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Novel erbium-doped TeO_2-based oxysulfide glasses: thermal and spectroscopic properties

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Abstract

Er^{3+}-doped TeO_2-based oxysulfide glasses have been prepared in argon atmosphere in carbon crucibles. The thermal analysis and spectroscopic properties of Er^{3+} have been considered in terms of sulfide influence. As a function of composition, we have principally measured optical absorption, spontaneous emission and lifetime measurements. Judd-Ofelt theory was introduced to calculate bandwidth and emission cross-section. The results show the product FWHM$\times\sigma_e$ increase from 476.88 to 635.04 10^{-21} cm^2 nm evidently with the addition of 10 mol% PbS into tellurite glass, which indicates a perfect effect on spectra property of Er^{3+} ions.

Keywords: Glasses; Optical materials and properties; Thermal properties

1. Introduction

Tellurite glasses have scientific and technological interest due to their relatively higher refractive indices and dielectric constants and lower phonon energies compared for instance with the well known silicate or phosphate glasses. The refractive indices allow the utilization of these glasses for non-linear optical materials [1] and the phonon energies have at least two important consequences improved infrared (IR) transmission (up to 6 μm) and low multiphonon decay rates for rare earths excited states as compared to silicate and phosphate glasses. Tellurite glasses are therefore potential candidates for IR transmitting devices [2], especially for potential applications in wavelength division multiplexing system of telecommunication network [3].

The transmission from 0.5 to 10 μm makes sulfide glasses a promising host for rare earth dopants [4]. Research in the rare-earth oxysulfide systems of glasses has been focuses mainly on the oxysulfides of lanthanum with varying proportions of Ga_2S_3 [5,6]. These glasses show much better chemical stability and are more resistant to atmospheric attack in comparison with the corresponding sulfide glasses [7]. The main drawback to the effective application of oxysulfide glasses is the reliance on preparation routes requiring heat treatments in closed systems [8].

It maybe takes on perfect physical and spectroscopic properties as adding sulfide to tellurite glasses. In this paper, we firstly report a synthesis method of TeO_2-based oxysulfide glasses. For evaluating spectroscopic properties, the absorption and emission spectra were determined and interpreted with the aid of the Judd-Ofelt theory [9,10], which has been successfully applied to most of the lanthanide ions. The three strengths parameters Ω_t (t=2, 4, 6) were determined from the UV/visible absorption spectra of the glasses. From these parameters, the emission cross-section, bandwidth and lifetime were estimated.

2. Experimental

Glasses samples were prepared according to the following compositions in mol%: $65TeO_2$–$5B_2O_3$–$(30-x)$PbO–xPbS–

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$0.5Er_2O_3$ (x=0, 10) with the purity of Er^{3+} ions being 99.99%. The appropriate mixtures were put into a tubular furnace and gradually heated. In order to avoid volatilization of sulfur and sulfide chemical attack of the silica tubes during the melting process, the starting materials have been placed in carbon crucibles, which were placed inside a silica tube for melting under argon atmosphere. The glasses were obtained by melting at 850 °C for 20 min, then the melts were annealed to room temperature under argon atmosphere in 48 h. All the glass samples obtained were homogeneous and transparent as seen with the naked eyes. Samples for optical and spectroscopic properties measurements were cut and polished to the size of $20\times10\times1$ mm^3.

The index of refraction was measured at 656.3 nm, with a precision V-prism refractometer (made in China) using H_2 and Na lamps as spectral source. DSC scans were conducted with a Perkin-Elmer DSC7 instrument, at a heating rate of 10 °C min^{-1}, between 200 and 700 °C. The absorption spectra were measured using a Perkin-Elmer 900 spectrophotometer in the range 400–1700 nm. The emission spectra were obtained by exciting the samples with LD980 nm as pumping laser. The fluorescence lifetimes were measured by exciting the samples with the same LD980 nm as above and detected by a S-1 photomultiplier tube. All the measurements were taken at room temperature.

