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Optical absorption and photoluminescence properties of Eu^{3+}-doped ZnF_2–PbO–TeO_2 glasses

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Several physical, optical absorption and photoluminescence properties of Eu^{3+}-doped ZnF_2–PbO–TeO_2 glasses have been studied. From the measured intensities of various absorption bands of these glasses the Judd–Ofelt parameters Ω_2, Ω_4 and Ω_6 have been computed. The Judd–Ofelt theory has been applied to characterize the photoluminescence spectra of these glasses. From this theory, various radiative properties, such as transition probability, *A*, branching ratio, β_r, and emission cross-section, σ_P^E, for various emission levels of these glasses, have been determined and reported.

1. Introduction
The optical characterization of ZnF_2–PbO–TeO_2 glasses, i.e. the study of optical properties such as glass transparency (in the ultraviolet, visible and infrared regions) and their ability to accept rare-earth ions as the luminescent centres, is essential for their use in glass laser technology. During the last few years, a large variety of inorganic glasses has been developed and characterized [1–5]. ZnF_2–PbO–TeO_2 glasses are well known due to their excellent transparency in the 3–18 μm region and have been considered as good materials for use as optical components such as infrared domes, filters and laser windows. Recently, we have reported the results of our studies on electrical and elastic properties of these glasses [6–9]. The studies have yielded valuable information regarding the electrical resistance and mechanical strength of these glasses.

Tellurite glasses are advantageous as laser hosts in view of their optical transparency, both in the short wavelength region (necessary for getting the optimum efficiency from optical pumping of lasing ions) and high wavelength region (necessary for getting the maximum output intensity from laser radiation). Further, these glasses possess very low rates of crystallization, high transparency, low toxicity and they resist moisture. It was therefore felt worthwhile to investigate the optical properties of ZnF_2–PbO–TeO_2 glasses after incorporation of Eu^{3+}. Most of the studies available [10–12] on optical properties of tellurite glasses are aimed at understanding the fundamental absorption edge, though a few studies [13, 14] on spectroscopic and thermoluminescence properties of some binary tellurite glasses are available.

2. Experimental procedure
For the present study, a particular composition 45 ZnF_2–8 PbO–45.4 TeO_2–9.6 PrF_3 has been chosen. Our earlier study on a series of ZnF_2–PbO–TeO_2 glasses prepared by simultaneously decreasing the PbO and TeO_2 contents (starting from high concentrations of PbO and TeO_2) has indicated that glasses prepared with the composition 45 ZnF_2–8 PbO–46 TeO_2 possess a particularly high electrical resistance and high mechanical strength. We have therefore chosen this composition for Eu^{3+} doping. Appropriate amounts of Analar grade reagents of ZnF_2, PbO, TeO_2 and EuF_3 powders were thoroughly mixed and melted in a platinum crucible at 600 °C for about 30 min until a bubble-free liquid was formed. The resultant melt was poured on a brass mould and subsequently annealed at 200 °C. The amorphous state of the glasses was checked by X-ray diffractometry using a Seifert Diffractometer Model SO-Debye-Flux 2002 having a copper target with nickel filter and operated at 40 kV, 30 mA. The density, *d*, of the glasses was determined by the standard principle of Archimedes using xylene (99.98% pure) as the buoyant liquid. The refractive index, n_d, of the optically polished glasses was measured using a sodium vapour lamp ($\lambda = 589.3$ nm) on a precession refractometer with an organic liquid, namely monobromonaphthalene, as the

contact layer between the glass and refractometer prism.

The optical absorption of ZnF_2–PbO–TeO_2 glasses containing Eu^{3+} was recorded on a Shimadzu UV–VIS-NIR 3101 PC spectrophotometer in the wavelength range 300–800 nm. By using a xenon arc lamp, the intense line $\lambda_{exc} = 396$ nm, was identified and used to record the photoluminescence spectrum. The photoluminescence spectrum of the glasses was recorded on a Hitachi-F 3010 fluorescence spectrophotometer in the wavelength range 450–700 nm.

