

The influence of nanocrystallization process on thermal and optical parameter in oxyfluoride glasses

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The influence of nanocrystallization process in oxyfluoride glasses $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{LaF}_3-\text{NaF}$ doped with rare earth (RE) ions on their thermal and optical properties is studied. The thermal characteristics of oxyfluoride glasses (OG) with Tm^{3+} , Yb^{3+} are presented. The effect of the glass crystallization on thermal stability of the glass and crystallizing phases formed upon heat treatment is investigated by DTA/DSC and XRD methods. It has been found that the effect of nanocrystallization of LaF_3 and incorporation of RE elements in formed upon heat treatment nanocrystallites depends on the kind of rare earth elements and is determined by factors of crystallochemical nature and requires adequate proportions between the components forming glass structure.

The ellipsometric investigations are performed by M2000 spectroscopic ellipsometer. These measurements allowed us to determine dispersion of refractive indices in the range 190–1700 nm and depolarization coefficients. The influence of nanocrystallization process on refractive indices is discussed.

Keywords: oxyfluoride glasses, rare earth elements, thermal and optical properties.

1. Introduction

In recent years, an increasing interest has been devoted to rare earth doped oxyfluoride glasses, particularly oxyfluoride transparent glass ceramic, because of their potential use for making optical devices, such as solid lasers and optical amplifiers, transparent host materials based on rare earth (RE) ions [1]. Among numerous host materials, transparent oxyfluoride glass ceramics, which combine the advantages of the excellent optical properties of fluoride and high chemical and thermal stability of oxide, have attracted a great deal of attention [2]. An RE doped LaF_3 single crystal, characterized

by the low phonon energy and large transfer coefficient between the RE ions, has been revealed to be a suitable host to achieve laser and up-conversion. It is well known that up-conversion is difficult to generate in conventional oxide glasses due to their high phonon energies, corresponding to the stretching vibrations of the oxide glass network former. But oxide glasses might be much better for practical applications because of their high thermal stability, chemical durability and not complicated fabrication [3]. Rare earth ions are preferentially incorporated into crystalline phases with small phonon energies of 350 cm^{-1} . Consequently, excited-state lifetimes and optical absorption cross-sections of the doped RE ions become substantially larger in them than in vitreous environments [4]. The glass host matrices are based on silicates with mechanically and chemically desirable characteristics. The lanthanum trifluoride LaF_3 is a classical host for studying thermal and optical properties of the trivalent RE ions.

1.1. Spectroscopic ellipsometry measurements

Ellipsometry technique uses light of known polarization incident on a surface under study and detects the polarization state of the reflected light [5].

Spectroscopic ellipsometry (SE) data can be acquired from ultraviolet to near infrared. SE determines two angles Ψ and Δ , with:

$$\rho = \tan \Psi = \frac{r_p}{r_s} e^{i\Delta} \quad (1)$$

where r_p and r_s are complex Fresnel reflection coefficients for p and s polarizations, respectively, and Δ is a phase shift between both polarized waves. The fundamental ellipsometry equation (1) allows determination of thickness of a film and the spectral dependences of optical constants (*i.e.*, the refractive index n and extinction coefficient k). Ellipsometric measurements also permit determination of the depth profile and surface roughness, as has been done in this work. In each spectral range, different properties of materials are studied. However, the data must be analyzed to obtain useful information.

An optical model representing the assumed physical geometry and microstructure is developed, and Fresnel reflection coefficients calculated, allowing predictions of Ψ and Δ to compare with measured values. Model parameters, such as n , k and roughness σ , vary in regression until the comparator function, such as mean square error, is minimized. The resulting parameters are the “best fit” values of n , k , and σ .

1.2. Experimental details

For each batch, the starting materials of high purity were fully mixed and melted in a covered platinum crucibles in an electric furnace at the temperature range from 1400 to 1450 °C in air. The melts were poured out onto a steel plate forming a layer thickness of 2 to 5 mm and then cast into a brass mould followed by annealing at a temperature of 100 °C below the glass transition temperature determined by differential scanning calorimetry (DSC) to relinquish the inner stress. The following

Table 1. Composition of the rare earth doped oxyfluoride glasses.

