RT- and AN-film glasses.

	[Te]	[Zn]	[Er]	[O]	[F]
Bulk	23.7 ± 2.4	11.6 ± 1.2	0.3 ± 0.1	58.4 ± 6.0	6.0 ± 0.6
RT-film	22.4 ± 2.2	8.3 ± 0.8	0.1 ± 0.1	65.9 ± 6.6	3.3 ± 0.3
AN-film	24.4 ± 2.4	8.6 ± 0.9	0.1 ± 0.1	64.0 ± 6.4	2.7 ± 0.3

We observe an increase of [O] in the films with respect to the bulk glass that is in the range of ≈10-20 %, whereas [F] decreases by a ≈50 %. In the case of the cations, [Zn] shows a moderate decrease with respect to [Te], whereas a precise comparison between bulk and film glasses in the case of [Er] is difficult since its content is very small.

However, from the results obtained we can conclude that [Er] does not show a significant variation in the films with respect to the bulk glass. Finally, annealing at $T_{\text{ann}} \leq 315$ °C does not induce significant compositional changes.

The increase of [O] in the films indicates a change in the stoichiometry with respect to the bulk glass. In the case of TeO_x sputtered films, the increase of the oxygen content led to the formation of TeO_3 [35]. Thus, XPS and Raman analysis have been performed to clarify the chemical nature of the glasses and the effect of the excess of oxygen on the glass structure. Figure 3 shows the O *1s* and Te *3d* photoelectron spectra for bulk, RT-film and AN-film glasses. The O *1s* core spectrum (Fig. 3a) shows the existence of two types of bonds: a main contribution from oxides (which appears at 530.2 ± 0.1 eV) and a smaller shoulder (≈ 531.9 eV) that is related with hydroxides and C-O/C=O compounds. The area of the shoulder band is $\approx 25\%$ of the total area and it peaks at 531.9 ± 0.2 eV in all cases. In the case of the Te *3d* core-level spectrum, the peak positions do not show a significant variation in the films with respect to the bulk glass, corresponding to TeO_2 in all cases. However, when looking in detail at the Te $^3d_{5/2}$ band (Fig. 3b), a shoulder at the low BE side of the band can be observed. In the case of bulk glass for which this shoulder is much more intense than for glass films, this contribution is attributed to the presence of a small fraction of a Te suboxide ($\sim 6\%$) and metallic Te ($\sim 6\%$). In the case of RT- and AN-film glasses, $\sim 97\%$ of Te is present in the form of TeO_2 , while the rest is in the form of a Te suboxide. Table II summarises the obtained BE for O *1s* core electrons and Te $^3d_{5/2}$ core-level transitions.

Figure 3. (a) O $1s$ and (b) Te $3d_{5/2}$ photoelectron spectra for the bulk, RT-film and AN-film glasses. The deconvolution of the O $1s$ and Te $3d_{5/2}$ spectra is illustrated in the figure for the case of AN-films and the bulk glass, respectively.

Table II: Binding energies (BE in eV) and areas (A in %) of the O $1s$ and Te $3d$ XPS peaks for the bulk, RT-film and AN-film glasses. The values given in the parenthesis correspond to the shoulder peaks in the case of O $1s$ and Te $3d_{5/2}$.

Sample	O $1s$ BE	O $1s$ A	Te $3d_{5/2}$ BE	Te $3d_{5/2}$ A
Bulk	530.19	69.3	575.83	84.6
	(531.66)	(26.3)	(574.00)	(5.6)
			(573.04)	(6.1)
RT-film	530.37	77.1	576.14	95.3
	(532.02)	(22.9)	(574.20)	(2.8)
AN-film	530.26	76.5	576.01	97.5
	(531.92)	(23.5)	(574.00)	(2.5)

Figure 4 shows the normalized reduced Raman spectra measured for the bulk glass, RT- and AN-film glasses in the $250\text{--}900\text{ cm}^{-1}$ range. Raman spectra of similar bulk glasses have been previously reported and discussed [9, 13, 20, 36], and thus here we compare them with the results obtained for the thin film glasses. Like in other tellurite glasses, the cut-off frequency of the optical phonon modes is $\approx 850\text{ cm}^{-1}$, which reduces multiphonon relaxation of Er^{3+} ions with respect to silica glasses (cut-off at $\approx 1100\text{ cm}^{-1}$) [6, 8, 9] and the spectra present the distinctive bands of tellurite glasses at $400\text{--}500\text{ cm}^{-1}$ (A), $600\text{--}700\text{ cm}^{-1}$ (B) and $700\text{--}800\text{ cm}^{-1}$ (C).

Figure 4. Normalized Raman spectra of bulk, RT- and AN-film glasses.

