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Effect of optical basicity on broadband infrared fluorescence in erbium-doped germanate glasses

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ABSTRACT

In the case of alkali and alkaline earth germanate glasses, the effect of optical basicity on emission spectra at 1.55 μm of Er^{3+} ions is investigated. The results indicate that the bandwidth and intensity of emission spectra at 1.55 μm of Er^{3+} are controlled by the optical basicity of the host glasses. As the increase of the optical basicity, the 1.55 μm emission intensity of Er^{3+} ions is decreased. Based on the experimental results, the optical basicity, which is calculated from glass composition, could act as a guiding principle to obtain broadband fiber amplifier in wavelength division multiplexing systems.

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1. Introduction

Rapidly increasing Internet and data traffic are stimulating the demand for greater information transmission capacity of backbone and "metro" optical networks. To meet the needs of the capacity demand, wavelength division multiplexed (WDM) datacom transmission, has been proposed and used practically [1,2].

In order to increase the channel counts of WDM, one of the key technologies is to broaden the bandwidth limitation by erbium-doped broadband fiber amplifiers (EDFA). Thus, there are strong incentives to develop new broadband luminescent materials that can cover the whole WDM band and possess much larger FWHM. Much effort has been exerted to broaden and flatten the bandwidth of optical amplified materials [3–7]. The choice of appropriate glass host is very critical to achieve broadband luminescent materials at 1.55 μm. Considering the fact the spectral shape of 1.55 μm emission of erbium arise from the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition, which is related with both the electric-dipole (ED) transition and the magnetic-dipole (MD) transition, For Er^{3+} ion [8,9], the line strength S_{ED} of $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition is described by the Judd–Ofelt parameters Ω as follows:

$$S_{ED}[^4I_{13/2};{}^4I_{15/2}] = 0.019\Omega_2 + 0.118\Omega_4 + 1.462\Omega_6 \quad (1)$$

In Eq. (1), the Judd–Ofelt Ω_6 parameter plays a dominant role to enhance the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ optical emission. Therefore, in order to increase the emission bandwidth, the increase of the Ω_6 could effectively enhance the ED transition [10]. According to Judd–Ofelt theory, the parameter Ω_6 in glasses is in inverse proportions to covalence of the Er–O bond. And the covalence of the Er–O bond is related with the local cation field around the rare-earth sites, which can be adjusted by the introduction of network-modifying cations [11]. In other words, the large Ω_6 value is probably obtained from the low basicity of glass that contains nominally no non-bridging oxygen ions. Optical basicity is fundamentally related to the chemical bonding in solid and the optical properties of a material through the polarizability of electron clouds around atoms (ions) [12]. Qian et al. [13] reported the spectroscopic properties of Er^{3+}-doped Sb_2O_3–B_2O_3 glass, with the increasing concentration of Sb_2O_3, the electronic oxide ion polarizability, optical basicity and the covalent bonding character in the local ligand environments around Er^{3+} increase, while the Ω_6 parameter decreases. In the 30–70 mol% Sb_2O_3 range, FWHM changes from 91 to 76 nm, and the peak emission cross-section increases from 6.01×10^{-21} to 7.47×10^{-21} cm^2. The Er^{3+}-doped antimony-borate glasses exhibit higher $\sigma_e \times$ FWHM (567×10^{-28} cm^3) than that of Er^{3+}-doped tellurite- and germanate-based glasses. Optical basicity, originating in the chemistry community and hence closely tied to chemical bonding, ionicity, and electronegativity, should be considered a material property of a system as much as the aforementioned concepts.

Recently we reported the effect of optical basicity on Er^{3+} up-conversion luminescence in GeO_2–R_2O glasses [14], it is indicated that the lower optical basicity is propitious to the higher up-conversion luminescence intensity. Therefore, the aim of this work is to investigate the relationship between the spectral shape of 1.55 μm emission of erbium and the optical basicity of the glass.

