Spectroscopic properties of Er^{3+}-doped AlF_3-La_2O_3-Al_2O_3-SiO_2 glasses

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Er^{3+}-doped fluoride lanthanum aluminosilicate glasses with compositions of $(65 - x/2)SiO_2 \cdot (25 - x/2)Al_2O_3 \cdot xAlF_3 \cdot 9.1La_2O_3 \cdot 0.6Er_2O_3 \cdot 0.3Yb_2O_3$ (x = 4, 8, 12, 20, 30) (mol%) were prepared and their glass transition temperatures and spectroscopic properties were investigated. The Ω_2, Ω_4, and Ω_6 intensity parameters of glasses were calculated by Judd-Ofelt theory from absorption curves. It was found that glasses transition temperature and melting temperature decreased with the increase of fluoride content in glass, Ω_2 decreased gradually with the increase of AlF_3 content, but both Ω_4 and Ω_6 did not increase until AlF_3 content increased to 30 mol%. The quantum efficiency of $^4I_{13/2}$ to $^4I_{15/2}$ transition of Er^{3+} ions increases with the increase of AlF_3 content in glass. Fluorescent lifetime is longer in glass containing more AlF_3 content.

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Rare earth doped glasses have recently attracted more investigations due to their potential technological applications[1−5]. Some Er^{3+}-doped glasses have been widely used not only as fiber amplifier material[6] but also as bulk laser material[7,8]. For more efficient laser excitation, the improvement of host glasses' optical, thermal, and mechanical properties is needed. Lanthanum aluminosilicate (LAS) glass under investigation is a good host for Er^{3+} ions. These glasses present broad emission spectra, high transformation temperature, high mechanical strength, and high thermal conductivity coefficient.

However, LAS glasses have a high melting temperature of 1680 °C[9], which leads to the fabrication difficulty. This work aims at introducing aluminum fluoride into LAS glasses to decrease the melting temperature as well as to investigate the effect of AlF_3 content on the spectroscopic properties of Er^{3+}-doped LAS glasses.

The glasses with compositions $(65 - x/2)SiO_2 \cdot (25 - x/2)Al_2O_3 \cdot xAlF_3 \cdot 9.1La_2O_3 \cdot 0.6Er_2O_3 \cdot 0.3Yb_2O_3$ (x = 0, 4, 8, 12, 20, 30) (mol%) were melted at temperatures around 1450−1680 °C and annealed at temperatures near glass transition temperature for 4 hours. Then the glasses were cut and polished to dimensions of $5 \times 10 \times 20$ mm^3 for spectroscopic measurements. It was found that glass melting temperature decreases from 1680 °C in glass without AlF_3 to 1450 °C in that with 30 mol% AlF_3.

The refractive index was measured by V prism method, and the density measurements were made by the Archimedes method using the distilled water as the immersion liquid. The glass transition temperature (T_g) was determined from differential thermal analyzer (DTA) measurement. The absorption spectra were measured with a Perkin Elmer Lambda 900 spectrophotometer in 300 − 1700 nm wavelength range. The fluorescence spectra measurements were carried out at room temperature using a JY Spex TriAx 550 spectrofluorimeter equipped with a 974-nm, 2-W InGaAs laser diode as excitation source and an InGaAs detector. The fluorescence lifetime was measured with a Hitachi 100M oscillograph. The infrared (IR) transmission spectra of glasses, shown in Fig. 1, were measured by a Nicolet Nexus FT-IR Spectrometer.

The glass transition temperatures are listed in Table 1. We did not observe the crystal trend according to DTA curves of all samples. It can be found that T_g decreases with the increase of AlF_3 content in glass.

