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Optical and luminescence studies of Pr^{3+} and Er^{3+} doped different phosphate glasses

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ABSTRACT

Optical absorption and emission spectra of Pr^{3+} and Er^{3+} doped different chlorophosphate glasses have been studied. Optical properties of these two rare earth ions were characterized through optical absorption and emission spectra using Judd–Ofelt theory. Judd–Ofelt intensity parameters Ω_λ (λ=2, 4 and 6) are calculated for both the ions from their absorption spectra, which in turn used to derive the radiative properties such as radiative transition probabilities (A_T), radiative lifetimes (τ_R), branching ratios (β) and integrated absorption cross-sections (Σ). An attempt has been made to discuss structural changes considering the hypersensitive transitions and covalency of rare earth oxygen (RE-O) bonds for the present glass systems. From emission spectra, peak emission cross-sections (σ_P) are obtained for the observed emission bands of Pr^{3+} and Er^{3+} ions in all these chlorophosphate glasses. Variation of peak emission cross-sections with the glass matrix has been studied.

1. Introduction

In recent years extensive research work has been done for improved functionality of new materials for various applications. In particular, spectroscopic and laser characteristics of rare earth doped glass materials are optimized for broad band fiber amplifier, efficient lasing and frequency up conversion process [1–3]. Rare earth ions are used to probe the local structural variations in the host glass matrices because of their unique spectroscopic properties resulting from the radiative transitions in the 4f intra-configuration. Among various rare earth ions, Pr^{3+} and Er^{3+} have been recognized as most efficient rare earth ions for obtaining laser emission, frequency up conversion, waveguide lasers and in optical amplifiers [4,5]. Recently, Ratnakaram et al. [6] reported optical absorption and emission properties of Pr^{3+} and Er^{3+} in lithium–cesium mixed alkali borate glasses. Moorthy et al. [7] reported optical properties of Er^{3+} doped alkali fluorophosphates glasses. Bodyl et al. [8] studied optical properties of Pr^{3+}, Sm^{3+} and Er^{3+} ions in apatite, fluorite and phosphate glasses. Optical absorption, fluorescence and decay properties of Pr^{3+} doped $PbO–H_3BO_3–TiO_2–AlF_3$ glasses were reported by Jamalaiah et al. [9]. Optical spectra and Judd–Ofelt analysis of Pr^{3+} and Er^{3+} in different phosphate glasses have been reported by Seshadri et al. [10].

The host glass matrix is very important factor for the development of rare earth doped optical devices. Among different host glass matrices, phosphate glasses are important hosts for Pr^{3+} and Er^{3+} ions because of their spectroscopic characteristics such as laser emission cross-section; weak interaction among active ions and may cause concentration quenching which have been extensively used for lasers and fiber amplifiers [11,12]. Recently, the authors reported spectroscopic properties and Judd–Ofelt analysis of Sm^{3+} and Dy^{3+} doped phosphate glasses [13]. In the present work, characterization of Pr^{3+} and Er^{3+} doped different chlorophosphate glasses has been reported. Various spectroscopic parameters (Racah (E^1, E^2 and E^3), spin–orbit (ξ_{4f}) and configuration interaction (α)) are deduced for both the ions in different chlorophosphate glasses. Using Judd–Ofelt theory and from the measured absorption spectra, the local environment of Pr^{3+} and Er^{3+} ions and bond covalency of RE-O bond have been studied. Judd–Ofelt intensity parameters (Ω_2, Ω_4 and Ω_6) have been used to calculate radiative transition rates (A), radiative lifetimes (τ_R), branching ratios (β) and integrated absorption cross-sections (Σ) for certain excited states of Pr^{3+} and Er^{3+} in different chlorophosphate glasses. Peak stimulated emission cross-sections (σ_p) of the observed emission transitions of both the ions in all the glass matrices are reported.

2. Experimental

Pr_2O_3 and Er_2O_3 (0.2 mol%) doped different chlorophosphate glass matrices of the glass compositions $69.8P_2O_5 \cdot 20Na_2HPO_4 \cdot 10RCl$ (R=Na, K, Mg and Ca) and $69.8P_2O_5 \cdot 20Na_2HPO_4 \cdot 5NaCl \cdot 5RCl$ (R=K, Mg and Ca) were prepared using melt quenching

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method. All these chemicals are reagent grade with 99.9% purity. The anhydrous chlorides were dried by heating at appropriate temperatures under vacuum. A small amount of ammonium chloride was added to these dehydrated chlorides in order to drive off impurities. About 5–10 g batch compositions were thoroughly ground using agate mortar and heated in a silica crucible for 2 h in an electric furnace at a temperature of 400 °C. This allowed the phosphorus pentoxide to decompose and react with other batch constituents before melting. Then the crucible with the mixture was kept at 950 °C. During melting, the liquids were shaken at 15 min interval in order to obtain bubble free glass and ensure homogeneity. When the melting was completed, the liquid was poured and quenched between two well polished brass plates. The obtained glass samples were annealed at 400 °C for 3 h to eliminate the mechanical stress. Glass samples of about 1–2 mm thickness were obtained. Densities of the glass samples were determined using Archimedes principle (using xylene as immersion liquid) and the refractive indices of the samples were measured using Abbe-refractometer with sodium lamp. Optical absorption spectra were measured in the UV–Vis–NIR regions using JASCO V-570 spectrophotometer with the spectral resolution of 0.1 nm. Fluorescence spectra were measured using Fluoro-Max 3 fluorescence spectrophotometer under excitation wavelengths, 485 and 315 nm for Pr^{3+} and Er^{3+} ions, respectively, with the spectral resolution of 1 nm.

