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Influence of modifier oxide on Spectroscopic properties of Ho^{3+}: V^{4+} co-doped $Na_2O–SiO_2–ZrO_2$ glasses

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ABSTRACT

$Na_2O–SiO_2–ZrO_2$ glasses co-doped with variable concentrations of Ho^{3+}: V^{4+} have been synthesized, characterized by different techniques and finally their luminescence characteristics were investigated. The EDS spectra of the glass samples indicate all the elements are intact in the final composition of prepared glass. The infrared and Raman spectral studies are carried out and the existence of conventional structural units are analyzed. The ESR and optical absorption spectra indicated that a considerable proportion of vanadium ions do exist in V^{4+} state in addition to V^{5+} state. The absorption and emission spectra of Ho^{3+} ions were characterized using J–O theory. The radiative transition probabilities and branching ratio were evaluated from luminescence spectra. The analysis these results indicated the highest values of radiative probabilities and branching ratios for the green emission transition viz., $^5S_2 \rightarrow {}^5I_8$ transition among various other transitions of Ho^{3+} ions. However, the presence of higher concentration of V_2O_5 in the glass matrix seems to be a hindrance for getting the high luminescence efficiency especially in the red region.

1. Introduction

Oxide glasses doped with trivalent rare earth ion have been paid much attention due to their potential applications in developing solid state and glass lasers, optical applications such as fibers, amplifiers and visible display devices. Among the rare earth ions Ho^{3+} are expected to give high luminescence output to view the characteristics of the glasses. These Ho^{3+} doped glasses which emit emission bands in the ultraviolet, visible region are of great interest and it is used for eye-safe source in atmosphere, wind shear, laser radar, medical and surgery [1–3]. An alkali oxide like sodium is added to glasses, the optical density in the ultraviolet wavelength longer than the absorption edge is directly proportional to the alkali concentration and the intensity of absorption increases. Addition of sodium oxide in to glasses provides suitability for the fabrication of optical wave guide devices [4–7]. Silica has been the most commonly used host glass and having many applications in semiconductor technology, optical devices such as optical data storage, color display, optical communication and other related areas of opto-electronics [8–10].

The incorporating of intermediate oxides like Zirconium in to the glasses leads to an enormous extension of possible vitreous materials with special physical properties. The presence of network modifier effects fundamentally to the glass properties; consequently the molar volume and the glass transition temperature is lowered due to the reduced degree of cross linking. The addition of alkali and alkaline metal oxide to silicate, zirconate mixed oxides have high alkaline resistance and alkali glass durability of the glass system are used as fibers reinforcing cement [11–13]. Among the various semiconducting transition metal oxide glasses, vanadate glasses are widely used in memory switching devices. Vanadium containing glasses are well known as the n-type semiconductors which show the semiconducting behavior with electrical conductivity of 10^{-3} to 10^{-5} ($\Omega\,cm^{-1}$) due to electron hopping between V^{4+} and V^{5+} ions. Vanadium ions are mixed with trivalent rare earth ions increase the laser efficiency of the glasses due to the energy transfer process and takes place radiative and non radiative transitions within the glass network [14–18].

The objective of the present study is to investigate how the transition metal oxides (V_2O_5) influence the optical properties of RE^{3+} ion and the energy transfer probably takes place between Ho_2O_3:V_2O_5 co-doped sodium, silicon, zirconium (NSZ) glasses by using EDS, FT-IR, Raman, EPR, Optical Absorption and Luminescence studies.

2. Experimental technique

The following compositions are chosen for the present study. Appropriate amounts of analytical grade reagents of Na_2CO_3, SiO_2, ZrO_2, Ho_2O_3 and V_2O_5 with 99.9% purity are used to prepare the glasses. Here holmium and vanadium are considered as dopants in the glass network. The melt quenching method is used for the preparation of glass samples; in this, definite amount of powders in mol% were

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thoroughly mixed in an agate mortar and to get homogeneous mixture and it is melted in silica crucible in the temperature range 1350–1450 °C in an automatic temperature controlled furnace about 1 h. The resultant bubble free melt was quickly poured in to preheated brass mould and subsequently annealed at 450 °C temperature. Later the prepared samples were ground and optically polished to final dimensions of 1 cm × 1 cm × 0.2 cm. The composition of the prepared glasses containing variable amount of contents are given in Table 1.

The refractive index of the glass sample is measured by using Abbe's refractrometer with monobromo naphthalene as the contact layer between the glass and the refractrometer prism. The density of the glasses was determined by the standard Archimedes principle using o-xylene (99.9% pure) as buoyant liquid. The energy dispersive spectroscopy measurements were conducted on a thermo instruments model noran system 6 attached to scanning electron microscope. The electron spin resonance (ESR) spectra of the fine powder of the sample were recorded at room temperature using E11Z Varian X-band (υ = 9.5 GHz) ESR spectrometer of 100 kHz field modulation. Infrared transmission spectra are recorded on a JASCO-FT-IR -53000 spectrophotometer with resolution of 0.1 cm^{-1} in the spectral range 400–4000 cm^{-1} using KBr pellets (300 mg) containing the pulverized sample (1.5 mg). The Raman spectra (model Nexus 670 Nicolet – Madison –W.I.USA) is recorded on fourier transform Raman spectrometer with resolution of 4 cm^{-1} in the 400–1500 cm^{-1}. The optical absorption (UV–Vis) spectra are recorded on JASCO, V-570 spectrophotometer from 200 to 1800 nm with spectral resolution of 0.1 nm. The luminescence Spectra are recorded at room temperature on a photon technology international (PTI) spectroflurometer with excited wavelength 400 nm from 300 to 1200 nm.

