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Luminescence properties of Nd^{3+} in mixed alkali fluoride glasses

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Three indium trifluoride based neodymium glasses (abbreviated as A, B and C) with the mixed dual alkali fluorides as network modifiers have been newly prepared to characterize their absorption and photoluminescence spectra, both at room and liquid nitrogen temperature. By performing a least squares fit analysis, the Judd–Ofelt parameters and the spectroscopic quality factor (Ω_4/Ω_6) have been computed from the absorption levels. The Judd–Ofelt parameters (Ω_λ) have been used to derive the radiative properties of these glasses in the determination of the predicted radiative lifetime of the measured excited state. The recorded low temperature photoluminescence spectra have revealed an intense emission peak $^4F_{3/2} \rightarrow {}^4I_{11/2}$ at $\lambda = 1.05$ μm and for this level, the lifetime has been measured by the use of an Ar^+ ion laser. The fluorescence characteristics of these mixed alkali fluoride glasses have been compared with the results obtained on the Nd-glasses possessing the individual alkali fluorides as the modifiers.

1. Introduction

We recently prepared and characterized the terbium doped InF_3 based multicomponent glasses with the alkali fluorides (both mixed and unmixed) to examine the effects of these alkali fluorides on the physical and optical properties [1,2]. Since neodymium is a potential laser ion, the above glass systems have been synthesized and studied first with the individual alkali fluorides as the property modifiers [3], and now, as a continuation of the study of these Nd-doped devices, we report new results on Nd^{3+} in mixed alkali fluoride systems (LiF–NaF, NaF–KF and KF–LiF) in order to understand the effects on the physical and luminescence properties at 300 and 77 K.

2. Experimental details

The method of preparation of the fluoride glasses with Nd^{3+} as the dopant is similar to that given in our earlier paper [3]. The compositions are:

Glass A: $30InF_3 + 30BaF_2 + 10ThF_4 + 9ZnF_2 + (10LiF + 10NaF) + 1NdF_3$.
Glass B: $30InF_3 + 30BaF_2 + 10ThF_4 + 9ZnF_2 + (10NaF + 10KF) + 1NdF_3$.
Glass C: $30InF_3 + 30BaF_2 + 10ThF_4 + 9ZnF_2 + (10KF + 10LiF) + 1NdF_3$.

In our earlier paper [3], the compositions of the glasses were:

Glass A′: $30InF_3 + 30BaF_2 + 10ThF_4 + 9ZnF_2 + (20LiF) + 1NdF_3$.

Glass B′: $30InF_3 + 30BaF_2 + 10ThF_4 + 9ZnF_2 + (20NaF) + 1NdF_3$.
Glass C′: $30InF_3 + 30BaF_2 + 10ThF_4 + 9ZnF_2 + (20\ KF) + 1NdF_3$.

The glass compositions of the present and previous work are given here, for the purpose of comparing their properties. The densities of these glasses have been measured at room temperature with xylene as the immersion liquid. The refractive indices have also been measured on a standard

3. Results and discussion

3.1. Absorption properties

Eight absorption levels have been identified from the recorded room temperature absorption spectra in all three Nd-glasses. Though we observed eight absorption states, only the five most well defined absorption bands have been selected to carry out the spectral intensity measurements to apply the Judd–Ofelt procedure [5] for estimating with the 487.9 nm line of the Ar^+ ion laser. Since the room temperature photoluminescence spectra did not give a satisfactory profile, only the low temperature recordings have been used in the present work. Of the ${}^4F_{3/2} \to {}^4I_J$ (where $J = 15/2$, 13/2, 11/2 and 9/2) transitions, the ${}^4F_{3/2} \to {}^4I_{11/2}$ transition would be the best for laser emission ($\lambda = 1.05$ μm). Because of this the J–O parameters listed in table 1 have been used to determine the spontaneous emission probability of each of these four emission levels from the expression [6]

$$A = \frac{64\pi^4 e^2 \nu^3}{3h(2J+1)} \left[\frac{n(n^2+2)^2}{9} \right] S_{ed}.$$

The total transition probability of the ${}^4F_{3/2} \to {}^4I_J$ manifolds was obtained from [6]

$$A_T = \sum A.$$

With the estimation of the values of A and A_T, the branching ratio (β_R) was evaluated from [6]

$$\beta_R = (A/A_T).$$

Both figs. 1(a) and (b) describe the relationships between the spectroscopic factor (Ω_4/Ω_6) and te fluorescence branching ratio (β_R) values for the Nd-glasses with the mixed alkali fluorides (present work) and the unmixed alkali fluorides (previous work, ref. [3]). The predicted radiative lifetimes (T_R in μs) of the luminescent state ${}^4F_{3/2} \to {}^4I_{11/2}$ have been computed and compared with the measured values in calculating the quantum efficiency as follows [6]

$$\eta = (T_m/T_R).$$

From the recorded photoluminescence spectral profiles, the stimulated emission cross-sections (σ_p) of ${}^4F_{3/2} \to {}^4I_{11/2}$ state was obtained from the equation [6]

$$\sigma_p = \frac{\lambda_p^4}{8\pi C n_d^2 \, \Delta\lambda} A\left({}^4F_{3/2} \to {}^4I_{11/2}\right),$$

where λ_p is the wavelength of the transition and $\Delta\lambda$ is the bandwidth obtained by integrating the intensity of the luminescence shape and dividing

