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ABSORPTION AND FLUORESCENCE PROPERTIES OF Eu^{3+} DOPED ALKALI MIXED HEAVY METAL FLUORIDE GLASSES

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In this paper, we report the preparation of Eu^{3+} doped ZrF_4–AlF_3–BaF_2–RF (where RF = LiF–NaF or NaF–KF pairs) glasses in six different RF chemical compositions. For these europium glasses, we made a systematic study on the various physical properties namely the refractive index, density, dielectric constant, non-linear refractive index co-efficient based on the chemical composition. By combining the Judd–Ofelt results obtained from optical absorption studies with those of the fluorescence measurements at 300 K and 77 K, we verified the suitability of chemical composition of the glass in the selection of an ideal optical glass for the characterisation of efficient laser emission from the europium ion. The lifetimes of the luminescent state $^5D_0 \rightarrow {}^7F_2$ of europium glasses were measured both at room and liquid nitrogren temperatures by using an argon ion laser source.

1. INTRODUCTION

THE LAST few years have been the most exciting in the preparation of optical glasses. The range of glasses made wider than ever before and now includes chalcogenides, fluorides, oxides and oxyhalides. At present, there has been a strong interest in the research and development of heavy metal fluoride (ZrF_4, ThF_4, InF_3, HfF_4) based glass systems doped with rare earths. Among the various heavy metal fluoride glasses, the mixed alkali fluorozirconate glasses appear to be very promising, because of its good transparency and resistance from the moisture. These optical glasses could be used as fibre waveguides, laser-windows and infrared lenses [1, 2]. About two years ago, the synthesis and elastic properties of the glass systems of $48ZrF_4$–$24BaF_2$–$8AlF_3$–20RF: (RF = NaF–LiF, NaF–KF) were carried out [3, 4]. Quite recently, we published our results on the absorption and fluorescence properties of Ho^{3+}-doped alkali mixed ZrF_4-based glasses [5]. Now, we report the preparation of Eu^{3+}-doped ZrF_4 based glasses in six different mixed alkali fluoride combinations and these glasses have been used to understand the various physical properties, concerning the absorption and the laser emission characteristics.

2. EXPERIMENTAL

2.1. *Europium glass preparation*

Extra pure reagents of $(NH_4)_2\,ZrF_4$, BaF_2, AlF_3, LiF, NaF, KF and EuF_3 were used as starting materials for preparing Eu-doped alkali mixed fluoride glass systems for the present work. The chemical compositions of these glasses are given in Table 1. The mixture of raw materials containing about 10% (W/W) NH_4HF_2 as fluorinating agent, was preheated at about 450° C for an hour and then melted at 900–950° C for about 20 min in a platinum crucible under nitrogen atmosphere in an electrically heated furnace. The melts were quenched between two steel plates and allowed to cool to room temperature. The europium glasses, thus, obtained are in excellent transparency. The crucible containing the glasses was weighed before removing the glass materials and cleaning. The weight of the glass always was in close agreement with the anticipated in that batch, and found that there was about 0.2% weight loss in each case. These results

Table 1. Various physical properties of Eu-doped fluoride glasses

Parameters	Glass-A [5LiF+15NaF]	Glass-B [10LiF+10NaF]	Glass-C [15LiF+5NaF]	Glass-D [5NaF+15KF]	Glass-E [10NaF+10KF]	Glass-F [15NaF+5KF]
Density [Dgm cm^{-3}]	4.502	4.485	4.47	4.457	4.442	4.431
Refractive index [n at 5893 Å]	1.571	1.566	1.56	1.551	1.546	1.54
Eu-ion concentration [Nions cm^{-3}] $\times 10^{19}$	0.976	0.986	0.995	0.963	0.973	0.981
Non-linear refractive index [n_2 esu]	0.874	0.861	0.861	0.868	0.856	0.855
Non-linear refractive index coefficient [γ cm^2/Weber] $\times 10^3$	2.331	2.304	2.312	2.346	2.318	2.327
Abbe number [ν]	86	86	85	83	83	82
Mean atomic volume [V]	7.904	7.888	7.868	8.172	8.152	8.125
Reflection losses [R%]	4.9	4.9	4.8	4.7	4.6	4.5
Molar refractivity [R_M]	9.999	9.906	9.794	10.0.38	9.938	9.815
Dielectric constant [ε]	2.468	2.525	2.434	2.406	2.39	2.372
Optical dielectric constant [$\rho\partial\varepsilon/\partial\rho$]	1.468	1.524	1.434	1.406	1.39	1.372
Ionic radius [r_p in nm]	0.188	0.187	0.187	0.189	0.188	0.188
Ion-ion distance [r_i in nm]	0.467	0.466	0.464	0.469	0.468	0.467
Ionic field strength [Z/r_p^2] $\times 10^{17}$	8.443	8.497	8.551	8.362	8.416	8.461
Molecular polarizability [$\alpha \times 10^{21}$]	8.031	7.896	7.755	7.901	7.769	7.635

