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# Optical properties of $Sm^{3+}$ ions in zinc potassium fluorophosphate glasses

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ABSTRACT

In the present work, different concentrations of $Sm^{3+}$ ions doped zinc potassium fluorophosphate glasses (PKAMZFSm: $P_2O_5 + K_2O + MgO + Al_2O_3 + ZnF_2 + Sm_2O_3$) were synthesized via melt quench technique. Physical properties and refractive indices of the present glasses were evaluated. Optical characterization of $Sm^{3+}$: PKAMZF glasses through absorption, excitation, emission and decay spectra had been carried out. Nephelauxetic ratios, bonding parameter and energy band gap of the 1.0 mol% $Sm^{3+}$-doped PKAMZF glass were evaluated using absorption spectra. Judd–Ofelt (JO) intensity analysis had been presented and JO parameters were evaluated for 1.0 mol% $Sm^{3+}$-doped zinc potassium fluorophosphate glass. Radiative properties such as transition probabilities, branching ratios and radiative lifetime were estimated by using JO parameters. Stimulated emission cross-sections and effective bandwidths of each transition were obtained from the luminescence spectra. The experimental lifetime, quantum efficiency and donor–acceptor interaction parameters were also estimated using decay curves of $^4G_{5/2}$ level of $Sm^{3+}$ ions in the present glasses. The influence of $Sm^{3+}$ ion concentrations on the luminescence intensity, lifetime and energy transfer parameters for PKAMZFSm glasses was investigated. The results obtained have been compared with the other $Sm^{3+}$-doped glasses.

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## 1. Introduction

Optical studies of rare earth (RE) doped glasses provide precious insights that is comprised of energy level structure, bonding character, radiative properties, stimulated emission cross-sections, energy transfer mechanism, lifetimes, quantum efficiencies, etc. These informations play a momentous role to update the existing or to build up novel optical devices like optical fibers, optical amplifiers, light converters, sensors, lasers, optical detectors, hole burning high-density memories, etc. [1,2]. The optical properties of RE ions in glasses are kindred to the 4f–4f transitions and vary with the structure and nature of bonds which are determined by the chemical composition of the glass matrix. In general, phosphate glasses are hygroscopic whereas incorporation of fluoride enhances the resistance to water. Since fluorophosphate glasses have the advantages of both phosphate and fluoride glasses, fluorophosphate glasses are salient among different glass matrices. High transparency in UV–Vis–NIR region, physical and chemical stability, good moisture resistance, low non-linear refractive index and low phonon energy are the staple attributes of fluorophosphate glasses [3,4]. OH absorption in the host matrix emphatically attenuates due to the reaction of fluorine with OH group [5]. Numerous researchers have reported that fluorophosphate glasses incorporated with RE ions are effective as laser hosts [6–8]. The RE ion preferred for the present work is $Sm^{3+}$ and it is lucrative for spectral hole burning investigations [9]. The $Sm^{3+}$ ions doped glasses have many applications in solid state lasers, various fluorescent devices, high density optical storage devices, solid corrosion free glass matrices for undersea communications, etc. [10,11]. In the present work, we prepared a novel zinc potassium fluorophosphate glass incorporated with different concentrations of $Sm^{3+}$ ions for obtaining various efficient optical properties. The absorption, excitation, emission and decay spectra of these glasses are recorded and analyzed. Optical energy band gap, bonding parameter, Judd–Ofelt intensity analysis and radiative properties of the glasses are discussed. The results of the investigations suggest the realization of the present glasses as optical fiber amplifiers and visible lasers due to the higher values of branching ratios and stimulated emission cross-sections.

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## 2. Experimental

### 2.1. Sample preparation

Samarium doped zinc potassium fluorophosphate (PKAMZFSm) glasses were prepared by using conventional melt quench technique. The molar composition of glasses investigated in the present work is $(53 - x/2)P_2O_5 + 15K_2O + (14 - x/2)MgO + 8Al_2O_3 + 10ZnF_2 + xSm_2O_3$, where $x$ = 0.0, 0.1, 0.5, 1.0 and 2.0 mol%. About 20 g of the chemicals were thoroughly crushed in an agate mortar. This homogenous mixture was heated in an electric furnace at 1050–1100 °C for about 90 min in a platinum crucible. The melt was poured onto a preheated brass plate and annealed at a temperature 350 °C for about 12 h for thermal stability and then cooled to room temperature (RT). The prepared glasses have good transparency and are polished for optical measurements.

### 2.2. Measurements

Refractive indices ($n$) of the glasses were measured using Abbe Refractometer at Na wavelength with 1-bromonaphthalin as the contact liquid. The physical parameters and refractive indices of the present glasses are shown in Table 1. Absorption spectra of the PKAMZFSm glasses were recorded on Perkin Elmer Lambda-950 UV–Vis–NIR spectrophotometer in the wavelength region 200–2500 nm. Excitation, emission and lifetime measurements were recorded on Jobin Yvon Fluorolog-3 spectrofluorimeter by using xenon arc lamp as excitation source. All these measurements were made at room temperature.