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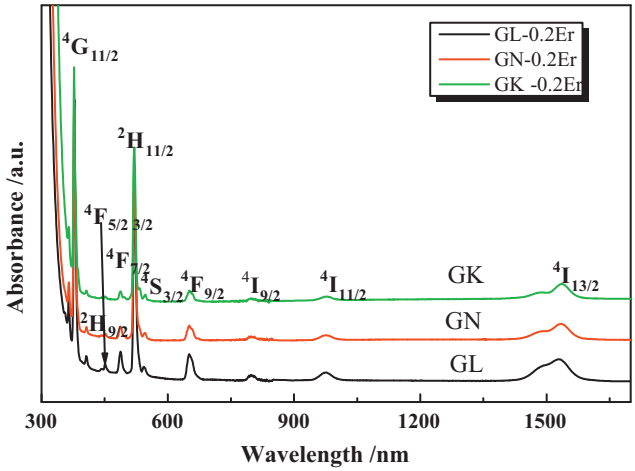

Fig. 1. Absorption spectra of Er^{3+}-doped germanate glasses.

In this paper, we measure emission spectra of Er^{3+} in alkali or alkaline earth germanate glasses, and discuss the correlation between emission bandwidth and optical basicity of the samples.

2. Experimental details

The compositions of the prepared glass were $85GeO_2$–$15R_2O$–$0.2Er_2O_3$ (R = Li, Na and K), $85GeO_2$–15RO–$0.2Er_2O_3$ (R = Mg, Ca, Sr, and Ba) and $(100-x)GeO_2$–xLi_2O–$0.2Er_2O_3$ (x = 5, 10, 20, 25, 30, 35). In this article, these samples are labeled by GL, GN, GK, GM, GC, GS, GB, GL5, GL10, GL20, GL25, GL30 and GL35, respectively. High purity Li_2CO_3, Na_2CO_3, K_2CO_3, $MgCO_3$, $CaCO_3$, $SrCO_3$, $BaCO_3$, GeO_2 and Er_2O_3 were used as starting materials. The weighed starting materials (about 10 g) were firstly ground and mixed thoroughly by using a mortar. Then, the mixture was compacted into a platinum crucible. After fusion at 900 °C for 30 min in an electric furnace, the mixture was melted at 1500 °C in a platinum crucible for an hour in air. When the melting was completed, the liquid was poured on a preheated stainless steel plates. The obtained glasses were annealed at the glass-transition temperatures. Finally, the glass samples were shaped into 10 mm × 10 mm × 3 mm and its surface was polished.

The optical absorption spectra were carried out in the wavelength range of 400–2000 nm at HITACHI U-4100 spectrophotometer. The fluorescence spectra in the wavelength range of 1400–1700 nm were measured at ZOLIX SBP300 spectrophotometer under 980 nm LD excitation. The fluorescence decay curves in near-infrared regions were recorded by using a FLS920 fluorescence spectrophotometer made by Edinburgh Instruments Ltd., UK. All the spectral measurements were performed at ambient temperature.

3. Results and discussion

The absorption spectrum of Er^{3+}-doped GL, GN and GK glasses is shown in Fig. 1. All relevant internal 4f–4f electronic transitions of Er^{3+} ions in the range of 300–1700 nm have been identified in this figure. The absorption spectrum consists of 10 absorption bands, each of which corresponds to the absorption from the ground level of $^4I_{15/2}$ to the excited levels. As can be seen in Fig. 1, the absorption intensity at 1.55 μm is decreased, with the increasing of the radius of alkali ion. In the case of GM, GC, GS, GB glasses, a similar phenomenon is observed. This result implies that the absorption intensity at 1.55 μm is related with the radius of alkaline earth ion.

To further investigate the relationship between near infrared fluorescence around 1.55 μm and the radius of alkali or alkaline earth ion, the fluorescence spectra in the near infrared region in the glasses pumped by 980 nm laser are shown in Fig. 2. The fluorescence decay curve of the GM, GC, GS and GB glasses are also shown in Fig. 2(c). As shown in Fig. 2(a) and (b), the emission intensity at 1.55 μm is decreased, with the increasing of the radius of alkali (or alkaline earth) ion. The curves of the singly 0.2 mol% doped Er^{3+} glasses exhibit nearly single exponential decay, as shown in Fig. 2(c). With the increasing of the radius of alkaline earth ion, the radiative lifetime of Er^{3+} at the excited level $^4I_{13/2}$ is decreased.

