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Optical, photoluminescence and physical properties of Sm^{3+} doped lead alumino phosphate glasses

Preet Kaur, Devinder Singh *, Tejbir Singh

Department of Physics, Sri Guru Granth Sahib World University, Fatehgarh Sahib, 140407, Punjab, India

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ABSTRACT

Sm^{3+} doped lead alumino phosphate glass samples have been synthesized by melt quenching technique. XRD pattern confirm non-crystalline structure of all the synthesized glass samples. These samples were further used to measure some physical and optical properties viz. density, molar volume, optical band gap, refractive index and polarizability. Absorption, excitation and emission spectra of the selected glass samples were obtained using UV–visible and photoluminescence spectrophotometers. A shift in excitation wavelength range to short wavelength region (208 nm) at high concentration of PbO is observed owing to the energy transfer mechanism from Pb^{2+} ion to Sm^{3+} ion; which confirm enhanced energy down conversion. In addition to four prominent emission transitions at 565 nm, 595 nm, 640 nm and 709 nm, one more peak appears at 685 nm which attributes the transitions from $^5D_0$ to $^7F_0$ in Sm^{2+} ion. The high absorption intensity in UV region and strong emission of red light has been observed for all the glass samples. Higher densities for the synthesized glass samples were observed due to presence of lead ($_{82}Pb$). The glasses have potential application in developing high energy electromagnetic radiation sensors.

1. Introduction

Phosphate glasses have a wide range of applications owing to its properties such as low melting point, low optical dispersion, low refractive indices, high transparency, high thermal expansion coefficient and high gain density due to high solubility for lanthanide ions [1]. Among the low melting point glasses, phosphate glasses have been the attraction of many researchers due to its low phonon energy in comparison to borate glasses [2]. Moreover, the chemical stability of phosphate glasses can be improved with the addition of metal oxides such as Li_2O, Al_2O_3 etc. These glasses can be considered as good candidates for radiation shielding [3]. Further, phosphate glasses are found to be advantageous over silicate glasses for being good host to high concentration of doping rare earth ions for optical, display and LED devices [4]. Rare earth doped phosphate glasses have numerous applications in optoelectronic devices such as lasers, fluorescent devices, optical detectors, optical amplifiers and high density memories etc. [5].

The addition of PbO in phosphate glasses increases the moisture resistant capabilities. As compared to the conventional alkali or alkaline earth oxide modifiers, PbO forms more stable glasses due to its dual role-one as glass former with PbO_4 structural units and other as modifier with PbO_6 structural units [6]. Moreover, the addition of PbO in glasses leads to increase its density as well as refractive index; which further affects the optical properties of the glass systems [7]. The addition of PbO also helps in decreasing the phonon energy and thereby reducing the non-radiative losses [8]. The scope of phosphate glasses were also explored in environmental applications for the burial of some radioactive wastes [9]. Further, the addition of Al_2O_3 in lead phosphate glasses not only reduces its hygroscopic nature, but also improves the glass quality and enhances the transmission of radiations [10].

With the increasing demand of optical devices, Sm^{3+} ions doped glasses are gaining significance. Optical and luminescence properties of Sm^{3+} doped CdO-Al_2O_3-SiO_2 glasses were explored for its use in infra-red lasers and optical amplifiers. It has been also reported that heavy metal oxide glasses possess lower phonon energies as compared to other oxide glasses [11]. Sm^{3+} doped phosphate glasses with composition $60P_2O_5$-$4B_2O_3$-$7Al_2O_3$-$10K_2O$-$18BaO$-Sm_2O_3 exhibit strong fluorescence intensity, large stimulated emission, large absorption cross-section, long fluorescent life time, high luminescence efficiency and rich energy levels [12]. Samarium doped glasses with composition $(60-x)P_2O_5$-$20PbO$-$20ZnO$-xSm_2O_3 where $x = 0, 0.5, 1.0, 3.0$ mol%) were prepared by melt quenching technique. Sm^{3+} ions doped glasses show strong emission in the orange-red region originating from $^4G_{5/2}$ level which is populated non-radiatively by $^6P_{3/2}$ state and its sublevels [13]. Lead fluoro phosphate glasses of composition $44P_2O_5$-$17K_2O$-$9Al_2O_3$-$(24-x)PbF_2$-$6Na_2O$-xSm_2O_3, where $x = 0.01, 0.05, 0.1, 0.5, 1.0$ and 2.0 mol% shows relatively high quantum efficiency due to larger energy gap (of the order of 7200 cm^{-1}) between the metastable $^4G_{5/2}$ level and the next lower lying energy level $^6F_{11/2}$ [14]. The lasing efficiency for Sm^{3+} doped phosphate (P_2O_5-K_2O-BaO-Al_2O_3-Sm_2O_3) and fluoro-phosphate (P_2O_5-K_2O-BaO-BaF_2-Al_2O_3-Sm_2O_3) glasses were

* Corresponding author.
E-mail address: drdevinderphysics@gmail.com (D. Singh).

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investigated for its applications in high density optical storage, under sea communication, color display, temperature sensors and medical diagnostics [15]. Recently, alumino-phosphate glass with chemical composition $50P_2O_5$–$20Li_2O$–$7Al_2O_3$–$10Sb_2O_3$–8MnO–$1.5Eu_2O_3$–$1Er_2O_3$–$2.5Yb_2O_3$ has been explored for glass greenhouse, which can convert sunlight to red light emission with high efficiency [16].

Considering the advantages of phosphate glasses, an attempt has been made to synthesize lead-alumino phosphate glass matrix doped with Sm^{3+} ions in different compositions to explore its feasibility as high energy electromagnetic sensor. Further, the variation of different physical and optical properties with the molar percentage of PbO has been explored.