3. Results

From the measured values of density, d, refractive index, n_d, and average molecular weight, $\bar{M}$, various other physical parameters such as Eu^{3+} ion concentration, N_i, molar refractivity, R_M, molecular polarizability, α_e, mean Eu^{3+} separation distance, r_i, and the field strength, F [11] were calculated and are presented in Table I for these glasses.

The optical absorption spectrum of Eu^{3+}-doped ZnF_2–PbO–TeO_2 glasses, recorded at room temperature in the visible region, exhibited four absorption levels (Fig. 1). These levels are assigned to the appropriate electronic transitions as follows:

$$^7F_0 \rightarrow {}^5I_6, {}^5D_2$$

and

$$^7F_1 \rightarrow {}^5D_3, {}^5D_1$$

TABLE I Various physical properties of Eu^{3+}-doped ZnF_2–PbO–TeO_2 glasses

Property	
Refractive index, n_d (measured at $\lambda = 589.3$ nm)	1.566
Density, d ($g\,cm^{-3}$)	4.28
Average molecular weight, $\bar{M}$ (g)	129.41
Pr^{3+} ion concentration, N_i (10^{22} ions cm^{-3})	0.55
Molar refractivity, R_M (cm^{-3})	9.98
Molecular electronic polarizability, α_e ($10^{24}\,cm^3$)	3.90
Mean Eu^{3+} separation, r_i (nm)	0.566
Field strength, F ($10^{-10}\,cm^{-3}$)	0.57

The photoluminescence (PL) spectrum has been recorded at room temperature for Eu^{3+}:ZnF_2–PbO–TeO_2 glasses. The luminescence spectrum shown in Fig. 2 for these glasses displays the following emission transitions:

$$^5D_1 \rightarrow {}^7F_2 \text{ (575 nm)}$$
$$\rightarrow {}^7F_3 \text{ (500 nm)}$$
$$\rightarrow {}^7F_5 \text{ (650 nm)}$$
$$^5D_0 \rightarrow {}^7F_2 \text{ (610 nm)}$$

4. Discussion

It is well known that there is a shielding of the 4f electrons of rare-earth ions and this shielding allows these ions to serve as active centres in solid-state laserhosts, such as the present tellurite glasses. These ions exhibit sharp absorption and luminescence transitions, sharp because these 4f ions are weakly perturbed by the surrounding ligands [15]. The spectral intensities for the observed absorption bands of these glasses, which are often expressed in terms of oscillator strength, f, have been analysed with the help of Judd–Ofelt theory [16]. Experimentally, the values of f have been calculated from the following expression

$$f_{exp} = 2.303(mc^2/N_A)\pi e^2 \int \varepsilon(\nu)\,d\nu \qquad (1)$$

where N_A is Avogadro's number and $\varepsilon(\nu)$ is the molar absorption coefficient which can be evaluated from Beer's law after correcting for reflection loss etc.