Bands A and B are associated to the vibration of symmetric and antisymmetric Te–O–Te linkages, respectively, which are related to a continuous network built up by $[\text{TeO}_4]$ trigonal bipyramids (tbp's), whereas band C is related to symmetric stretch of non-bridging oxygen (NBO) bonds associated to $[\text{TeO}_{3+1}]$ polyhedrons and $[\text{TeO}_3]$ trigonal pyramids. The addition of Zn deforms and breaks $[\text{TeO}_4]$ groups to form $[\text{TeO}_{3+\delta}]$ and $[\text{TeO}_3]$ units, which increases the relative intensity of band C and leads to a large distribution of structural sites [8, 9, 13, 36]. We have analyzed the structural changes in the thin film glasses by deconvoluting the Raman spectra in three Gaussian bands (Table III).

Table III: Peak position (in cm^{-1}), relative intensity (I_p) and Area of Raman bands determined for bulk, RT- and AN-film glasses.

Band	Bulk glass			RT-film			AN-film		
	Peak	I_p	Area	Peak	I_p	Area	Peak	I_p	Area
A	438	27	40	455	24	30	457	17	23
B	658	70	62	662	63	58	663	59	58
C	760	100	106	769	100	108	766	100	97

Raman spectra of RT- and AN-films are very similar. We observe a shift toward higher wavenumbers of the band peaks with respect to the bulk glass in both cases. In addition, the relative area of bands A and B with respect to band C decreases. Finally, we qualitatively compare the fraction of NBO in the bulk and film glasses from the ratio of the intensities of peak C (related to NBO) to the peak B (related to $[\text{TeO}_4]$ tbp's) [28]. This ratio (I_C/I_B) increases from 1.42 in the case of the bulk to 1.59 (RT-film) and 1.69 (AN-film), which indicates the breaking of the 3-D network of $[\text{TeO}_4]$ tbp's and the formation of $[\text{TeO}_3]$ groups in the films.

To conclude the structural characterization, the surface morphology of the film glasses and the concentration of OH^- groups both in the bulk and film glasses were studied. SEM micrographs of RT- and AN- films are presented in Figs. 5a and 5b, respectively. They show a uniform surface composed by small particles with typical diameters $\varnothing < 100$ nm, that belong to the same plane. Only few large particles and clusters of agglomerated particles are observed in both cases. However, the boundaries between the particles can be distinguished clearly in the case of the RT-film (Fig. 5a). This implies that its microstructure presents interconnection voids which increase the film porosity. On the contrary, the AN-film shows a more compact microstructure where only few boundaries between adjacent particles are observed (Fig. 5b). This fact should lead to both a reduction of the surface roughness and the porosity of the annealed film. AFM measurements allowed determining the mean surface roughness (root mean squared, rms) of RT- and AN- films that is ~ 12 nm and ~ 8 nm, respectively, thus confirming that annealing treatments improve film quality. It is worth noting that the mean surface roughness of the RT-film is lower than the typical mean roughness (16 nm) reported for oxyfluoride silicate films synthesized by PLD at 200 °C [24].

Figure 5. Plane-view SEM images of: (a) RT-film and (b) An-film.

We have finally studied the mid-IR absorption spectrum of the different samples in order to analyse the evolution of OH⁻ content upon film deposition and subsequent annealing. Figure 6 compares the experimental spectrum of the bulk glass with those of the RT- and AN-films. All the spectra exhibit a broad band in the range from 2500 cm⁻¹ to 3500 cm⁻¹, which can be assigned to stretching vibrations of OH⁻ groups [9,15]. It is clearly seen that the absorbance of the bulk glass ($\alpha_M = 0.2 \text{ cm}^{-1}$) is much smaller than that of the as-grown ($\alpha_M = 600 \text{ cm}^{-1}$) or annealed film glasses ($\alpha_M = 50\text{-}160 \text{ cm}^{-1}$).

Figure 6. Near Infrared absorption spectra of bulk, RT- and AN-film glasses.

We have deconvoluted the IR absorption spectra into three bands related to strongly bounded ($\sim 2200 \text{ cm}^{-1}$), weakly bounded ($\sim 2900 \text{ cm}^{-1}$) and free ($\sim 3400 \text{ cm}^{-1}$) OH^- groups. Weakly bounded OH^- groups dominate the absorption band of the bulk glass; however, the main contribution to IR absorption in the case of RT-films is related to free OH^- groups. The intensity of the OH^- absorption decreases as we increase the duration of the thermal treatment to reach a value that is only 150 times the absorbance of the bulk glass for the films step annealed up to 315°C (AN-film). In this case, the band related to free OH^- groups has almost disappeared and only the bands related to bounded OH^- groups are observed. We have estimated the concentration of OH^- groups using the expression [14]:

$$N_{\text{OH}} = \frac{N_{\text{Av}}}{\epsilon} \alpha \quad [1]$$

$$\text{with} \quad \alpha = \frac{1}{L} \ln\left(\frac{1}{T}\right)$$

where N_{Av} is the Avogadro constant, α the sample absorption coefficient (in cm^{-1}), L the sample thickness (in cm) and T its transmittance. Finally, ϵ is the molar absorptivity

corresponding to OH⁻ groups in silicate glasses ($49.1 \times 10^3 \text{ cm}^2/\text{mol}$) [12]. Table IV presents the relative area of the bands corresponding to OH⁻ groups, the maximum α and the calculated concentration of OH⁻ groups both for bulk and film glasses.