Table 1. Properties and Parameters of FLAS Glasses

Sample	[AlF_3]	T_g	n_D	$N_{Er^{3+}}$	Ω_2	Ω_4	Ω_6	δ_{rms}
	(mol%)	(°C)		(10^{20} cm^{-3})	(10^{-20} cm^2)			(%)
LAS[8]	0	886	1.6110	1.560	6.65	1.52	1.02	1.52
FLAS4	4	760	1.6024	2.278	6.76	1.61	1.07	0.83
FLAS8	8	760	1.5949	2.264	6.28	1.62	1.00	0.92
FLAS12	12	755	1.5970	2.306	6.26	1.69	1.03	0.96
FLAS20	20	740	1.5938	2.356	5.91	1.62	1.02	1.33
FLAS30	30	710	1.5909	2.351	5.94	1.74	1.19	2.37
Oxyfluoride[10]	—	—	—	—	3.22	1.34	0.61	—
Fluoride[10]	—	—	—	—	2.54	1.39	0.96	—
Fluoride[11]	—	—	—	—	2.91	1.27	1.11	—

T_g: glass transition temperature; n_D: refraction index; $N_{Er^{3+}}$: Er^{3+} ions concentration; δ_{rms}: root mean square deviation.

Table 2. Spectroscopic Properties and the OH^- Absorption Coefficient of FLAS Glasses

Sample	τ (ms)	A (s^{-1})	A_{rad} (s^{-1})	τ_{rad} (ms)	W_{nr} (s^{-1})	η (%)	$\sigma_{abs1530}$ (10^{-21} cm^2)	FWHM (nm)	$\alpha(OH^-)$ (cm^{-1})
LAS	5.7	175.40	140.00	7.00	35.40	74.00	—	60.0	—
FLAS4	5.4	185.19	127.26	7.86	57.92	68.72	5.57	49.5	1.25
FLAS8	6.4	156.25	120.18	8.32	36.07	76.91	5.43	49.5	0.70
FLAS12	4.4	227.27	123.41	8.10	103.87	54.30	5.64	50.5	1.77
FLAS20	5.6	178.57	121.15	8.25	57.42	67.84	5.50	50.5	0.93
FLAS30	6.1	163.93	132.58	7.54	31.36	80.87	6.22	54.0	0.83

τ: fluorescent lifetime; A: emission probability; A_{rad}: spontaneous emission probability; τ_{rad}: spontaneous emission lifetime; W_{nr}: non-spontaneous emission probability; η: fluorescence quantum efficiency; $\sigma_{abs1530}$: absorption cross-section at 1530 nm; FWHM: full width at half maximum; $\alpha(OH^-)$: absorption coefficient of OH^-.

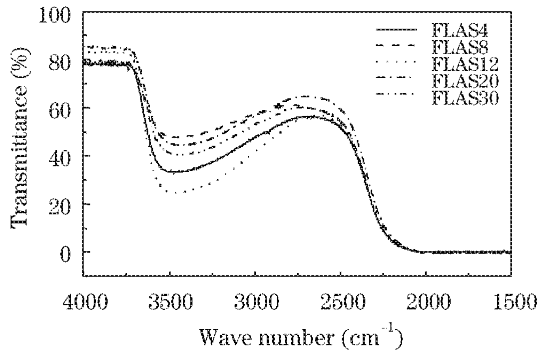

Fig. 1. IR transmission spectra of FLAS glasses.

Judd-Ofelt analysis[12,13] was performed using six absorption bands of the absorption spectra. The reduced matrix elements calculated by M. J. Weber[14] were used. The determined Judd-Ofelt intensity parameters Ω_t (t = 2, 4, 6) and the root mean square deviations (δ_{rms}) of least-square fitting are listed in Table 1. The Judd-Ofelt intensity parameters are important for investigation of local structure and bonding in the vicinity of rare-earth ions. Ω_2 parameter is sensitive to the local environment that is affected by asymmetry of the coordination structure. Ω_6 parameter is related to covalent bonding in the vicinity of the rare earth ions[15]. In Table 1, Ω_t ($t = 2, 4, 6$) parameters in Er^{3+}-doped non-fluoride LAS glass, fluoride glass, oxyfluoride glass, and fluoride lanthanum aluminosilicate (FLAS) glasses in this work are compared. As can be seen from Table 1, with the increase of AlF_3 content in FLAS glasses, Ω_2 parameter decreases slowly. This indicates that the asymmetry of coordination around Er^{3+} ions changes with the increase of fluoride content. It is known from Table 1 that the Ω_2 parameter decreases in the order of LAS glass, oxyfluoride glasses, and fluoride glass. The more the fluoride content the glass contains, the smaller the Ω_2 parameter. The unobvious change of Ω_4 and Ω_6 indicates that the covalent bonding in the vicinity of the Er^{3+} ions in the FLAS glasses is insensitive to the fluoride content except FLAS30 glass that shows higher Ω_4 and Ω_6 than other FLAS glasses.