Glass No.	Composition [mol%]						
	SiO ₂	Al ₂ O ₃	Na ₂ O	LaF ₃	NaF	Tm ₂ O ₃	Yb ₂ O ₃
O	42.55	31.32	10.08	14.50	1.55	–	–
O1	36.56	26.89	9.33	25.32	1.81	0.09	–
O2	36.56	26.89	9.33	25.32	1.81	–	0.09
O3	36.57	26.89	9.33	25.32	1.82	0.03	0.03

raw materials were used to prepare the batches: SiO₂, Al₂O₃, Na₂CO₃, LaF₃, NaF, Tm₂O₃ and Yb₂O₃. The compositions of the glasses are listed in Tab. 1. The crystallization ability of the glasses obtained was determined by DTA/DSC measurements conducted on the Perkin–Elmer DTA-7 System operating in heat flux DSC mode. The samples (60 mg) were heated in platinum crucibles at a rate 10 °C/min in dry nitrogen atmosphere to the temperature 1000 °C. All glasses revealing the effect of ceramization process were selected for further thermal treatment. To obtain the ceramming effect the glasses were heated 20 min at a temperature of the maximum of the exothermal peak. The transparent glassy samples with 2–5 mm in thickness so produced were then cut into square coupons of about 1 cm², and heated to the ceramming temperature at a rate of 10 °C/min, held for 10 min, then cooled down to room temperature naturally to obtain transparent glass ceramics.

1.3. Ellipsometric study

The spectroscopic measurements of Ψ and Δ for the layers presented were performed with the use of Woollam M2000 spectroscopic ellipsometer in spectral range from 190 to 1700 nm. The samples were measured for two angles of incidence (60°, 65°). To analyze the data, we combined all angular spectra and we fitted all data simultaneously. The data have been analyzed using CompleteEASE 3.65 software. Also, the depolarization coefficient versus light wavelength has been determined.

2. Experimental results

The DTA and DSC thermal analysis are sensitive to changes in the chemical composition of the glass and they are very easy methods to determine the characteristic temperature of glasses. From DTA/DSC curves the vitreous state transformation (glass transition temperature T_g), crystallization temperature T_{cryst} , as well as the thermal effect accompanying them can be determined. In the course of cooling or heating the glass demonstrates the phenomenon of jump-like change of the molar heat C_p similarly to the phase transition of the 2-nd order according to Ehrenfest's thermodynamic classification. The change in the value of C_p accompanying the glassy state transition (ΔC_p), determined from the DSC curves is related to the degree of rearrangement of the glass structure connected with this transition and depends on the strength of modified bonds with the components of the glass network.

Figure 1 shows the DSC curve of an as-prepared oxyfluoride glass doped with 0.09 mol% of Tm_2O_3 and Yb_2O_3 , respectively. The DSC curve shows a glass transition temperature T_g and exothermal effects, one just above T_g temperature which is connected with ceramming process and the second one which occurs in higher temperatures. These exothermal effects indicate the same crystallization phases but the first crystallization effect is connected with crystallization of LaF_3 as a nanocrystallite and the second one with crystallization of LaF_3 but in micro-sizes. The thermal stability factor ΔT has been frequently used as a rough estimate of the glass stability. To achieve a large working range of temperature during sample fiber drawing, it is desirable for a glass host to have ΔT as large as possible.

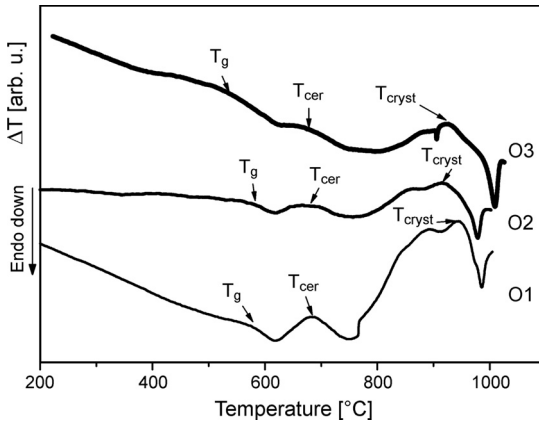


Fig. 1. DTA/DSC curves of rare earth doped oxyfluoride glasses.