Table IV: Maximum absorption coefficient (α_{MAX}), relative area (in %) of the absorption bands related to free (Free OH⁻), weakly bounded (Weak OH⁻) and strongly bounded (Strong OH⁻) OH⁻ groups for bulk, RT- and AN-film glasses. The OH⁻ concentration (N_{OH}) calculated from Eq. 1 is included for the different samples.

	α_{MAX} (cm^{-1})	Area (%)	N_{OH} (10^{20} cm^{-3})
Bulk:			
Strong OH ⁻	0.25	14	0.03
Weak OH ⁻	0.56	80	0.07
Free OH ⁻	0.11	6	0.01
Total OH ⁻			0.11
RT-film:			
Strong OH ⁻	192	7	24
Weak OH ⁻	960	72	118
Free OH ⁻	520	21	64
Total OH ⁻			206
AN-film:			
Strong OH-	132	20	16
Weak OH-	212	70	26
Free OH-	49	10	6
Total OH ⁻			48

4. Discussion

The experimental results presented in Fig. 1 show that PLD at room temperature allows the synthesis of thin film glasses (RT-film) with good optical properties (high n , low k) and transparency range. Moreover, the observation of well-defined interference fringes in the experimental transmission spectrum (Fig. 1) evidences the deposition of homogeneous thin films [24, 35] with a large refractive index contrast with respect to the substrate ($n_{\text{SiO}_2} \approx 1.44$ at $1.53 \mu\text{m}$). The structure of film glasses is characterized by an increase on the relative concentration of [TeO₃] groups and a decrease of the glass

network connectivity with respect to the bulk glass that is evidenced by the increase of the I_C/I_B ratio and the decrease of the area of band associated to the vibration of symmetric Te–O–Te linkages (band A in Fig. 4 and Table III). This should lead to an increase of the refractive index of film glasses (n_F) with respect to the bulk glass (n_B) [8,28]. Instead, as we observe in the inset of Fig. 1, n_F is slightly smaller than n_B ($\sim 3\%$ at 1500 nm). This behavior has been previously observed for other thin films glasses fabricated by PLD [26, 28, 37] or TeO_x films produced by rf-sputtering [35] and it has been attributed to a reduction of the glass density. This is likely related to the decrease of the kinetic energy of the laser generated species that reach the substrate and the incorporation of oxygen to the growing film during the deposition process, as it has been previously observed in either oxide or oxyfluoride tellurite thin film glasses, such as $\text{TeO}_2\text{-WO}_3\text{-La}_2\text{O}_3$, $\text{TeO}_2\text{-TiO}_2\text{-Nb}_2\text{O}_5$ or $\text{TeO}_2\text{-P}_2\text{O}_5\text{-Na}_2\text{O-ZnF}_2$ [27, 28, 37], produced by PLD in an O_2 environment.

However, the significant [O] enrichment observed in the films ($\approx 5\text{-}10$ at. %) cannot be compensated by the relative loss of [F] during film deposition (≈ 3 at.%) (Table I). Thus, the question is: Where the excess of oxygen can be accommodated? There are several possibilities. Oxygen adsorption on the thin film glass surface is one of them; but the low k value measured for thin film glasses, the observation of well defined interference fringes in their transmission spectra (Fig. 1) and the surface morphology (Fig. 5) suggests the deposition of homogeneous thin films with low porosity, which lead us to discard oxygen adsorption as the responsible process.

The formation of oxygen rich defects, such as NBO hole-center, peroxy linkage/radical or interstitial oxygen that can take place in the case of silica could also account for the oxygen enrichment [38]. However, the presence of oxygen rich defects is unlikely to occur in tellurite glasses. A third alternative would be a further oxidation the cations,

which in our case should be related to the oxidation of tellurium from Te^{+4} to Te^{+6} , as it has been observed in tellurium oxide thin films produced by rf-sputtering [35]. However, as it is shown in Figure 3, XPS analysis of the deposited film glasses clearly demonstrates the absence of Te^{+6} in either RT- or AN-films.