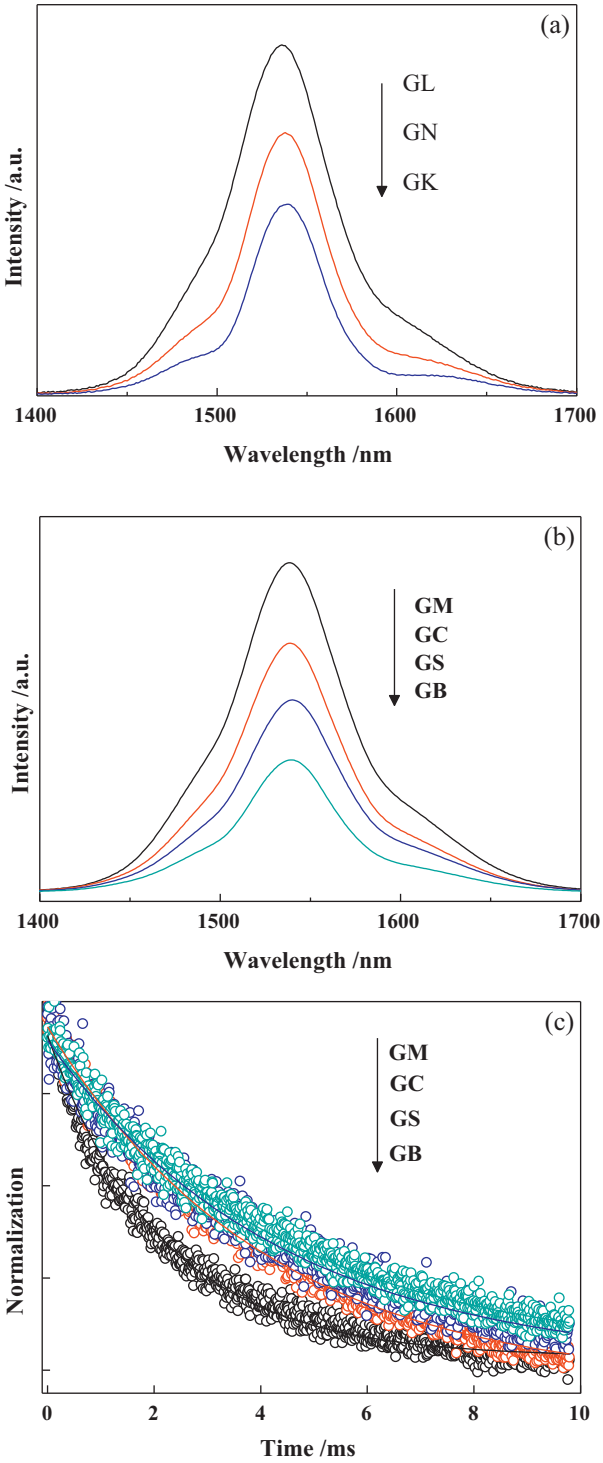

Fig. 2. Infrared fluorescence spectra of Er^{3+}-doped germanate glass under 980 nm laser excitation. (a) Er^{3+}-doped alkali germanate glasses GL, GN, GK and (b) Er^{3+}-doped alkaline earth germanate glasses GM, GC, GS and GB. (c) Fluorescence decay curve of GM, GC, GS and GB glass when pumped by 980 nm LD. Solid line shows the first-order exponential decay fitting result.

The lowest radiative lifetime is 2.10 ms of the GB glass. It is well known that ionic radius variety in the glasses can change glass local structures of Er^{3+} ions. Duffy and Ingram defined the optical basicity that is fundamentally related to the chemical bonding in solid and the optical properties of a material through the polarizability of electron clouds around atoms (ions) by electromagnetic waves [15]. The ionic radius changes, accompanies by a change in