2. Experimental

2.1. Sample preparation

The chemical composition of different glasses samples synthesized by melt-quenching technique has been listed in Table 1. Analytical grade chemicals viz. ammonium dihydrogen phosphate ($NH_4H_2PO_4$), lead oxide (PbO), aluminum oxide (Al_2O_3) and samarium oxide (Sm_2O_3) were weighed in an electric balance (least count 0.1 mg) and grinded to fine powder in an agate mortar and mixed well. The mixture was then put into a silica crucible and heated at 1000 °C for 2 h in an electric furnace. The glasses were obtained by pouring the melt onto a preheated graphite mould of dimensions 1.5 cm (inner diameter) × 1.5 cm (thickness). The glass samples were then annealed at 350 °C for 12 h to eliminate any mechanical and thermal stress. All the samples were grinded and well-polished before performing further investigations.

2.2. X-ray diffraction

The characterization of glass samples was performed by X-ray diffraction (XRD) studies using Rigaku Miniflex Table Top spectrometer with $Cu-k\alpha$ line of width $=1.5418A^{\circ}$ at the scanning rate of 2°/min and 2θ was varied from 5° to 70°.

2.3. Density and molar volume

The densities of the glass samples was measured by Archimedes principle at room temperature using sensitive microbalance (Shimadzu ELB300) with benzene (density $= 0.876$ g cm^{-3}) as an immersion liquid. The accuracy in the measurement of weight was ± 0.1 mg. The experiment was repeated four times to get an accurate value of density. The corresponding molar volumes were calculated by the formula $V_m = M/\rho$, where M is molecular weight and ρ is the density of corresponding glass samples.

2.4. Optical studies

2.4.1. Energy band gap

UV absorption spectra of as prepared glass samples were obtained by spectrophotometer (Shimadzu UV-2600/UV-2700) in the wavelength range of 250–900 nm. Mott and Davis [17] reported experimental results for optical absorptions in non-crystalline materials. There are two types of transitions, i.e. direct and indirect, that occur at absorption edges. These transitions occur as a result of interaction of electromagnetic waves with valence electrons thereby raising it across the energy gap to conduction band. Indirect transitions involve simultaneous interaction with lattice vibrations and the wave vector of the electron. In crystalline semiconductors, the absorption coefficient varies with incident photon energy for indirect allowed transitions by the relation [18]

$$\alpha(\nu)\mathrm{h}\nu = \mathrm{B}\left(h\nu - E_g\right)^2 \tag{1}$$

where B is a constant, E_g is the optical band gap energy and hν is the incident photon energy.

The optical absorption coefficient $\alpha(\nu)$was calculated for each sample at various photon energies by the relation $\alpha(\nu) = \frac{A}{d}$, where A is the absorbance and d is the thickness of the sample. The value of indirect energy gap was obtained by plotting $(\alpha h\nu)^{1/2}$ as a function of $h\nu$ and then extrapolating the linear part of each curve to energy axis [19].

2.4.2. Refractive index

Refractive index (n) studies of the glass samples was obtained by the relation [20]

$$\frac{(n^2-1)}{(n^2+2)} = 1 - \sqrt{\frac{E_g}{20}} \tag{2}$$

2.4.3. Polarizability

Polarizability (α_m) of the oxide ions of the glass samples was obtained by Lorentz-Lorentz relation [21].

$$\frac{(n^2-1)}{(n^2+2)} V_m = \frac{4}{3}\pi N \alpha_m \tag{3}$$

where V_m and N are the molar volume and Avogadro's number respectively.

2.5. Photoluminescence studies

Excitation and emission spectra of the prepared glass samples were observed by applying a xenon flash lamp in Fluorescence Spectrometer (FLS980) in the wavelength domain 200 to 450 nm for excitation spectra and 400 to 750 nm for emission spectra with step 1 nm and integration time 0.2 s.

All the above said properties were recorded four times, which were further used to compute mean and standard deviation using the following expressions:

$$\mathrm{S.D} = \sqrt{\Sigma\left(\mathrm{X_i} - \overline{\mathrm{X}}\right)^{2/N}} \tag{4}$$

where

Table 1
Nominal Composition, density (ρ), molar volume (V_m), optical band gap (E_g), refractive index (n) and polarizability (α_m) along with standard deviation of oxide ion of Al_2O_3-Sm_2O_3-PbO-P_2O_5 glass system.

Sample name	Composition [mol%]				Density (ρ) [g/cm^3]	Molar volume (V_m) [cc/mol^{-1}]	Optical band gap (E_g) [eV]	Refractive index (n)	Polarizability (α_m)$\times 10^{-24}$ [cc]
	PbO	P_2O_5	Al_2O_3	Sm_2O_3					
PbPAS1	38	60	1.8	0.2	4.411 ± 0.092	39.387 ± 0.825	3.85 ± 0.029	2.199 ± 0.0058	8.768 ± 0.192
PbPAS2	48	50	1.8	0.2	5.066 ± 0.073	35.984 ± 0.514	3.56 ± 0.026	2.261 ± 0.0058	8.251 ± 0.105
PbPAS3	48	51.8	0	0.2	4.584 ± 0.011	39.417 ± 0.099	4.05 ± 0.028	2.160 ± 0.0053	8.599 ± 0.046
PbPAS4	58	40	1.8	0.2	5.416 ± 0.021	34.782 ± 0.132	3.52 ± 0.024	2.270 ± 0.0055	8.008 ± 0.039