$$\varepsilon(\nu) = (1/N_m t)\log(I_0/I) \qquad (2)$$

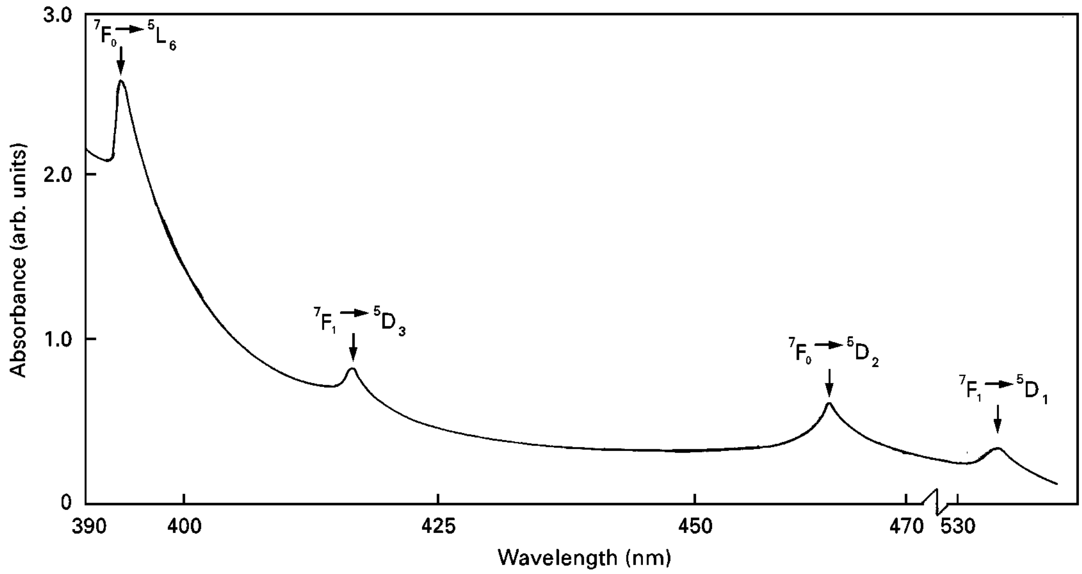

Figure 1 Optical absorption spectra of Eu^{3+}-doped ZnF_2–PbO–TeO_2 glasses.

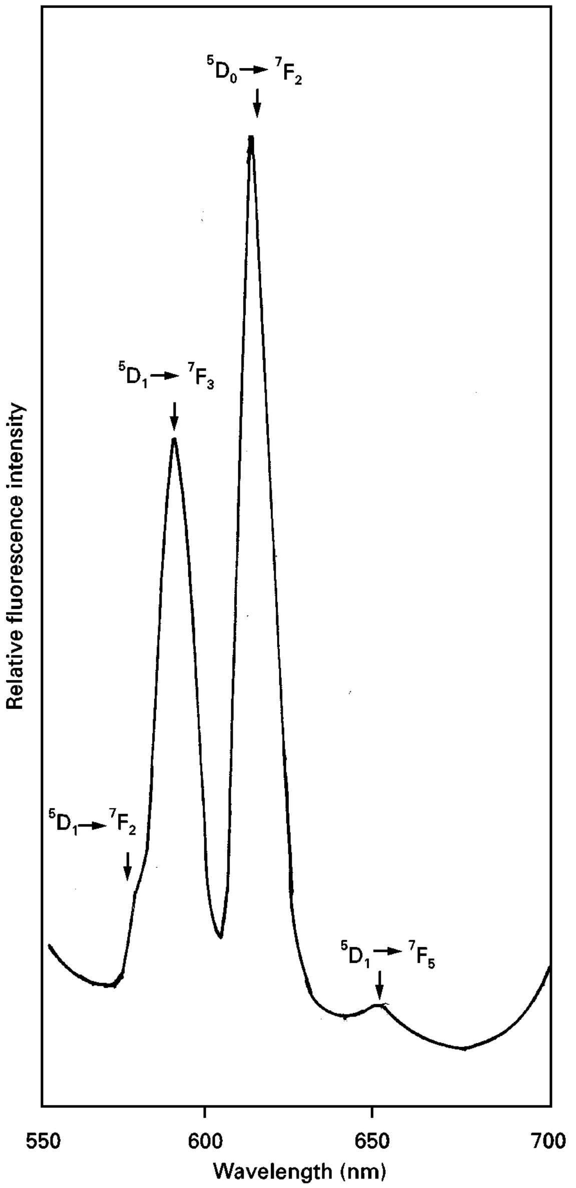

Figure 2 Luminescence spectrum of Eu^{3+}-doped ZnF_2–PbO–TeO_2 glasses recorded at room temperature.

where N_m is the concentration of Eu^{3+} ions (mol %) and t is the thickness of the sample.

Using these oscillator strengths, the original Judd–Ofelt (J–O) parameters, T_λ have been calculated by performing a least-square analysis for the present glasses using

$$f = \sum_{\lambda = z}^{\sigma} T_\lambda \nu (\psi_J \| U^\lambda \| \psi_{J'})^2 \tag{3}$$

where ν is the energy of the transition (cm^{-1}), $\psi_J \rightarrow \psi_{J'}$ and $\| U^\lambda \|^2$ is the squared reduced matrix element of the rank $\lambda = 2$, 4 and 6.