From Table 2, it could be observed that the values of T_g , T_{ceram} , T_{cryst} , and ΔT of O1, O2 glass increased evidently compared to reference glass samples O. From DTA/DSC curves of O1, O2, O3 glass it can be seen that the kind of rare earth ions has a great influence on ceramming process. The maximum of ceramming temperatures increases with addition of Tm^{3+} and Yb^{3+} ions. Simultaneously, the enthalpy (ΔH_{cer}) of this process becomes reduced. This is the evidence of an increasing ability of the glass for ceramization, manifested by a decreasing value of the thermal stability index of the glass ΔT_2 . Simultaneously, the glass transition temperature is

Table 2. Thermal characteristics of rare earth doped oxyfluoride glasses ($\Delta T_1 = T_{max.cer} - T_g$, $\Delta T_2 = T_{max.cryst} - T_g$).

Glass No.	T_g [°C]	ΔC_p [$Jg^{-1}°C^{-1}$]	$T_{max.cer}$ [°C]	ΔH_{cer} [Jg^{-1}]	1-st stage of crystal. (ceram.)	$T_{max.cryst}$ [°C]	ΔH_{cryst} [Jg^{-1}]	ΔT_1 [°C]	ΔT_2 [°C]
O	576	0.810	664	18.04	LaF_3	908	41.15	88	332
O1	593	0.491	671	53.25	LaF_3	953	69.59	78	360
O2	592	0.251	668	21.61	LaF_3	933	78.85	76	341
O3	560	0.252	657	19.69	LaF_3	959	159.34	97	399

shifted towards higher temperatures with addition of RE ions compared to glass O without RE. The addition of Tm^{3+} and Yb^{3+} ions causes the reduction of the specific heat (ΔC_p) accompanying the glass transition region, which may be the evidence of an increased flexibility of the glass network.

The XRD measurements were performed on as-prepared glass and its corresponding glass-ceramic. The XRD pattern for as-prepared glass presented in Fig. 2, does not show diffraction peaks, indicating its amorphous structure by nature. But in Fig. 3a, the mild diffraction peaks for sample O1 heat treated at 671 °C for 10 min have appeared. The marked peaks are matched with the diffraction peaks of crystalline LaF_3 reported earlier [2, 4, 6]. From XRD studies one can see in the case of glass O1 doped with Tm^{3+} ions that the heat treatment of this glass in the ceramming temperature 671 °C for 10 min causes appearance of very weak diffraction peaks of crystalline LaF_3 . In the case of glass O2, the addition of Yb^{3+} ions causes appearance of very well visible diffraction peaks of crystalline LaF_3 , when the glass is heat treated at the maximum ceramization temperature of 668 °C for 10 min (Fig. 3b).

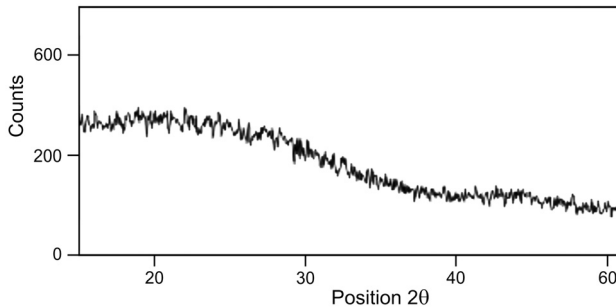


Fig. 2. XRD pattern for the host matrix glass prepared.