indicate that the actual glass compositions are essentially identical to those based on the glass batch. Glass formation was confirmed by the polarizing microscopic observation and X-ray diffraction analysis.

2.2. *Physical properties of the Eu-doped glasses*

The refractive index (n) of the glass was measured on the Abbe-refractometer at a wavelength of λ = 5893 Å. A thin-film of monobromonapthalene was used as a contact layer between the prism of the refractometer and the glass sample that is to be examined. The density of the glass sample was determined at room temperature by the Archemede's principle on a sensitive microbalance with xylene as an immersion liquid. The mean atomic volume (V) of each glass was obtained from the values of densities (D) and average molecular weights ($\bar{M}$). The europium ion concentration (N) in each of the six glasses was determined from the chemical composition and density values. The estimated Eu^{3+}-ion concentrations of these glasses were found to be in between 0.9639×10^{19} (for glass-D) and 0.9553×10^{19} (for glass-C) as the maximum and minimum values respectively. In addition to the measurement of both the refractive indices and densities, we have determined several other important physical properties by using the mathematical equations available in literature [6–16]. The estimated values of these parameters are collected in Table 1.

2.3. *Absorption and fluorescence spectral recordings*

The absorption spectral measurements of europium fluoride glasses were made at the room temperature in the wavelength range of 350–450 nm on a Cary Model 17 Spectrophotometer. The absorption spectral recordings for our samples were made by the laboratories of physics and Chemistry of Hull University, Hull, England, following our collaboration with these two departments. Both the excitation and photoluminescence spectra of these glasses were carried out in the laboratories of the Changchun Institute of Physics, Changchun, People's Republic of China. The recorded luminescence spectra of six europium glasses have been identified with the appropriate assignments for the measurements emission states.

2.4. *Lifetime of the fluorescent state* $^5D_0 \rightarrow {}^7F_2$

The lifetime of this fluorescent state of the europium ion was in milliseconds both at room and liquid nitrogen temperatures. The excitation source used in the lifetime measurement was an argon ion (AR^+) laser with the wavelength 478 nm. The lifetime measurements were made using by a Biomation 610B transient recorded and a Nicholet 1070 signal averager.

3. RESULTS AND DISCUSSION

3.1. *Absorption and fluorescence properties*

From the recorded spectra of Eu-doped glasses, we observed four absorption states of transitions $^7F_0 \rightarrow {}^5D_4$, $^5G_3$, $^5L_6$ and $^5D_3$ at the wavelengths of about 360, 380, 390 and 400 nm. To characterise the spectral intensities of these states, the Jubb–Ofelt theory has been considered as an ideal model following two good articles published by Tanimura *et al.* [17a] and Weber [17b] to verify the suitability in correlating the measured values with the computed data. This Judd–Ofelt model permits relatively rapid determination of luminescence characteristic parameters and also explains the dependence of these properties on the systematic variations in glass composition. We have, therefore, combined the absorption characteristic parameters with the measured photoluminescence spectra of Eu^{3+}-doped alkali mixed fluoride glasses to investigate the effectiveness of the laser emission from these materials. From the measured spectrophotometric profiles, the band intensities have been estimated and a computer least-squares routine has resulted in a set of best fit Judd–Ofelt intensity parameters as listed in Table 2. The unit tensor operators for the various absorption and emission levels of Eu^{3+}-free-ion have already been reported in the literature (18, 19). From this table we have noticed the trend of $\Omega_2 > \Omega_6 > \Omega_4$ in all six europium glasses reported here.

