Spectroscopic and photoluminescence properties of Sm^{3+} ions in Pb–K–Al–Na phosphate glasses for efficient visible lasers

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ABSTRACT

The Sm^{3+}-doped lead phosphate glasses (PKAPbNSm:$44P_2O_5$–$17K_2O$–$9Al_2O_3$–$(24-x)$ PbO–$6Na_2O$–xSm_2O_3, where $x=0.1$, 0.5, 1.0 and 2.0 mol%) have been prepared by conventional melt quenching technique and are characterized through absorption and emission spectra and decay rate analysis. The partial energy level structure of Sm^{3+} ions in these glasses have been evaluated from the measured absorption and emission spectra using free-ion Hamiltonian model. The emission spectra of Sm^{3+} ions in these glasses have been measured using 488 nm line of Ar$^+$ laser as an excitation source. The decay rates for $^4G_{5/2}$ level of Sm^{3+} ions have been measured and are found to exhibit single exponential nature at lower concentration (0.1 and 0.5 mol% Sm_2O_3-doped glass) and turns into non-exponential at higher concentrations (≥ 1.0 mol% Sm_2O_3-doped glasses). The experimental lifetimes for $^4G_{5/2}$ level of Sm^{3+} ions are found to decrease from 2.34 to 1.24 ms when the concentration is increased from 0.1 to 2.0 mol% Sm_2O_3 due to cross-relaxation energy transfer. The non-exponential decay rates are well-fitted to Inokuti-Hirayama model for $S=6$, indicates that the energy transfer is of dipole–dipole type.

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1. Introduction

Currently, extensive research is going on glasses doped with rare earth (RE) elements. The RE-doped glasses have long been the topic of research owing to their prominent and desirable optical and magnetic properties. Typically trivalent RE elements have very stable emissions, due to the 4f electrons which are deeply buried and hence well shielded from the outer shells. This property makes it possible to incorporate the RE elements into various hosts with different lattices and still preserve the typical RE emissions. The sharpness of many lines in the emission spectra of RE-doped glasses enable us, in principle to investigate interactions in a solid by optical means with a degree of accuracy similar to that usually possible with free atoms. In search of new lasing materials for optical devices such as upconvertors, light emitting diodes (LEDs), fibre amplifiers, memory devices, fluorescent display devices, etc., RE-doped inorganic glasses with suitable formers and modifiers are being studied [1–8]. Glasses based on heavy metals, viz., incorporating lead oxide, lead fluoride, bismuth oxide, etc., give opportunities for realization of more efficient laser systems in view of their low-phonon energy. The introduction of these compounds in conventional glasses, e.g., silicate, borate,

phosphate, etc., is also of interest as their presence can enhance the resulting fluorescence.

Phosphate glass is an excellent material for optical amplifier due to properties of good chemical durability, ion-exchange-ability, high gain co-efficient, wide band width capability and low upconversion emission. Phosphate glasses are technologically important materials because they generally have higher thermal expansion co-efficients, lower transition temperatures, low preparation temperatures and higher electrical conductivities than silicate and borate glasses [2,3]. These properties have made them ideal materials for fundamental studies of the glass transition and devitrification effects. However, their chemical durability limits their diverse users. Addition of different types of metal oxides like PbO, Al_2O_3, B_2O_3 etc., to binary phosphate glasses [4,5] has been found to improve their chemical durability and alter the physico-chemical properties like electrical conductivity and thermal expansion.

Among the glass components, Al_2O_3 has received significant consideration as the most likely useful matrix composition due to its high solubility of RE ions [9]. RE has a structure similar to that of Al_2O_3, in which RE ions have a preference for eight fold or nine-fold coordination. The charge of the RE ions is compensated by the oxygen's surrounding the Al^{3+} ions, which results in a homogeneous dispersion of the RE ions in the glass structure. However, in the meantime, it is difficult to prepare a glass containing large amounts of Al_2O_3 because of its high melting temperature. Addition of PbO to these glasses makes them to be

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more moisture resistant, in contrast to the conventional alkali oxide modifiers. Also PbO based glasses got the ability to form stable glasses due to its dual role, one as a modifier (if Pb–O is ionic) and the other as a glass former (with PbO_4 structural units, if Pb–O is covalent). The covalent character of PbO in the glass network is attributed to the strong interaction of easily polarizable valence shells of Pb^{2+} ions with the highly polarizable O^{2-} ion [10,11]. PbO mixed glasses may also be of particular interest for non-linear optical effects, when doped with RE ions. The IR harmonic and anharmonic electron–phonon modes are expected to contribute significantly to the non-linear optical susceptibilities in these glasses [12,13]. Lead phosphate glasses and derived samples doped with some metal oxides not only have high co-efficients of thermal expansion but can also exhibit good optical properties while having an improved chemical durability [3,14,15]. The strong absorption in the ultra-violet range is assumed to be caused by electron transition in the divalent lead ion [3]. Also the shift of the position of the absorption edge to longer wavelengths in these glasses is attributed to the increase in the concentration of non bridging oxygens.