3. Results

3.1. Physical properties

To know the physical properties of the glasses, the calculated values of density (d) and refractive index along with other physical parameters [19–21] such as vanadium ion concentration (N_i), mean ionic separation (r_i), polaron radius (r_p), field strength (F_i), electronic polaraizability (α), reflection loss, molar refractivity (R_M) and optical dielectric constant (ε) are calculated by using conventional formulae and are presented in Table 2. Fig. 1 shows the variation of density and refractive index as a function of V_2O_5 concentration. Fig. 2 represents the ionic concentration and electronic polaraizability as a function of *x* mol% of dopant.

3.2. Energy dispersive spectroscopy

Results from the energy dispersive spectroscopy (EDS) reveals the chemical makeup of the samples; the analysis indicates the presence of sodium (Na), silicon (Si), zirconium (Zr), samarium(Sm), oxygen (O), carbon(c), and vanadium (V) elements in various phases. Fig. 3 shows the chemical composition of the glasses with 0.2% and 1 mol% of V_2O_5. The inset figure shows the electronic image spectrum of the glass sample.

3.3. Fourier transforms infrared transmission spectra (FT-IR)

Fig. 4 shows the Fourier transforms infrared transmission spectra of undoped and doped Ho^{3+}/V^{4+}: NSZ glasses; which gives the information about the various vibrational modes and also provides different structural units. The observed IR spectral bands are given in Table 3. The spectra exhibit a series of bands [22] one at about 483 cm^{-1}, the second band at around 630 cm^{-1} and the third at around 700 cm^{-1}. Another two bands are located at around 850, 880 cm^{-1} and one sharp band with a peak is located at about 1012 cm^{-1}.

3.4. Raman spectra

Fig. 5 represents the Raman spectra of the undoped and doped Ho^{3+}/V^{4+}: NSZ glasses. Raman spectra analyses the local arrangement of the glasses and also give information about the structural properties that would support the infrared transmission spectra. The Raman spectra of the glasses and band positions are presented in Table 4. The spectra of NSZ glasses have revealed a peak at round 340–365 cm^{-1} and structural vibrations are observed at 800 cm^{-1}. In the spectrum contains V_2O_5, stretching vibrations are observed at around 600 cm^{-1} and another two band is observed at 950 cm^{-1} and 1080 cm^{-1} [23–25].

3.5. Electron paramagnetic resonance spectra

The EPR spectra recorded at room temperature for the present investigated NSZ: Ho^{3+}/V^{4+} co-doped glasses. No signals are observed for the undoped glasses. When V_2O_5 enter into the glass matrix, the EPR resonance spectra exhibit eight parallel and eight perpendicular lines arising from the unpaired $3d^1$ electron of VO^{2+} ions with ^{51}V (I = 7/2) isotope in an axially symmetric field. The axial spin-Hamiltonian for hyperfine interaction is used to describe the spectra of V^{4+} ions [26].

$$H = \beta\left[g_{\parallel}B_zS_z + g_{\perp}(B_xS_x + B_yS_y)\right] + A_{\parallel}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) \quad (1)$$

Here β denotes Bohr magneton, $g_{\parallel}$, $g_{\perp}$ and $A_{\parallel}$, $A_{\perp}$ denotes the components of the hyperfine coupling tensor, B_x, B_y and B_z denotes components of the magnetic field, S_x, S_y, S_z and I_x, I_y, I_z are the spin operator of the electron and the nucleus. The magnetic field positions for the parallel and perpendicular hyperfine peaks are based on the second order perturbation terms are

$$B_{\parallel}(m) = B_{\parallel}(0) - mA_{\parallel}\left[\frac{A\perp^2}{1B_{\parallel}(0)}\right]\left[\left(\frac{63}{4}\right) - m^2\right] \quad (2)$$

$$B\perp(m) = B_{\perp}(0) - mA_{\perp}\left[\frac{A_{\parallel}^2 + A_{\perp}^2}{4B_{\perp}(0)^2}\right]\left[\left(\frac{63}{4}\right) - m^2\right] \quad (3)$$

From the above equation m refer to the nuclear spin magnetic quantum number, bearing values ±7/2, ±5/2, ±1/2; $B_{\parallel}(0) = h\nu/g_{\parallel}\beta$ and $B_{\perp}(0) = h\nu/g_{\perp}\beta$. From the above parameters, the dipolar hyperfine coupling parameters $P = 2\delta\beta\beta_N\langle r^{-3}\rangle$ and the Fermi contact interaction (K), are evaluated [27] using the expression

$$A_{\parallel} = P[(-4/7) - K + (g_{\parallel} - g_e) + (3/7)(g_{\perp} - g_e)] \quad (4)$$

$$A_{\perp} = P[(2/7) - K + (11/14)(g_{\perp} - g_e)] \quad (5)$$

In the equation, g_e = 2.0023 and refer to the *g* factor of the free electron. The term *P* and *K* in the above equation result from the

Table 1
Composition of the studied glasses (batch mol%).

S. No.	Glass	Na_2O (mol%)	SiO_2 (mol%)	ZrO_2 (mol%)	Ho_2O_3 (mol%)	V_2O_5 (mol%)
1	Pure	40	55	5	–	–
2	Hov0	40	54	5	1	–
3	Hov1	40	54	4.8	1	0.2
4	Hov2	40	54	4.6	1	0.4
5	Hov3	40	54	4.4	1	0.6
6	Hov4	40	54	4.2	1	0.8
7	Hov5	40	54	4	1	1.0