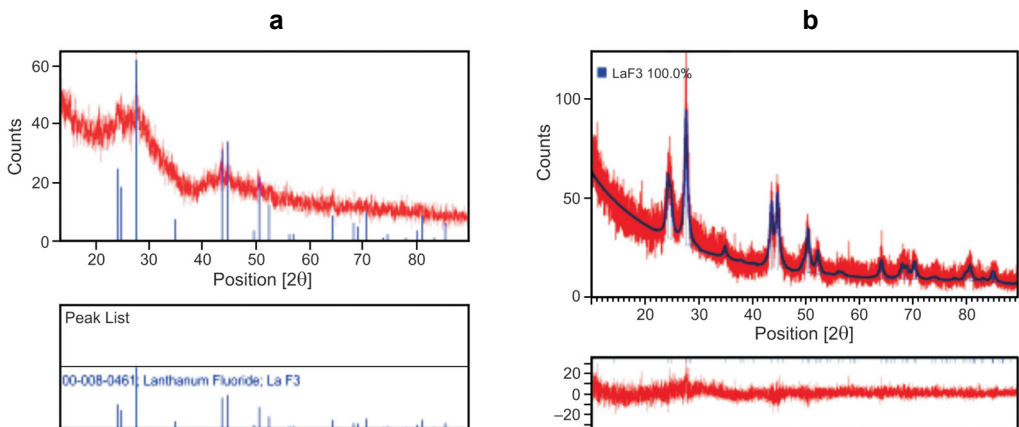


Fig. 3. XRD pattern of glasses O1, O2 after ceramization process; O1, 671 °C, 10 min (a), O2, 668 °C, 10 min (b).

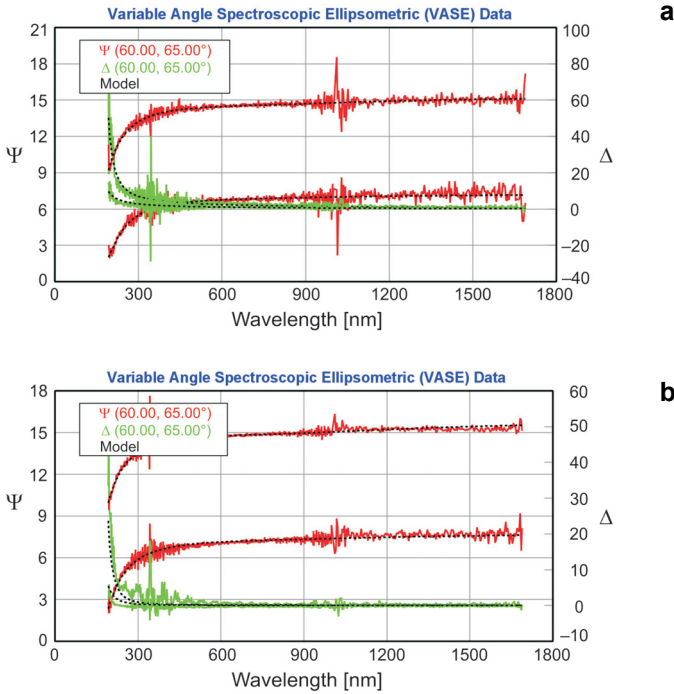


Fig. 4. Spectral dependence of ellipsometric angles measured for O1 (a) and O2 (b) samples, respectively.

The spectral dependence of ellipsometric angles for samples O1 and O2 is shown in Fig. 4. In the same figure, the values of Ψ and Δ generated using the fitting Cauchy model are given.

The Cauchy model describes dispersion relations for n and k indices namely:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \tag{2}$$

$$k(\lambda) = ke^{\beta\left(\frac{hc}{\lambda} - E_{\text{bandedge}}\right)} \tag{3}$$

where A , B , C and β are constant terms. The k and E_{bandedge} are the fit parameters which describe Urbach’s tail absorption and allow the shape of dispersion of extinction

T a b l e 3. Values of parameters determined from ellipsometric measurements.

Sample no.	A	$B \times 10^{-4}$	$C \times 10^{-4}$	$k \times 10^{-4}$	Roughness [nm]	n at 633 nm
O1	1.306±0.017	2.21±0.3	1.77±0.16	3.4±0.2	4.19±0.29	1.312
O2	1.366±0.018	28.7±0.2	1.40±0.10	7.1±0.5	1.13±0.10	1.374