3.2. *Luminescent properties*

From the recorded photoluminescence spectra of Eu-doped glasses, the following emission transitions have been measured.

$$^5D_0 \rightarrow {}^7F_2;\ {}^5D_1 \rightarrow {}^7F_{5,3,2};\ {}^5D_2 \rightarrow {}^7F_6.$$

Of these five fluorescent levels, $^5D_0 \rightarrow {}^7F_2$ emission state at the approximate wavelength of λ = 606 nm was observed to be very prominent. Following the application of Judd–Ofelt model, we have evaluated the radiative parameters for all the possible emission transitions to ^7F_J (J = 0, 1, 2, 3, 4, 5, 6) from the measured excited states namely $^5D_0$, $^5D_1$ and $^5D_2$ respectively. In this approach, firstly the value of the transition probability for each of the fluorescent transitions was evaluated from the equation [20–22],

$$A_{JJ'} = \frac{64\pi^4 e^2 v^3}{3h(2J+1)}\left[\frac{n(n^2+2)^2}{9}\right]S_{ed},$$

where S_{ed} is the electric-dipole linestrengths, n is the refractive index, J = is the J value of the excited level, v is the energy of the transitions (cm^{-1}) and other factors have their standard meanings. To evaluate the

Table 2. The electric dipole line strengths[1], integrated absorption co-efficients[2] and the oscillator strengths[3] of Eu^{3+}-doped fluoride glasses

Transitions SLJ S′L′J′	Wavenumber (cm^{-1})	Glass-A			Glass-B			Glass-C			Glass-D			Glass-E			Glass-F		
		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
$^7F_0 \rightarrow {^5D_3}$	24030	0.12	0.99	1.53	0.11	0.86	1.32	0.09	0.69	1.05	0.11	0.82	1.28	0.09	0.71	1.11	0.07	0.53	0.9
$\rightarrow {^5L_6}$	25000	0.79	6.06	9.96	0.70	5.36	8.86	0.56	4.30	7.07	0 67	5.00	8.47	0.59	4.43	7.40	0.47	3.56	5.9
$\rightarrow {^5G_3}$	26185	0.12	0.91	1.66	0.11	0.79	1.43	0.09	0.63	1.14	0.11	0.75	1.39	0.09	0.65	1.20	0.07	0.19	1.0
$\rightarrow {^5D_4}$	27300	0.04	0.30	0.60	0.04	0.26	0.52	0.03	0.21	0.41	0.04	0.25	0.50	0.03	0.21	0.43	0.03	0.17	0.3
Judd–Ofelt Intensity parameters																			
$\Omega_2 \times 10^{20}$ cm^2		1.27			1.10			0.88			1.07			0.94			0.75		
$\Omega_4 \times 10^{20}$ cm^2		0.61			0.53			0.42			0.52			0.45			0.36		
$\Omega_6 \times 10^{2}$ cm^2		0.88			0.77			0.67			0.75			0.65			0.53		

[1]($S_{ed} \times 10^{22}$); [2]($\int K(\lambda)\, d\lambda$) and [3]($f_{jj} \times 10^8 = (mc^2/\pi N \lambda^2) \int K(\lambda) d\lambda$).