## 3. Theory

### 3.1. Physical properties

Density ($\rho$), concentration ($N$) and refractive index ($n$) have been used to calculate various physical properties of the glasses using suitable expressions [12,13]. In terms of RE ion concentration, the polaron radius ($r_p$) can be calculated as

$$r_p = \frac{1}{2}\left(\frac{\pi}{6N}\right)^{1/3} \tag{1}$$

and the interionic distance ($r_i$) for RE doped glasses is given by

$$r_i = \left(\frac{1}{N}\right)^{1/3} \tag{2}$$

Field strength ($F$) is expressed as

$$F = \frac{Z}{{r_p}^2} \tag{3}$$

where $Z$ is the charge of the ion and reflection loss ($R$) is given by

$$R = \left(\frac{n-1}{n+1}\right)^2 \times 100 \tag{4}$$

Dielectric constant ($\varepsilon$) is given by

$$\varepsilon = n^2 \tag{5}$$

Molar refractivity ($R_\mu$) is determined as

$$R_\mu = \left(\frac{n^2-1}{n^2+2}\right)\frac{M}{\rho} \tag{6}$$

where $M$ is the average molecular weight of the glass. Electronic polarizability ($\alpha_e$) is given by the Lorentz–Lorenz equation

$$n = \left(\frac{1 + 2\frac{4\pi N_A}{3}\frac{\alpha_e}{V_m}}{1 - \frac{4\pi N_A}{3}\frac{\alpha_e}{V_m}}\right)^{1/2} \tag{7}$$

where $V_m$ is the molar volume.

### 3.2. Judd–Ofelt analysis

The experimental oscillator strength ($f_{\exp}$) of an absorption transition from the ground state to an excited state is expressed as

$$f_{\exp} = 4.32 \times 10^{-9} \int \varepsilon(\nu)d\nu \tag{8}$$

where $\varepsilon(\nu)$ is the molar absorptivity of a band at a wavenumber $\nu$ ($cm^{-1}$) and $d\nu$ is the half-band width [14]. According to Judd–Ofelt

**Table 1**
Glass code, composition and physical properties for PKAMZFSm glasses.

| Glass code | PKAMZF | PKAMZFSm01 | PKAMZFSm05 | PKAMZFSm10 | PKAMZFSm20 |
|---|---|---|---|---|---|
| Composition | $53P_2O_5$, $15K_2O$, 14MgO, $8Al_2O_3$, $10ZnF_2$ | $52.95P_2O_5$, $15K_2O$, 13.95MgO, $8Al_2O_3$, $10ZnF_2$, $0.1Sm_2O_3$ | $52.75P_2O_5$, $15K_2O$, 13.75MgO, $8Al_2O_3$, $10ZnF_2$, $0.5Sm_2O_3$ | $52.5P_2O_5$, $15K_2O$, 13.5MgO, $8Al_2O_3$, $10ZnF_2$, $1.0Sm_2O_3$ | $52P_2O_5$, $15K_2O$, 13MgO, $8Al_2O_3$, $10ZnF_2$, $2.0Sm_2O_3$ |
| Density $d$ (gm/cc) | 2.6298 | 2.6434 | 2.6552 | 2.6842 | 2.7482 |
| Optical path length $t$ (mm) | 2.32 | 3.47 | 3.57 | 3.03 | 4.00 |
| Refractive Index $n$ | 1.515 | 1.515 | 1.516 | 1.517 | 1.519 |
| Concentration of $Sm^{3+}$ $N$ ($\times 10^{20}$ ions/cc) | 0.0000 | 0.2795 | 1.3829 | 2.7501 | 5.4508 |
| Polaron radius $r_p$ (nm) | – | 1.33 | 0.78 | 0.62 | 0.49 |
| Electronic polarizability $\alpha_e$ ($\times 10^{-24}$) | 8.58 | 8.54 | 8.55 | 8.52 | 8.43 |
| $\alpha_e/V_m$ ($\times 10^{-25}$) | 1.195 | 1.195 | 1.197 | 1.199 | 1.204 |
| Molar refractivity $R_\mu$ ($cm^3$) | 21.64 | 21.55 | 21.57 | 21.48 | 21.26 |
| Dielectric constant $\varepsilon$ | 2.295 | 2.295 | 2.298 | 2.301 | 2.307 |
| Interionic distance $r_i$ (nm) | – | 3.30 | 1.93 | 1.54 | 1.22 |
| Field strength $F$ ($\times 10^{15}$ $cm^{-2}$) | – | 0.17 | 0.49 | 0.78 | 1.25 |
| Reflection losses $R$ (%) | 4.19 | 4.19 | 4.21 | 4.22 | 4.25 |

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