The values of $\|U^\lambda\|^2$, which will not change with the host for the Ln^{3+} ions, are taken from the literature [17] for different absorption levels of Eu^{3+} ions.

Using the refractive index, n_d, the parameters T_λ can be transformed into Ω_λ [18] using the equation

$$\Omega_\lambda = \frac{3h(2J+1)}{8\pi^2 mc} \frac{9n_d}{(n_d^2+2)^2} T_\lambda \tag{4}$$

TABLE II The absorption band energies, the electric dipole line strength, S_{ed}, the oscillator strength, f_{exp}, for some transitions and Judd–Ofelt intensity parameters and spectroscopic quality factor (Ω_4/Ω_6) of Eu^{3+}:ZnF_2–PbO–TeO_2 glasses.

Absorption	Energy (cm^{-1})	S_{ed} ($\times 10^{20}$)	f_{exp} ($\times 10^6$)	Judd–Ofelt parameters, Ω (10^{20} cm^2)
$^7F_0 \rightarrow {}^5I_6$	25 375	8.25	0.075	$\Omega_2 = 49.49$
$^7F_1 \rightarrow {}^5D_3$	24 040	3.38	0.061	$\Omega_4 = 0.60$, $\Omega_6 = 13.64$
$^7F_0 \rightarrow {}^5D_2$	21 449	7.69	0.039	
$^7F_1 \rightarrow {}^5D_1$	18 676	3.67	0.385	$\Omega_4/\Omega_6 = 0.044$

where h is Planck's constant, m is the mass of the electron, c is the velocity of light and J is ground state J value.

Then the electric dipole line strengths, S_{ed}, for various absorption transitions have been estimated using the expression

$$S_{ed} = \sum_{\lambda = z}^{\sigma} \Omega_\lambda (\psi_J \| U^\lambda \| \psi_{J'})^2 \tag{5}$$

The J–O parameters, namely Ω_2, Ω_4 and Ω_6, and the dipole line strengths, S_{ed}, for the Eu^{3+}: ZnF_2–PbO–TeO_2 glasses, are presented in Table II along with the other pertinent data. The values of Ω_λ are found to be in the order: $\Omega_2 > \Omega_6 > \Omega_4$.

Using J–O parameters, Ω_λ, the radiative properties of the various fluorescence levels observed for the present glasses have been determined. The spontaneous emission probability for electric dipole transition has been obtained from [19]

$$A = \frac{64\pi^4 e^2 \nu^3}{3h(2J+1)} \left[\frac{n_d(n_d^2+2)^2}{9} s_{ed} \right] \tag{6}$$

The values of $\| U^\lambda \|^2$ for various luminescent states of the Eu^{3+} ion are taken from the literature [17].

Then the total emission probability, A_T, involving all the intermediate terms is calculated using [20, 21]

$$A_T(\psi_{J'}) = \sum_{\psi_J}^{\psi_{J'}} A(\psi_{J'}, \psi_J) \tag{7}$$

and the fluorescent branching ratio, β_r, is obtained from

$$\beta_r = \frac{A(\psi_{J'}, \psi_J)}{A_T(\psi_{J'})} \tag{8}$$

Finally, the stimulated emission cross-sections of the measured fluorescence levels are calculated using

$$\sigma_P^E = \frac{A(\psi_{J'}, \psi_J)\lambda^4}{8\pi c n_d^2 \Delta\lambda} \tag{9}$$

where λ is the peak position of the emission line and $\Delta\lambda$ is the effective band width of the emission transition.

The obtained values of the transition probability $A_T(\psi_{J'}, \psi_J)$, the total transition probability, $A_T(\psi_{J'})$, and the fluorescence branching ratio, β_T, using equations 6–8 for some of the transitions, are presented in Table III.