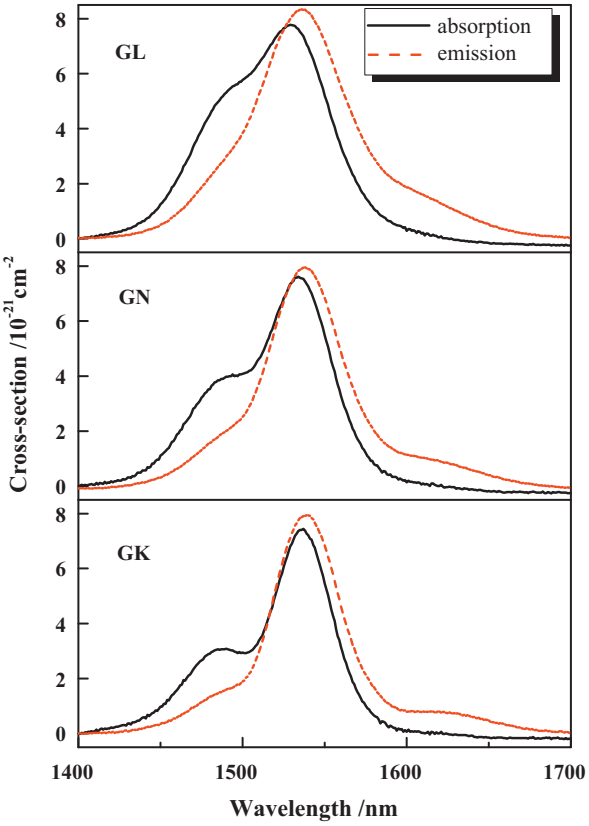

Fig. 3. Absorption and emission cross-sections of Er^{3+}-doped germanate glasses.

optical basicity. So, we calculated the optical basicity of each glass and examined the relationship between the optical basicity and the emission bandwidth.

The optical basicity Λ of glasses calculated from the empirical formula is follows [15]:

$$\Lambda = \frac{X_A^{a+}}{\gamma_A} + \frac{X_B^{b+}}{\gamma_B} + \cdots \quad (2)$$

where $X_A^{a+}, X_B^{b+}, \ldots$ are the equivalent fractions of $A^{a+}, B^{b+}, \ldots$ and $\gamma_A, \gamma_B, \ldots$ are the corresponding moderating parameters. Duffy clearly demonstrated the definition and utility of γ parameters in many glass systems [15–19]. This formula allows Λ to be calculated for many oxide glasses from its chemical constitution and the basicity moderating parameters of the various cations. The value of Λ obtained theoretically is an ideal optical basicity. The Λ values of each sample are listed in Table 1. As can be seen in Table 1, with the increasing of the radius of alkali (or alkaline earth) ion, or the concentration of Li_2O, the optical basicity is increased, and the radiative lifetime is decreased. According to optical basicity theory [12], the optical basicity can affect the refractive index of glasses. That is, with the increasing of the optical basicity, the refractive index is increased. Meanwhile, based on Judd–Ofelt theory, the radiative lifetime is decreased, when the refractive index is improved [20]. Therefore, with the increasing of optical basicity, the radiative lifetime at the 1.55 μm emission is decreased.

In order to make a deep research on the relationship between optical basicity and the spectral of 1.55 μm emission of Er^{3+} in the glasses. The absorption and emission cross-sections of Er^{3+}-doped germanate glasses will be calculated. Fig. 3 shows absorption and emission cross-sections of 1.55 μm fluorescence in Er^{3+}-doped

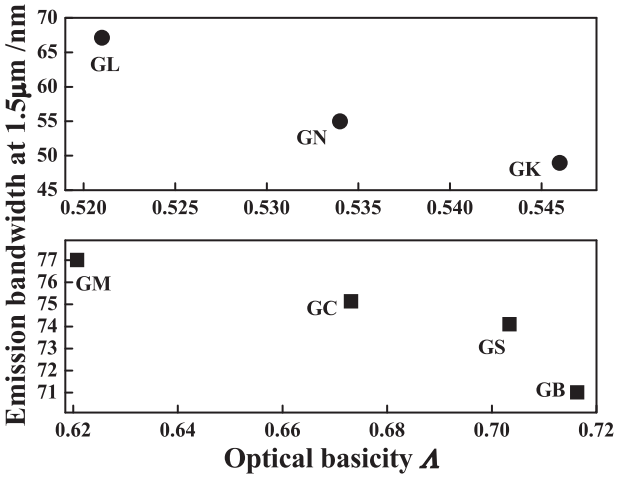

Fig. 4. Correlation between the calculated optical basicity and observed emission bandwidth in alkali and alkaline earth germanate glasses.