The comparison of the PL response for RT- and AN-films gives a hint about the origin of the oxygen excess. As it is shown in Fig. 2, AN-films present a much large PL emission than RT-films. Thus, since $[\text{Er}]$ is similar for RT- and AN-films and slightly smaller than for the bulk glass, Er clustering [33] seems unlikely. Instead, the quenching of the near-infrared emission at $1.5\ \mu\text{m}$ is most likely related to the large concentration of OH^- groups observed in RT-films (Fig. 6). N_{OH} is more than 3 orders of magnitude higher in RT-films than in the bulk glass (Table IV). This leads to a very large N_{OH}/Er ions ratio (> 102) and suggests that. Thus, nonradiative energy transfer processes from excited RE ions to hydroxyl ions are likely to occur and they play a major role in the nonradiative decay of the $^4\text{I}_{13/2}\ \text{Er}^{3+}$ level since the energy gap between the $^4\text{I}_{13/2}$ and $^4\text{I}_{15/2}$ levels is bridged by the vibration of two OH^- groups ($\sim 6000\ \text{cm}^{-1}$) [34], which reduces dramatically the PL emission of RT-films.

The large OH^- content in glass films produced by PLD is not unusual. Irannejad et al. [37, 39], reported quenching of photoluminescence in Er-doped phospho-tellurite films synthesized by PLD on substrates held at $100\text{-}200\ ^\circ\text{C}$, which was related to post-deposition incorporation of molecular water that led to a IR absorption $10^3\text{-}10^4$ times larger than that of the bulk glass. The deposition of a silica capping layer reduced the molecular water content in the films. Yet, an IR absorption two orders of magnitude larger than that of the bulk glass was still observed, although in this case was related to weakly bounded OH^- groups [39]. Contrary to phospho-tellurite films, RT-fluorotellurite films deposited in the present work do not show any post-deposition

incorporation of molecular water, since no band 3700 cm^{-1} is observed (Fig. 6) and, moreover, the IR spectra of one year old films are similar to that of recently grown/annealed films. RT-films were produced from a bulk target having low OH^- concentration ($\sim 10^{19}\text{ cm}^{-3}$, Table IV). Thus, their large OH^- content suggests that the incorporation of OH^- groups to the produced films takes place during the deposition process itself.

Thermal annealing at temperatures above $300\text{ }^\circ\text{C}$ for a time long enough, but below the glass transition temperature ($< 320\text{ }^\circ\text{C}$) leads to the significant reduction of weakly bounded and free OH^- groups, while the effect on strongly bounded OH^- groups is much smaller (Fig. 6 and Table IV). This reduces the N_{OH}/Er ratio down to ≈ 30 and thus, the probability of radiative deexcitation of Er^{3+} increases and the PL emission experiences a large enhancement, as it is shown in Fig. 2. Moreover, annealing allows improving the optical quality of the films by smoothing their surface and reducing the interconnection voids between the grains as demonstrated by SEM analysis (Fig. 5). This aspect may also contribute to the improvement of the PL response of annealed films. However, as shown in Fig. 2, the PL lifetime is a $\approx 20\%$ shorter than that of the bulk, which clearly indicates that non-radiative deexcitation is still relevant and that further refinement of film glass deposition and thermal treatment is required.

Conclusions

Er^{3+} -doped $\text{TeO}_2\text{-ZnO-ZnF}_2$ thin film glasses having good optical properties (high refractive and broad transparency range) have been produced by PLD at room temperature in an O_2 atmosphere. Their glass structure is similar to that of the bulk glass, although the concentration of $[\text{TeO}_3]$ groups is slightly larger and they are oxygen rich. This excess of oxygen is not related to the presence of TeO_3 , but to the very large OH^- content ($\sim 10^{22}\text{ cm}^{-3}$), which is 10^3 times larger than in bulk glasses, observed in the

as-grown films. This leads to a strong quenching of the near-infrared $^4I_{13/2} \rightarrow ^4I_{15/2}$ Er emission at 1.53 μm .

Post-deposition thermal step-annealing in air at temperatures in the range 300-315 $^{\circ}\text{C}$ leads to a significant increase of PL intensity and lifetime. Thermal annealing affects neither the composition nor the glass structure of the films. Thus, the activation of the photoluminescence is related to the significant decrease of the OH^- concentration in the films upon annealing ($\sim 10^{21} \text{ cm}^{-3}$). OH^- concentration in the annealed films remains stable with time, which suggests that the incorporation of OH^- groups to the films takes place during film deposition and not after it. Upon the best annealing conditions considered in the present work we achieved a 20-fold increase of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ emission intensity with respect to as grown films and a single-exponential decay of the $^4I_{13/2}$ level with a maximum lifetime of 3.3 ms. However, even if the OH^- content of annealed films is strongly reduced it is still large enough to induce a non negligible nonradiative relaxation of excited Er^{3+} ions as the lifetime measured for the bulk glass is 3.8 ms. Thus, further refinement of the film glass deposition process is required.

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