TABLE III Transition probability and total transition probability and fluorescent branching ratio, β_r, for various emission transitions of Eu^{3+}-doped glasses

Emission transiton $\psi_{J'} \rightarrow \psi_J$	Transition probability	Branching ratio, β_r (%)
$^5D_0 \rightarrow {}^7F_6$	98.69	2.4
$\rightarrow {}^7F_4$	100.20	24.6
$\rightarrow {}^7F_2$	2951.30	72.8
$A_T (s^{-1})$	4050.19	
Radiative lifetime T_R (μs) = 246		
$^5D_1 \rightarrow {}^7F_6$	21.35	0.15
$\rightarrow {}^7F_5$	279.60	2.03
$\rightarrow {}^7F_4$	1676.00	12.21
$\rightarrow {}^7F_3$	4826.00	33.72
$\rightarrow {}^7F_2$	1001.00	7.29
$\rightarrow {}^7F_1$	6114.70	44.56
$A_T (s^{-1})$	13 718.70	
Radiative lifetime T_R (μs) = 72.8		

TABLE IV Other radiative properties of Eu^{3+}-doped ZnF_2–PbO–TeO_2 glasses

Emission transition	λ (nm)	Δλ (nm)	A (s^{-1})	A_T (s^{-1})	β_r (%)	Emission cross-section, σ_P^E (10^{20} cm^2)
$^5D_0 \rightarrow {}^7F_2$	610	10	2951.3	4056.19	72.8	2.28
$^5D_1 \rightarrow {}^7F_3$	590	16	4626.0	13 718.65	33.7	1.21

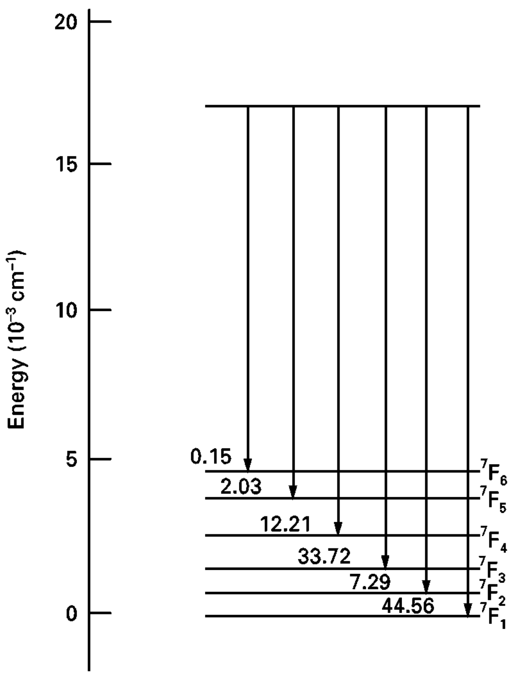

Figure 3 Energy level diagram for some of the emission transitions of Eu^{3+}-doped ZnF_2–PbO–TeO_2 glasses together with the values of fluorescent branching ratios, β_r (%).

The measured wavelength, λ, half-width, Δλ, and the computed value of the stimulated emission cross section, σ_P^E, for two prominent emission transitions, $^5D_0 \rightarrow {}^7F_2$ and $^5D_1 \rightarrow {}^7F_3$ are presented in Table IV for Eu^{3+}-doped glasses.

It has already been established that an emission level with β_r value near 50% becomes a potential laser emission transition [22]. Recollecting the data on the emission transitions of these Eu^{3+}-doped ZnF_2–PbO–TeO_2 glasses, the transition $^5D_0 \rightarrow {}^7F_2$ has got the highest β_r value. This transition can, therefore, be considered as a possible laser transition [2, 3]. The energy level diagram for various emission transitions of Eu^{3+}-doped ZnF_2–PbO–TeO_2 glasses is shown in Fig. 3. In conclusion, the J–O parameters combined with photoluminescence spectra of these luminescent materials have allowed calculations of induced emission cross-sections. These glasses are chemically stable, moisture-resistant over longer periods, and hence they can be used for practical applications.

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