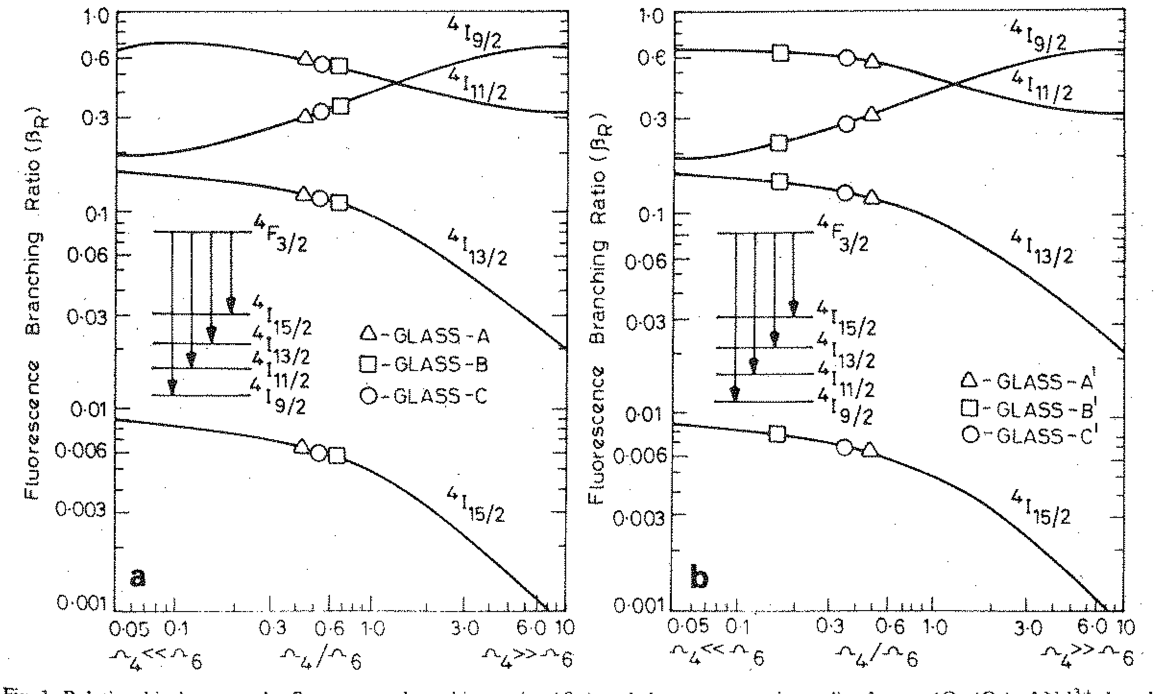

Fig. 1. Relationship between the fluorescence branching ratios (β_R) and the spectroscopic quality factors (Ω_4/Ω_6) of Nd^{3+}-doped HMF glasses of the present work (a) and the previous work (b).

this by the intensity at λ_p. This parameter is considered to be an important factor for understanding the lasing efficiency of the materials chosen in the present work.

4. Conclusions

A systematic study has been carried out on three InF_3 based Nd^{3+}-doped mixed dual alkali fluorides for their physical and optical properties and the results are tabulated in table 1. The Judd–Ofelt theory for the electric dipole transitions combined with the photoluminescence spectra has been used to understand the laser emission properties of these glasses. The comparison made in table 1, shows that the glasses of the present work have better laser emission properties than the systems already reported [3]. It is also shown that the alkali mixed glasses demonstrate a uniform trend in their optical behaviour without much variation. The magnitude of (Ω_4/Ω_6) has been found to be in the range 0.165–0.605 for the glasses of the present and previous work. The properties for laser emission at 0.9 μm ($^4F_{3/2} \rightarrow {}^4I_{9/2}$), 1.05 μm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$) and at 1.32 μm ($^4F_{3/2} \rightarrow {}^4I_{13/2}$) are given in table 1. Based on the luminescence properties shown in fig. 1 and the data in table 1, it is concluded that the Nd-doped mixed alkali fluorides show more favourable luminescence properties compared with the glasses having only a single alkali fluoride as a modifier.

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