S_{ed} values for the emission states $^5D_0$, $^5D_1$ and $^5D_2$ and their other lower lying states, the required squared reduced matrix elements have been collected from the tables of Carnall *et al.* [18] and Reisfeld *et al.* [19]. Secondly, the total transition probability of each emission state was obtained on taking the summation of individual probability values from this state to its next lower lying states [20–22].

$$A_T(JJ') = \sum A_{JJ'}.$$

Thirdly, the reciprocal value of this A_T was taken as the radiative lifetime of the concerned emission state. Finally, the branching ratio of the potential lasing transition $^5D_0 \rightarrow {}^7F_2$ was evaluated from [20–22].

$$\beta_R = \frac{A(^5D_0 \rightarrow {}^7F_2)}{A_T(^5D_0 \rightarrow {}^7F_{0,1,2,3,4,5,6})}.$$

Since the emission line $^5D_0 \rightarrow {}^7F_2$ of Eu-doped glasses appears to be a predominant fluorescent state, the lifetime T_m (milliseconds) measurement was carried out for this level, by using an argon ion laser both at room and liquid nitrogen temperatures. The quantum efficiency of the emission state was computed from [21].

$$\eta = \frac{T_m}{T_R}$$

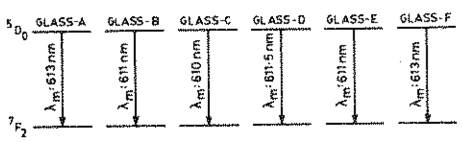
where T_m is the measured lifetime and T_R, the radiative lifetime. The laser characteristics of the luminescent state $^5D_0 \rightarrow {}^7F_2$ of Eu-doped glasses are clearly described in Fig. 1 by giving the values for A, A_T, β_R, T_R, T_m (300 K, 77 K) and η. Following the method of Weber *et al.* [14], the fluorescent state emission cross-section was determined from the expression

$$\sigma_E \Delta\lambda = \frac{A(^5D_0 \rightarrow {}^7F_2)}{8\pi n^2 c v^4}$$

where v is the emission transition energy (cm^{-1}), A: the transition probability, C: the velocity of light and n the refractive index of the glass at λ: 5893 Å. Fig. 1 also describes the effect of the alkali fluoride content on the emission cross-section values of the laser transition $^5D_0 \rightarrow {}^7F_2$.

4. CONCLUSIONS

Six new optical glasses of the chemical composition of $48ZrF_4 + 23BaF_2 + 8AlF_3 + 20RF + 1EuF_3$ (where RF = NaF–LiF, NaF–KF) were prepared. A detailed study was carried out on the different physical properties to examine the effects of mixed alkali fluoride (LiF–NaF, NaF–KF) content in all samples. The formation of glass was confirmed through the polarizing microscopic observation and



Laser characteristic parameters of the emission level $^5D_0 \rightarrow {}^7F_2$	GLASS-A	GLASS-B	GLASS-C	GLASS-D	GLASS-E	GLASS-F
A (s^{-1})	390	342	270	323	279	220
A_T (s^{-1})	536	461	363	438	376	296
β_R	0·74	0·74	0·74	0·73	0·74	0·74
T_R (ms)	1·86	2·16	2·74	2·28	2·65	3·37
T_m (ms) at 300 K	0·99	1·05	1·20	1·5	1·6	1·75
T_m (ms) at 77K	1·1	1·18	1·25	1·57	1·7	1·9
η	0·53	0·48	0·43	0·65	0·6	0·51
$\sigma_E \Delta\lambda \times 10^{29}$	101·82	88·15	70·12	84·90	73·71	58·56

Fig. 1. Laser characteristics of the emission level $^5D_0 \rightarrow {}^7F_2$ of Eu-doped alkali mixed fluoride glasses both at 300 K and 77 K.

also by carrying out X-ray diffraction analysis. By the estimation of Eu-ion concentration in each glass through its density and molecular weight, a good fitting of spectral intensities for the four absorption levels namely $^7F_0 \rightarrow {}^5D_4$, $^5G_3$, $^5L_6$ and $^5D_3$ between the measurement and theory was achieved. Such a fitting confirms the validity of Judd–Ofelt theory in the correlation of spectral intensity of both theory and experimental results. The root mean square deviation was within about an error of 5% only.