3. Results and discussion

3.1. Density, refractive index and thermal analysis

The density and refractive index of glass samples are presented in Table 1. It is shown that densities and refractive indices increase with PbO substituted by PbS of 10 mol%. Due to the molecular weight of S^{2-} is bigger than O^{2-}, with the replacement of the O^{2-} ions by S^{2-} ions, the average molecular weight of unit volume enhances, which results in densities increasing. Correspondingly, the refractive index also increases.

Fig. 1 compares the compositional dependence of the onset crystallization temperature (T_x), the glass transition temperatures (T_g) and the difference between T_x and T_g ($\Delta T=T_x-T_g$) between the two glass samples. The difference between T_x and T_g, ΔT, has been frequently used as a rough estimate of the glass formation ability or glass stability. Larger ΔT value, better glass stability [11]. It is shown that the ΔT is 142.3 °C as x=0, while the ΔT is 130.3 °C as x=10, which demonstrates that the thermal stability of the glass decreases with the replacement of O^{2-} by S^{2-} ion.

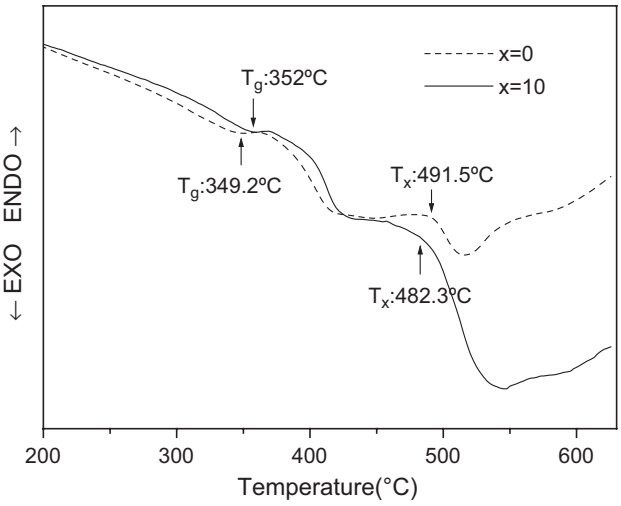

Fig. 1. DSC scans of the glasses with different content of PbS.

3.2. Effect of PbS on Judd-Ofelt parameters

Fig. 2 shows the absorption spectrum of Er^{3+} ion of the glass sample of x=10 mol% in the 400–1700 nm regions. The excited states responsible for observed bands were assigned on the basis of the reported energy level diagram of Er^{3+} in a LaF_3 host [12]. The part absorption corresponding to the transitions $^4I_{15/2}\rightarrow{}^4I_{13/2,11/2,9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$ and $^2H_{9/2}$ have been observed. Using these absorption spectra, we have calculated the Judd-Ofelt intensity parameters Ω_t (t=2, 4, 6) by least squares fitting. According to previous studies [13], the Ω_2 parameter is sensitive to the symmetry of the rare earth site and the covalency between rare-earth ions and ligand anions; the rigidity of the network surrounding the rare-earth ion was suggested to influence the magnitude of Ω_4 and Ω_6. The covalency between Er^{3+} and ligand anions is related with the local basicity around the rare-earth sites, which can be adjusted by the composition or structure of the glass host. Table 1 presents the Ω_t (t=2, 4, 6) parameters of Er^{3+} in the glasses with and without S^{2-}. Apparently, the three Ω_t (t=2, 4, 6) parameters increase from 6.48 to 6.53, from 1.99 to 2.02 and from 1.36 to 1.38, respectively, with PbS instead of PbO. Because the presence of S^{2-} around Er^{3+} should be probable resulting in an increase of the covalency between Er^{3+} and ligand anions, the value of Ω_2 increases accordingly. Moreover, the presence of

Table 1
Comparing with physical and spectroscopic properties between TBP and TBPS glasses

Series	ρ (g/cm^3)	n_d	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	Ω_6 (10^{-20} cm^2)	FWHM (nm)	σ_e (10^{-21} cm^2)	$\sigma_e\times$FWHM	Lifetime (ms)
x=0	6.01	2.13	6.48	1.99	1.36	71.8	6.6	473.88	3.4
x=10	6.05	2.19	6.53	2.02	1.38	78.4	8.1	635.04	3.1