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Structural, thermal and spectroscopic properties of highly Er3+-doped novel oxyfluoride glasses for photonic application

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ABSTRACT

The Er^{3+}-doped novel oxyfluoride glasses of composition $(43-x)SiO_2$–$10Al_2O_3$–24LiF–$23SrF_2$–xEr_2O_3, where x = 1.0, 2.0, 4.0 and 6.0 mol%, have been prepared by conventional melt quenching technique and are characterized through X-ray diffraction (XRD), differential thermal analysis (DTA), Raman, Fourier transform infrared (FT-IR) analysis, optical absorption spectra, visible (vis) and near-infrared (NIR) emission spectra measurements. Judd–Ofelt (JO) intensity parameters (Ω_λ, λ = 2, 4 and 6) have been derived from the absorption spectrum of 1.0 mol% Er_2O_3 doped glass and are in turn used to calculate radiative properties for the important luminescent levels of Er^{3+} ions. The studied glasses show intense green and weak red visible emissions under 365 nm excitation. The decrease in visible emission intensities with concentration of Er^{3+} ions has been explained due to energy transfer processes between Er^{3+} ions. Upon excitation at 980 nm laser diode, an intense 1.53 μm NIR emission has been observed with the maximum full width at half maximum (FWHM) for Er^{3+}-doped oxyfluoride glasses. The higher Er^{3+} ion doping capability and relatively high gain and broad emission at 1.5 μm are the most notable features of these glasses to realize efficient short-length optical amplifiers.

1. Introduction

In recent years, there has been an extensive research on glass hosts with low phonon energy and high stability, which are ideal for doping rare earth (RE) ions as they reduce multiphonon de-excitation between RE ion energy levels and favor the observation of some transitions with improved quantum efficiency in IR region. Such materials have numerous applications in the field of photonics [1]. Among the various oxide glasses, silicate glasses which are the most chemically and mechanically stable, have only very faint upconversion luminescence due to their large phonon energies [2]. However, oxyfluoride glasses are expected to have chemical durability and thermal stability that representing a compromise between pure fluoride and oxide glasses with flexible optical properties [3], particularly very intense up conversion.

Er^{3+}-doped glasses are especially attractive for numerous applications such as microchip lasers [4,5], erbium-doped fiber amplifier (EDFAs) in wavelength division multiplexing (WDM) systems [6,7], near infrared telecommunication windows [8], eye safe laser systems [9] and lidar transmitters [10]. In addition, the Er^{3+} and/or Tm^{3+} ion doped fibers make it possible to amplify signals in the range of C-band, 1530–1565 nm or S-band, 1460–1530 nm. Though single or co-doped RE based glass fibers/waveguides are of great promise, the focus has been concentrated mostly on silicate glasses although their amplified spontaneous emission (ASE) bandwidths are limited to few tens of nanometers (~40 nm). RE co-doped fluoride and tellurite glasses have shown ASE with considerably extended bandwidth, where the emission broadness arises due to inter-ion energy transfer. By and large, the suitability of RE doping and the proper choice of glass matrix are still unclear [11,12]. In general, the RE emission in glassy matrix is strongly dependent on crystal-field effects, local environment where the ion is situated, phonon energies, refractive index and precise details about defect energy levels (Urbach tails) extended into the band gap.

In the present paper, we investigated their XRD, DTA, Raman, FT-IR, optical absorption, visible and NIR emission properties of Er^{3+}-doped oxyfluoride glasses. XRD pattern is used to know the nature of the structure. Differential thermal analysis (DTA) curve have been measured to know the glass transition (T_g) and onset of crystallization (T_x) temperatures. Raman and FT-IR spectra are used to study the structure of vibration modes. The intensity of the

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transitions can be calculated by using the Judd–Ofelt (JO) theory [13,14]. This theory defines a set of three intensity parameters Ω_λ (λ = 2, 4 and 6) which are sensitive to the environment of the RE ions. These intensity parameters are used to calculate radiative properties for the important luminescent levels of Er^{3+} ions. A detailed study of visible and NIR emission properties has been carried out. The results are examined with respect to the concentration effects, and are compared with the other reported glass systems.

2. Experimental details

Er^{3+}-doped oxyfluoride glasses with a chemical composition of $(43 - x)SiO_2$–$10Al_2O_3$–24LiF–$23SrF_2$–xEr_2O_3 glasses (referred as SALSFEr10, SALSFEr20, SALSFEr40 and SALSFEr60 for x = 1.0, 2.0, 4.0 and 6.0 mol%, respectively) have been prepared by conventional melt quenching technique. About 20 g of the batch compositions was thoroughly mixed in an agate mortar and the homogeneous mixture was taken in a platinum crucible and kept in an electric furnace at a temperature of 1450 °C for about 90 min. The melt was then poured on to a preheated brass mold at a temperature of 450 °C and then the glass samples were annealed at this temperature for 15 h to remove thermal strains. The samples were then allowed to cool to room temperature and polished for optical measurements.