The intensity parameters (Ω_λ) showed the following situation for all glasses studied here as $\Omega_2 > \Omega_6 > \Omega_4$. For these glasses the photoluminescence spectra were recorded both at 300 K and 77 K by using a Xenon arc source and from these recordings, we measured the emission states such as $^5D_0 \rightarrow {}^7F_2$; $^5D_1 \rightarrow {}^7F_5$; $^7F_3$, $^7F_2$ and $^5D_2 \rightarrow {}^7F_6$. Of these fluorescence states, $^5D_0 \rightarrow {}^7F_2$ exhibited a significant bright emission intensities. We therefore, carried out measurement of the lifetimes of this particular state with an argon ion laser. The application of Judd–Ofelt theory to the photoluminenscence spectra has resulted in the computation of the values of the transition probability (A), relaxation rate (A_T), branching ratio (β_R), radiative lifetime (T_R) and the quantum efficiency (η) of the lasing transition $^5D_0 \rightarrow {}^7F_2$ at the room and liquid nitrogen temperatures. For this promising emission state of Eu-doped glasses, the emission cross-section values were also measured. The values of the lifetimes and emission cross-sections for the fluorescing state $^5D_0 \rightarrow {}^7F_2$ of Eu-ion showed significant variations with the change of mixed alkali fluoride content in all the glasses studied here.

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REFERENCES

1. H. Poignant & J. Lemellut, *Mater. Res. Bull.* **17,** 829 (1982).
2. D.C. Tran & G.H. Siegel, *Mater. Res. Bull.* **17,** 1177 (1982).
3. X. Zhao, K. Kosula & S. Sakka, *J. Mater. Sci.* **22,** 4103 (1987).
4. X. Zhao & S. Sakka, *J. Non-Crystalline Solids* **99,** 45 (1988).
5. S. Buddhudu & F.J. Bryant, *Spectrochemica Acta* **44A,** 1381 (1988).
6. Y. Ohisti, S. Mitachi & T. Tanabe, *Phys. Chem. Glasses* **24,** 135 (1983).
7. J.E. Shelby & J. Ruller, *Phys. Chem. Glasses* **28,** 262 (1987).
8. B. Bendow, P.K. Banerjee, J. Lucas, G. Fonteneau & M.G. Drexhage, *J. Amer. Ceram. Soc.* **65,** C92 (1985).
9. John Schroeder, *J. Non-Crystalline Solids* **40,** 549 (1980).
10. M.M. Ahmed, C.A. Hogarth & M.N. Khan, *J. Mater. Sci. Lett.* **19,** 4040 (1984).
11. P.W. MacMillan, *Glass Ceramics*, Academic Press Inc., London, W.J. 15 (1964).
12. A. Klonkowski, *J. Non-Crystalline Solids* **72,** 117 (1985).
13. M.D. Shinn, W.A. Sibley, M.G. Drexhage & R.N. Brown, *Phys. Rev.* **B27,** 6635 (1983).
14. M.J. Weber, J.E. Lynch, D.H. Blackburn & D.J. Cronin, *IEEE J. Quantum Electronics* **QE19,** 1600 (1983).
15. N.L. Boling, A.J. Glass, A. Owyoung, *IEEE J. Quantum Electronics* **QE14,** 605 (1978).
16. D. Milam & M.J. Weber, *J. Appl. Phys.* **47,** 2499 (1976).
17. (a) K. Tanimura, M.D. Shinn, W.A. Sibley, M.G. Drexhage & R.N. Brown, *Phys. Rev.* **B30,** 2429 (1984). (b) M.J. Weber, *Optical Properties of Ions in Crystals* (Edited by H.M. Crosswhite and Moss), Interscience publishers, John Wiley (1987).
18. W.T. Carnall, P.R. Fields & K. Rajnak, *J. Chem. Phys.* **49,** 4412 (1968).
19. R. Reisfeld, E. Greenberg, R.N. Brown, M.G. Drexhage & C.K. Jorgensen, *Chem. Phys. Lett.* **95,** 91 (1983).
20. A.A. Kaminiskii, K. Kurbano & A.J. Petrosyan, *Phys. Status Solidi (a)* **98(1),** K57–K62 (1986).
21. J.L. Adam & W.A. Sibley, *J. Non-Crystalline Solids* **76,** 267 (1985).
22. J. Sany, R. Casef & Q.R. Alcala, *J. Non-Crystalline Solids* **93,** 377 (1987).