Table 2 gives the fluorescence lifetime, radiative transition probability, radiative lifetime, quantum efficiency of Er^{3+}: $^4I_{13/2}$ in FLAS glasses and the absorption cross sections at 1530 nm. It is known that absorption cross section and quantum efficiency at 1530 nm in FLAS30 glass are largest among that in FLAS glasses. The general spectroscopic properties of FLAS30 glass are comparable to LAS glass. The absorption coefficient of OH^- groups in glass, $\alpha(OH^-)$, is also shown in Table 2. It is got from the measurement of IR transmission spectra in the range of 4000–1500 cm^{-1} in Fig. 1. The absorption band around 3500 cm^{-1} is due to fundamental vibrations arising from OH^- absorption. The absorption coefficient $\alpha(OH^-)$ is defined as[16]

$$\alpha(OH^-) = (1/d)\log(T_b/T), \quad (1)$$

where d is the thickness of glass sample, T_b is the maximum transmittance, and T is the transmittance at the OH^- absorption band position (~3500 cm^{-1}). Table 2 indicates that glass with high $\alpha(OH^-)$ has short fluorescent lifetime. The differences between the IR transmission spectra are due to the environment of glasses melting, especially air humidity. The existence of large amount of OH^- contents causes non-radiative transition of Er^{3+} ions. So it is important to remove the OH^- contents of the glasses.

Figure 2 shows the relation between absorption coefficient of OH^- and fluorescent lifetime in glasses. It is known from Table 2 and Fig. 2 that the fluorescent lifetime and quantum efficiency are seriously affected by OH^- contents in glasses. The reciprocal parameter k_{OH^-} between OH^- ions and Er^{3+} ions, calculated

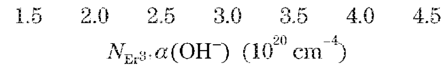

Fig. 2. The relationship between absorption coefficient of OH^- and fluorescent lifetime (τ_f) in FLAS glasses.

according to

$$\frac{1}{\tau_f} = k_{\mathrm{OH}^-} N_{\mathrm{Er}} \alpha(\mathrm{OH}^-) + \frac{1}{\tau_0}, \qquad (2)$$

and Fig. 2, is 2.78×10^{-19} $\mathrm{cm}^4 \cdot \mathrm{s}^{-1}$. It is bigger than the k_{OH^-} of LAS glass, which does not contain fluoride content[9].

The full width at half maximum (FWHM) of fluorescence spectra are also listed in Table 2. These glasses have similar FWHM except FLAS30 glass which has a large FWHM. In the case of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}, because the difference of the total angular momentum equals 1, there exists the contribution of magnetic dipole transition. The magnitude of magnetic dipole transition is independent on ligand fields while that of the electric dipole transition is a function of ligand fields[17]. It is considered that the fraction of electric dipole transition is bigger and then the bandwidth is wider. According to Judd-Ofelt theory, line strength of the electric dipole of Er^{3+} $^4I_{13/2} \rightarrow {}^4I_{15/2}$ is given by[11]

$$S_{\mathrm{ed}}[^4I_{13/2}, {}^4I_{15/2}] = 0.0188\Omega_2 + 0.01176\Omega_4 + 1.4617\Omega_6. \qquad (3)$$

From Eq. (3) it is known that for electric dipole transition of Er^{3+} $^4I_{13/2} \rightarrow {}^4I_{15/2}$, Ω_6 parameter is dominant. So FWHM of FLAS30 glass is larger than that of other glasses.

The glass transition temperature of FLAS glasses decreases with the increase of AlF_3 content. The spectroscopic properties of Er^{3+}-doped FLAS glasses, which contain various amounts of AlF_3 content, have been studied by Judd-Ofelt theory and absorption spectra. The intensity parameter Ω_2 of Er^{3+} doped FLAS glasses decreases slowly with the increase of AlF_3 content. The FWHM of fluorescence spectra FLAS glasses is narrow than that of LAS glass and does not change with AlF_3 content until it reaches 30 mol%. It is found that glass containing 30 mol% AlF_3 has the best spectroscopic properties in FLAS glasses.

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