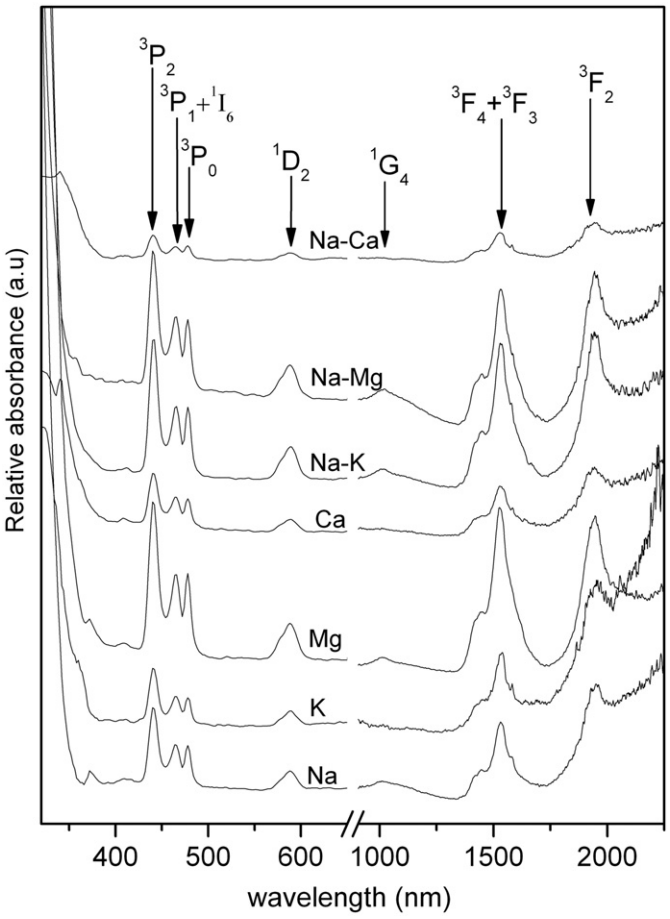

Fig. 1. Optical absorption spectra of Pr^{3+} doped different chlorophosphate glasses.

3. Results and discussion

3.1. Spectral intensities and intensity parameters

Figs. 1 and 2 show the optical absorption spectra of Pr^{3+} and Er^{3+} ions doped Na, K, Mg, Ca, Na–K, Na–Mg and Na–Ca chlorophosphate glass matrices measured at room temperature in the wavelength region 350–2200 nm. The precise transition energies are found and their absorption bands are assigned for both the ions as follows:

For Pr^{3+} ion, $^3H_4 \rightarrow {}^3P_2$, $^3P_1+{}^1I_6$, $^3P_0$, $^1D_2$, $^1G_4$, $^3F_4+{}^3F_3$, $^3F_2$

For Er^{3+} ion, $^4I_{15/2} \rightarrow {}^2G_{9/2}$, $^4G_{11/2}$, $^2H_{9/2}$, $^4F_{5/2}+{}^4F_{3/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$

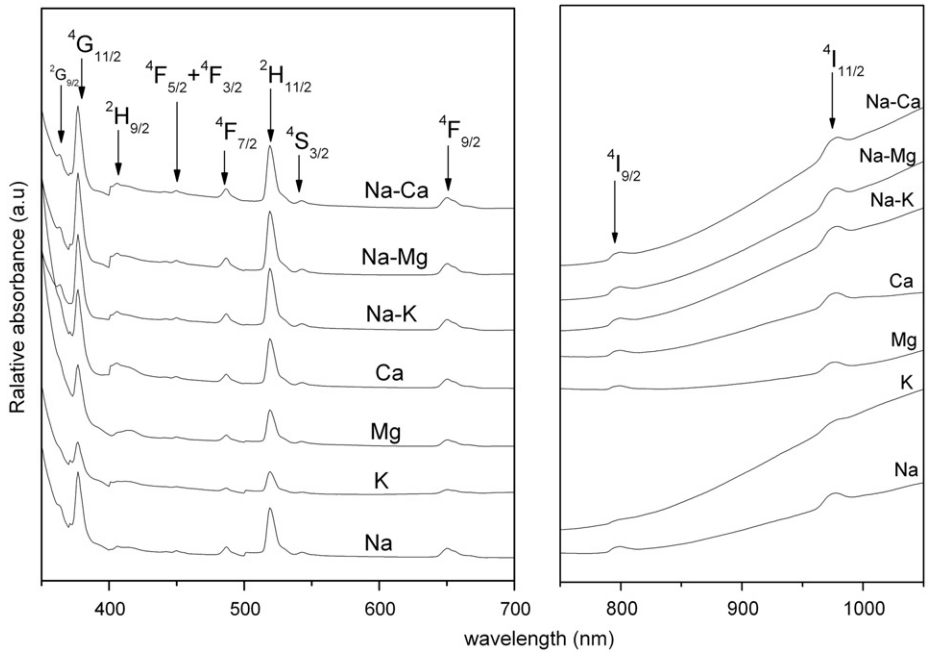

Fig. 2. Optical absorption spectra of Er^{3+} doped different chlorophosphate glasses.