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Investigations on spectroscopic properties of Er^{3+}-doped Li–Zn fluoroborate glass

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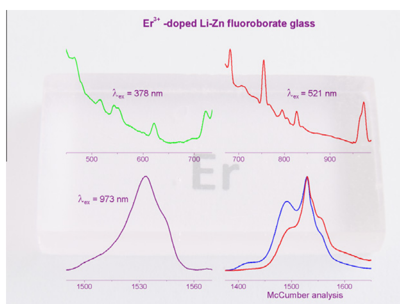
HIGHLIGHTS

- Er^{3+}:Li–Zn fluoroborate glass was fabricated for laser applications.
- Judd–Ofelt and radiative parameters were investigated.
- Broadband optical communications due to 1.5 μm emission.
- McCumber theory analysis for 1.5 μm region.

GRAPHICAL ABSTRACT



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ABSTRACT

Er^{3+}-doped Li–Zn fluoroborate glass was synthesized via melt quenching technique. Optical properties of the glass were investigated by UV–Vis-NIR absorption and emission spectra. To evaluate the nature of Er^{3+}-ligand bond in the glass network, nephelauxetic ratios and bonding parameter were calculated. Judd–Ofelt analysis and hence the radiative properties of the present glass system were evaluated for ascertaining the suitability of the glass for laser applications and compared those with the emission spectra. Absorption cross-sections have been calculated from the absorption spectrum and stimulated emission cross-sections were estimated using McCumber theory for $^4I_{13/2} \leftrightarrow {}^4I_{15/2}$ transitions. The results of the present glass were compared with those obtained for some other Er^{3+}-doped glass systems.

Introduction

Trivalent rare earth (RE^{3+}) doped optical glasses are key materials for the development of optical fibers, waveguide lasers, bulk lasers and optical amplifiers [1,2]. Out of many RE^{3+} ions, Er^{3+}-doped glasses have been extensively considered for laser applications due to their low loss in optical waveguide for $^4S_{3/2} \rightarrow {}^4I_{13/2}$ and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions [3]. Mostly, green emission by the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ion has led to successful outcomes with fiber and bulk structures [4]. The selection of proper glass host for Er^{3+} ion is an important factor for attaining good laser performance, i.e., low optical losses, energy storage capacity and high gain. Among different glass matrices, borate glass is an appropriate optical material due to its low melting point, high thermal stability, good rare earth ion solubility and high transparency [5,6]. Fluoride glasses are appropriate for fiber amplifiers owing to its ability to move IR cut off edge to low frequencies and also due to its reactivity with OH group to produce hydrogen fluoride, which in turn decreases the OH absorption in

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the glass matrix [7,8]. Heavy metal oxides embedded borate glasses have wide range of applications in solid state laser materials, electro-optic modulators, electro-optic switches and non-linear parametric converters [9,10]. The presence of Zn in the glass composition lowers the crystallization rate and enhances the glass forming ability [11]. Heavy metal fluoride (HMF) incorporated glasses possess some advantages over conventional borate, phosphate and silicate glasses. These advantages include low phonon energy, extended transparency from near-UV to mid-IR and capacity to incorporate large quantity of RE^{3+} ions [12,13]. The presence of ZnF_2 (HMF) in the glass network produces more efficient radiative emissions due to its ability to lower phonon energies [13].

The purpose of this work is to study the spectroscopic properties of Er^{3+}-doped Li–Zn fluoroborate glass through absorption and emission spectra. Judd–Ofelt [14,15] theory has been employed to investigate the radiative properties such as transition probabilities, branching ratios and lifetime for the various levels of Er^{3+} ions in the present glass system. The results are compared with other Er^{3+}-doped glasses and the potential of the present glass system as a laser material is discussed.

Fabrication and characterizations of the glass

In this work, we have prepared an Er^{3+}-doped Li–Zn fluoroborate glass, hereafter referred to as LBZnFEr, with a composition of $25Li_2O + 64.9B_2O_3 + 10ZnF_2 + 0.1Er_2O_3$ in molar fraction via melt quenching technique. The systematic procedures for glass synthesis, polishing and measurements of the physical properties are similar to our earlier work [16].

The absorption spectrum of the glass was recorded on Varian Cary 5000 UV–Vis–NIR spectrophotometer in the wavelength range 200–2500 nm. Emission spectra of the LBZnFEr glass were taken from Horiba Scientific Fluoromax-4 spectrofluorometer at excitation wavelengths 378 and 521 nm. The emission spectrum in the NIR region of LBZnFEr glass was measured using Jobin Yvon Fluorolog - FL3–11 spectrofluorometer at an excitation wavelength of 973 nm. All these spectroscopic measurements were done at room temperature (RT) with a spectral resolution of 1 nm. The details of theory and calculations adopted for this work have been described elsewhere [17,18]. Some of the physical parameters of LBZnFEr glass have been measured and are presented in Table 1.