The physical properties such as optical path length was measured by using screw gauge, density was determined by Archimedes's method using distilled water as an immersion liquid and refractive index was measured using an Abbe refractometer at sodium wavelength (589.3 nm) with 1-bromonapthalene ($C_{10}H_7Br$) as a contact liquid. The physical and optical properties of the Er^{3+}-doped oxyfluoride glasses are presented in Table 1. XRD curve were made with an X-ray diffractometer (Smart lab-RIGAKU) using the Cu-Kα radiation. Differential thermal analysis (DTA) measurements were determined by DTA at a heating rate of 10 °C/min using SDT Q600 V8.3 Build 101 Differential thermal analyzer. Raman spectrum was recorded by using a high resolution NRS-3300 laser Raman spectrophotometer (JASCO) system equipped with a DPSS green diode laser (532 nm) as the excitation source. FT-IR spectrum of the glass sample was recorded on a FT-IR-200E spectrometer (JASCO) with KBr pellet technique from 4000 cm^{-1} to 450 cm^{-1}. Absorption spectrum was measured on a Perkin Elmer Spectrophotometer (Lambda-950) in the wavelength range of 300–1700 nm. The visible and NIR emission spectra were measured with a monochromater (DK240) with a PMT by exciting at 365 nm LED and at 980 nm LD, respectively. All measurements were carried out at room temperature.

3. Results and discussion

3.1. XRD and DTA analysis

The XRD pattern of the Er^{3+}:SALSFEr10 glass, shown in Fig. 1, exhibits broad scattering at lower angles, which is the characteristic long range structural disorder and confirms the amorphous nature of the prepared glasses.

Table 1
Physical and optical properties of SALSF:Er^{3+}-doped oxyfluoride glasses.

Properties	SALSF:Er^{3+}			
	1 mol%	2 mol%	4 mol%	6 mol%
Optical path length, l (cm)	0.135	0.212	0.213	0.218
Density, d (g/cm^3)	3.398	3.636	3.878	4.141
Concentration, C (10^{20} ions/cm^3)	2.724	5.642	11.029	16.373
Refractive index (n)	1.582	1.593	1.612	1.634
Optical band gap, E_{opt} (eV)	3.62	3.58	3.55	3.45
Urbach energy, ΔE (eV)	0.28	0.35	0.42	0.49

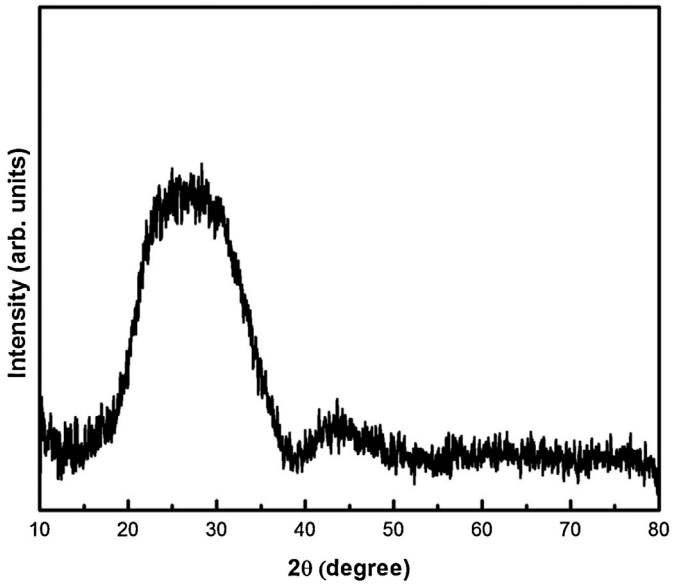

Fig. 1. XRD curve of SALSFEr10 glass.

Fig. 2 shows the DTA curve of 1.0 mol% Er^{3+}-doped SALSFEr10 glass. The glass transition temperature (T_g), the first (T_{x1}) and the second (T_{x2}) crystalline temperatures are found to be 480, 600 and 730 °C, respectively. Generally the difference between T_{x1} and T_g ($\Delta T = T_{x1} - T_g$) is usually chosen as a rough measure of glass formation ability or glass stability against crystallization [15]. The larger value of ΔT gives a larger working range during operations for fiber drawing. If $\Delta T > 100$ °C, the glass can be considered as a glass with relatively good thermal ability [16]. The ΔT for SALSFEr10 glass is found to be 120 °C. Therefore, the glasses which exhibit a higher thermal stability are the better candidates for rod/fiber fabrication due to the correspondingly small chance of crystallization problems. The fiber drawing is a reheating process and any crystallization during the process will increase the scattering loss of the fiber and then degrade the optical properties, hence, it is desirable for a glass host to have ΔT as large as possible. According to early reports [17,18], SiO_2 has long been recognized as a good glass former, adding SiO_2 into glass can enhance the thermal

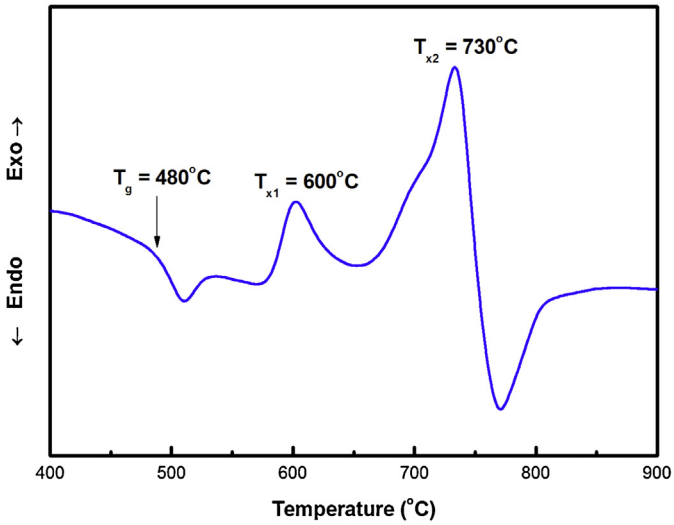

Fig. 2. DTA curve of SALSFEr10 glass.