RE ions such as Er and Tm-doped phosphate, silicate, germinate and tellurite glasses have been developed for infrared active optical devices. Recently, research focus on RE doped glasses is not limited to infrared optical devices, but there is a growing interest in visible optical devices. With the increasing demand of various visible lasers and light sources, further investigations of other RE ions, such as Dy^{3+}, Tb^{3+}, Sm^{3+} and Eu^{3+} ions, are becoming more important. It has been known for a long time that Sm^{3+} ion gives very strong fluorescence in the orange red spectral region in a variety of lattices, leading to potential high-power lasers, both in compact fibre and planar geometries. But only a few attempts have been made to explore the possibility of using orange-red luminescence of Sm^{3+} ions for the development of LED's in the visible spectral region as well as visible optical devices such as visible lasers and fluorescent devices. The main reason for not carrying on much spectral studies of Sm^{3+} ions doped in glasses is the complicated structure of $4f^6$ configuration of this ion. A large number of energy levels lying close to each other make the interpretation of the absorption spectrum of this ion rather difficult for the determination of meaningful intensity parameters needed in the calculation of various radiative properties which otherwise requires a suitable and skilful calculation technique. This could be made by properly grouping the closely observed transitions and carefully determining their intensities. In this work, the detailed optical and photoluminescence properties of Sm^{3+} doped lead phosphate glasses have been reported.

1.1. Experimental details

1.1.1. Glass preparation

Lead based phosphate glasses (PKAPbNSm) with composition of $44P_2O_5$–$17K_2O$–$9Al_2O_3$–$(24-x)$ PbO–$6Na_2O$–x Sm_2O_3, where $x=0.1$, 0.5, 1.0 and 2.0 mol% referred as PKAPbNSm01, PKAPbNSm05, PKAPbNSm10 and PKAPbNSm20, respectively, have been prepared. The stochiometric compositions of the batch materials were melted in a platinum crucible at 1100 °C for 1 h. The glasses were sufficiently annealed at 350 °C for 15 h and cooled slowly to release the thermal stress associated with these glasses during the quenching process. The refractive index was measured on an Abbe refractometer at wavelength 589.3 nm. The density was measured by the Archimedes method using water as an immersion liquid.

1.2. Spectroscopic measurements

Absorption spectra were measured on a Perkin-Elmer spectrometer (Lambda-950) in the wavelength range of 250–2500 nm

with a spectral resolution of 1 nm. The sample having the dimensions of 15 mm × 8 mm × 1.5 mm has been used for the optical measurements. Fluorescence spectra were obtained by exciting the samples with 488 nm line of a 10 W Ar^+ laser (2060-10 Beam lock Spectra Physics). The emission was collected with a convergent lens onto a 0.18 m single grating monochromator (Jobin Yvon Triax180) and then detected with the photomultiplier tube (Hamamatsu R928). The decay curves were measured by exciting the glass samples with the 476.5 nm radiation of optical parametric oscillator (EKSPLA/NT342/3/UVE) by monitoring the 600 nm emission. The laser power incidents on the samples during the luminescent measurements were 50 mW. The laser pulse width is 0.1 nm, pulse energy is 3 mJ, pulse duration is 10 ns and pulse interval is 10 Hz. The signal was acquired by a digital oscilloscope (LeCroy Wavesurfer 424, 200 MHZ Oscilloscope). The spectra were corrected from the instrument response and all the measurements were made at room temperature.

1.3. Theory

1.3.1. Energy level analysis, free-ion and bonding parameters

The free-ion Hamiltonian (H_{FI}) model that was used to study the energy level structure of Sm^{3+} ion can be written as [16,17]

$$\hat{H}_{FI} = E_{AVG} + \sum_k F^k \hat{f}_k + \xi_{SO} \hat{A}_{SO} + \alpha \hat{L}(\hat{L}+1) + \beta \hat{G}(G_2) + \gamma \hat{G}(R_7) + \sum_i T^i \hat{t}_i$$
$$+ \sum_k P^k \hat{p}_k + \sum_j M^j \hat{m}_j \tag{1}$$

where $k=2$, 4 and 6, $i=2$, 3, 4, 6, 7 and 8 and $j=0$, 2 and 4. This H_{FI} model accounts for two body electrostatic repulsion (F^k), two (α,β, γ) and three (T^i) body configuration interactions, spin–orbit coupling (ξ_{SO}), spin–other–orbit interactions (M^j) and electrostatically correlated spin–orbit interactions (P^k) and the spherically symmetric electron contribution is represented by a uniform energy shift of the $4f^n$ configuration (E_{AVG}). More detailed descriptions of the various operators and parameters which have become quite standard are available in the literature [18,19]. The quality of the parametric fit is generally described in terms of the root mean square (r.m.s.) deviation, σ, given by

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (E_i^{\exp} - E_i^{cal})^2}{N}} \tag{2}$$

where $E_i^{\exp}$ and E_i^{cal} are the experimental and calculated energies, respectively, for level i and N denotes the total number of levels included in the energy level fit.

1.3.2. Oscillator strengths: Judd–Ofelt theory

The intensity of an absorption band is generally expressed in terms of oscillator strength. The experimental oscillator strength (f_{exp}) of an f–f transition in the absorption spectra can be obtained by the following expression [6,20]

$$f_{\exp} = 4.318x10^{-9} \int \in(\upsilon) d\upsilon \tag{3}$$

where $\in$ is the molar absorptivity at a wavenumber υ (cm^{-1}). The theoretical oscillator strength of an f–f transition can be evaluated using the Judd–Ofelt (JO) theory [21,22]. In this theory, calculated oscillator strength (f_{cal}) for an induced electric-dipole transition from the ground state to an excited state is given by

$$f_{ed} = \frac{8\pi^2 mc\upsilon}{3h(2J+1)} \frac{(n^2+2)^2}{9n} S_{ed} \tag{4}$$

where

$$S_{ed} = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda \langle \Psi J || U^\lambda || \Psi' J' \rangle^2$$