Results and discussion

Optical absorption studies

Fig. 1 shows the absorption spectrum of 0.1 mol% Er^{3+} doped Li–Zn fluoroborate glass in the UV–Vis and NIR regions with the photograph of the prepared glass as inset. The spectrum shows 10 absorption transitions in the UV–Vis and 3 peaks in the NIR region. These inhomogeneously broadened bands at the wavelengths 356, 365, 378, 407, 442, 451, 488, 521, 543, 651, 797, 973 and 1529 nm are identified as transitions from the ground state $^4I_{15/2}$ to the different excited levels (1) $^2G_{7/2}$, (2) $^4G_{9/2}$, (3) $^4G_{11/2}$, (4) $(^2G,^4F,^2H)_{9/2}$, (5) $^4F_{3/2}$, (6) $^4F_{5/2}$, (7) $^4F_{7/2}$, (8) $^2H_{11/2}$, (9) $^4S_{3/2}$, (10) $^4F_{9/2}$, (11) $^4I_{9/2}$, (12) $^4I_{11/2}$ and (13) $^4I_{13/2}$ due to the 4f–4f interactions of Er^{3+} ions in the LBZnFEr glass, respectively (transitions are indicated in the figure with peak numbers labeled). Among these, the most intense $^4I_{15/2} \rightarrow {}^4G_{11/2}$ (378 nm) and $^4I_{15/2} \rightarrow {}^2H_{11/2}$ (521 nm) transitions follow the selection rules ($|\Delta S| = 0$, $|\Delta L| \leqslant 2$ and $|\Delta J| \leqslant 2$) for hypersensitive transitions (HSTs) and are found to be more sensitive to the environment. The absorption peaks, if any, could not be found below 350 nm due to the screening of higher energy levels of Er^{3+} ion in LBZnFEr glass by the upward sloping of Urbach edge of the glass matrix.

To investigate the nature of Er^{3+}-ligand bond in the LBZnFEr glass, nephelauxetic ratios (β) and the bonding parameter (δ) have been calculated. It is observed from Fig. 2 that the nephelauxetic ratio of most of the absorption transitions have a value >1, which indicates the observed energy values in LBZnFEr glass (ν_c) is higher than the corresponding energy values in aqua ion (ν_a). This shift depends on the bonding nature of the ligand of Er^{3+} ion. The obtained value for bonding parameter (δ) is -0.269 and this negative value is an indication of ionic nature of the Er^{3+}-ligand bond in the present glass system. Similar ionic nature of Er^{3+}-ligand bond was reported in some other glasses too [19,20].

Judd–Ofelt (JO) analysis of the LBZnFEr glass has been carried out from the absorption spectra. Fig. 3 shows the experimental and calculated oscillator strengths (f_{exp} and f_{cal}) along with their difference (Δf) for 13 transitions observed in absorption spectra. The root mean square (r.m.s) deviation (σ) of f_{exp} and f_{cal} is obtained as 0.649×10^{-6}. It is concluded from Fig. 3 and the r.m.s deviation (σ) that the experimental and calculated oscillator strengths agree very well and in turn leads to the accuracy of the JO analysis. It is observed that the oscillator strengths of the HSTs, $^4I_{15/2} \rightarrow {}^4G_{11/2}$ and $^4I_{15/2} \rightarrow {}^2H_{11/2}$ are larger than those for other absorption transitions. Also, the oscillator strengths of these HSTs are larger than those reported for other Er^{3+}-doped glasses [19,20], which indicates that the LBZnFEr glass possesses higher asymmetry around Er^{3+} ions. The JO intensity parameters, Ω_λ (where $\lambda = 2$, 4 and 6) were obtained by carrying out a least square fit for these f_{exp} and f_{cal} values and are presented in Table 2 along with JO parameters for other reported Er^{3+}-doped glasses [20–22]. Comparatively higher values of Ω_λ parameters for the present glass

Table 1
Physical parameters of 0.1 mol% Er^{3+}-doped Li–Zn fluoroborate glass.

Parameter	Value
Density (ρ)	2.6175 g/cm^3
Optical path length (t)	5.0 mm
Refractive Index (n)	1.473
Concentration of Er^{3+} (N)	0.4276×10^{20} ions/cm^3
Polaron radius (r_p)	1.1525 nm
Molar volume (V_m)	24.2122 cm^3/mol
Electronic polarizability (α_e)	2.6927×10^{-24}
Molar refractivity (R_μ)	6.7922 cm^3
Dielectric constant (ε)	2.1697
Electric susceptibility (χ)	0.0931
Interionic distance (r_i)	2.8597 nm
Donor–acceptor distance (R_{DA})	1.7740×10^{-8} cm
Field strength (F)	2.2588×10^{14} cm^{-2}
Reflection loss (R)	3.658%

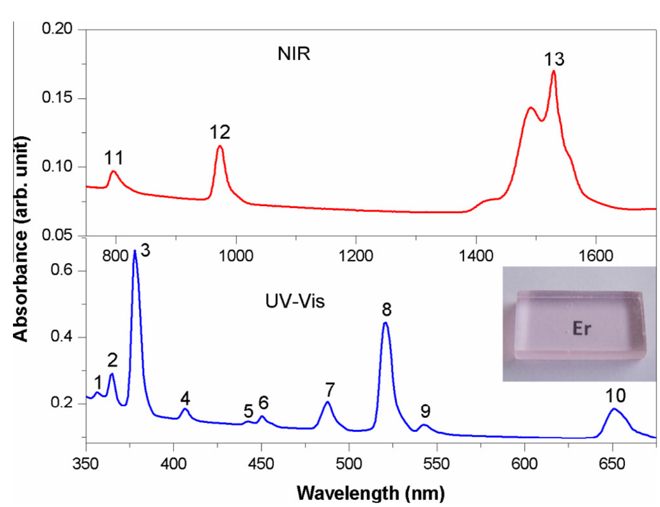

Fig. 1. Absorption spectra of LBZnFEr glass in the UV–Vis and NIR regions.