germanate glasses. The absorption cross-section of $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition could be obtained from the absorption spectra,

$$\sigma_{abs}(\lambda) = \frac{2.303 \log(I_0/I)}{Nl} \quad (3)$$

where $\log(I_0/I)$, l and N represent the optical density, sample thickness and RE-doping concentration, respectively. The stimulated emission cross-section of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition was calculated according to the McCumber theory [21]

$$\sigma_e(\lambda) = \sigma_a(\lambda) \exp\frac{(\varepsilon - h\upsilon)}{kT} \quad (4)$$

where σ_a and σ_e are absorption and emission cross-sections, respectively, h is the Planck constant, k is the Boltzmann constant, υ is the photon frequency, ε is the net free energy demanding to excite one Er^{3+} from $^4I_{15/2}$ to $^4I_{13/2}$ state at temperature T and can be calculated by the simplified procedure provided in Ref. [22]. The calculated values of absorption and emission cross-sections are listed in Table 1. The FWHM of each emission spectrum is also shown in Table 1.

In the alkali (or alkaline earth) glasses, with the increasing of the radius of the alkali ion, alkaline ion and the concentration of Li_2O, Maximum bandwidth of 67 nm, 81 nm and 66 nm are obtained when the alkali (or alkaline) oxide is Li_2O (or MgO) and the concentration of Li_2O is 5 mol%, respectively. Calculated peak emission cross-section σ_e^{peak} of the Er^{3+}-doped germanate glasses decrease with the increasing of optical basicity. This result indicates that the glass with lower optical basicity exhibits broader emission spectrum.

Fig. 4 shows the correlation between calculated the optical basicity and the emission bandwidth of the Er^{3+} doped germanate glasses. It is found that emission bandwidth of Er^{3+} becomes broader with decrease in optical basicity in the glasses. These results indicate that the basicity of host glass strongly affects the emission bandwidth of Er^{3+} ions that is independent on glass systems. Similar phenomena have been reported in Bi_2O_3 based, TeO_2 based, silicate and silica based glass systems [23]. In Bi_2O_3 based glasses, emission bandwidth showed tendency to increase with increase in B_2O_3 content, maximum bandwidth of 78 nm was reported, and the same emission bandwidth was obtained in the present investigated GM glass. Although the electronegativity of Bi (1.9) and Te (2.1) are larger than Ge (1.8), Bi_2O_3 based glasses and TeO_2 based glass show relatively small Λ. It is inferred that the effect of optical basicity on emission bandwidth is shown except only in the same glass matrix. Therefore optical basicity calculated

Table 1
Composition, optical basicity Λ, emission bandwidth and flourescence decay lifetimes of glasses.

	Glass											
	GL	GN	GK	GM	GC	GS	GB	GL5	GL10	GL20	GL25	GL30
Λ	0.521	0.534	0.546	0.621	0.673	0.703	0.716	0.489	0.505	0.537	0.553	0.585
FWHM (nm)	67	55	49	81	78	76	71	66	67	65	67	69
Decay lifetime (ms) ($^4I_{13/2} \rightarrow {}^4I_{15/2}$)	17.17	14.16	10.66	4.45	4.24	4.12	2.10	–	–	–	–	–
σ_a (10^{-21} cm^2)	7.78	7.61	7.44	8.01	7.82	7.67	7.56	7.84	7.80	7.59	7.48	7.30
σ_e^{peak} (10^{-21} cm^2)	8.34	8.05	7.94	8.55	8.38	8.13	7.89	8.22	8.20	7.99	7.91	7.83

from glass composition may work as a guiding principle to obtain broadband emission of Er^{3+} in the same glass matrix.

4. Conclusion

The correlation between the optical basicity and emission broadband infrared fluorescence of Er^{3+} is investigated in alkali and alkaline-earth germanate glasses. With the increasing of the radius of alkali and alkaline earth ion or the concentration of Li_2O, the optical basicity of the samples is increased. The emission bandwidth and intensity of Er^{3+} show well correlation to the optical basicity Λ; the samples with lower Λ show broadbander spectra and higher intensity. It is also inferred that the effect of optical basicity on emission bandwidth is shown except only in the same glass matrix, if not, it is necessary to lucubrate the relationship between the optical basicity and emission bandwidth. Therefore optical basicity calculated easily from the glass composition may work as a guiding principle to obtain broadband emission of Er^{3+} in the same glass matrix and to design EDF for broadband amplifier in WDM systems.

Acknowledgments

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