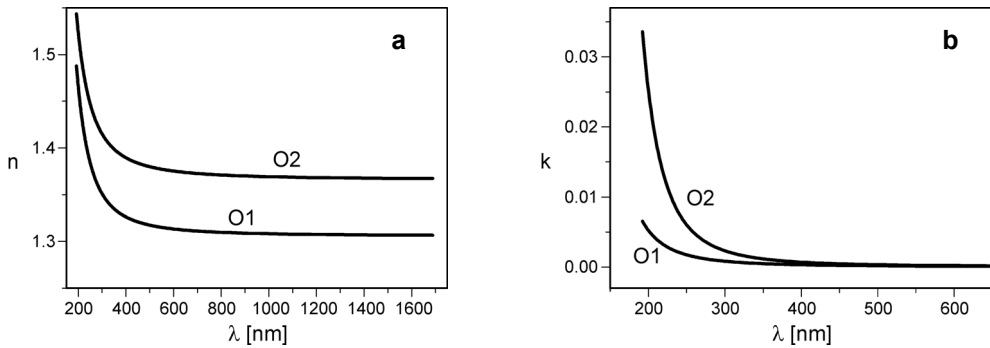


Fig. 5. Cauchy dispersion dependences for refraction indices n (a) and extinction coefficients k (b).

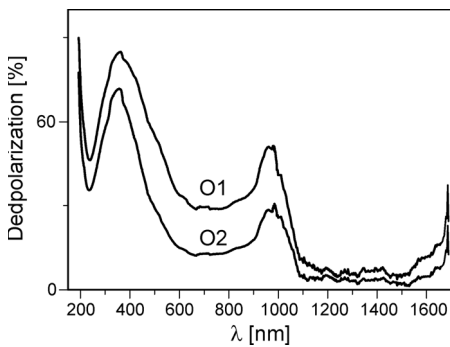


Fig. 6. Degree of depolarization of reflected radiation from O1 and O2 samples versus wavelength.

coefficient to be determined. The values of these fit parameters for O1 and O2 samples are presented in Tab. 3. Figure 5 shows the n and k dispersive relations in spectral range from 190 to 1700 nm for the samples under study. Ellipsometric results allow surface roughness to be determined. In the samples investigated we assumed the appearance of the surface roughness which can be described using the Bruggeman effective medium approximation (EMA) [7]. This approximation uses a 50:50 mixture of the material and air on the sample surface to get optical constants that approximate the effect of the surface roughness. The obtained values of σ are presented in column 6 of Tab. 3.

The oxyfluoride glasses (OG) doped with Tm ions exhibits lower optical parameters than the one with Yt ions. Generally, the OG host matrix shows higher refractive index in UV–VIS0–NIR range than rare earth doped glass.

Additionally, for the samples under investigation the depolarization coefficients [8] (ratio of incoherent part to the total reflected radiation) have been determined. The results of depolarization state of reflected radiation of the samples are showed in Fig. 6.

The reflected light beam may consist of two or more components with well defined polarization states. Yet, the resultant total beam does not exhibit a single well defined polarization state. There is so in the case of a nonuniform film, or transparent

substrate exhibiting back reflection effects as is for the glass samples [9]. However the depolarization coefficient of reflected beam is much bigger than other mentioned effect. This is because of depolarizing light in the bulk of OG glasses.

3. Conclusions

Stable glasses could be prepared in a relatively large composition domain of the NaF–LaF₃ system. Unfortunately, the effect of LaF₃ crystallization as the only nanocrystalline phase, which is indispensable from the optoelectronics point of view, is strongly dependent on the rare earth content with respect to the kind of those ions.

The thermal properties of rare earth (RE) ion doped glass depend strongly on local environment of RE, and therefore differences in the DTA/DSC curves are expected if they are placed in a glassy or in a crystalline surrounding of the glass ceramic. The advantages of oxyfluoride glass ceramic are that the rare earth ions would be incorporated selectively into the fluoride crystalline phase LaF₃ after crystallization, and these materials possess good transparency due to the much smaller size of precipitated crystals than the wavelength of visible light. The thermal stability factor ΔT has been frequently used as a rough estimate of the glass stability.

The index of refraction of oxyfluoride glasses is low (~ 1.4) in visible range. RE ions lower the refractive index of oxyfluoride host matrix. The doping of RE ions causes change in coefficients n and k . The Yt ions doped to modify optical constants enter the host matrix much more than the same quantity of Tb ions.

The depolarization of reflected beam results from light scattering in the bulk and backscattering from the bottom surface of OG wafer. Depolarized light comes mainly from scattering on nanocrystals appearing in the host matrix. The presence of RE ions enhance nanocrystallization in OG glasses.

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