1. Introduction

In recent years, rare earth doped glasses are found to be more useful materials for fiber amplifiers, sensors, high optical data storage/reading and solid state lasers [1, 2]. This is because of the fact, that the f-f electrons are shielded by the outer 5s and 5p electrons, which lead to sharp absorption and emission lines due to weak interaction with the environment. Glass is a very important host material for the doping of rare earth ions for the development of optical devices. Among different types of glass systems, the oxide glasses are more suitable for practical applications due to their high chemical durability and thermal stability. In oxide glass, silicate glasses are the most popular hosts and easy to draw into fibers for use in lasers and fiber amplifiers [3]. Silicate glasses possess high transparency from near UV to IR spectral range, and high melting point, but the maximum phonon energy (~1100 cm⁻¹) is a still major problem due to the stretching vibrations of the network forming oxides. In these glasses, K₂O is often used to modify the field strength of cations to improve mechanical properties which is prerequisite for a good laser glass [4]. Moreover, glasses containing Nb₂O₅ exhibit good non-linear optical properties, such as high non-linear refractive index (n₂), which make them attractive materials for ultrafast switching devices [5]. Among rare earth ions, the Sm³⁺ ions containing glass have stimulated extensive interest due their potential applications for high density optical storage, under sea communication and color displays [6]. In order to obtain optimum emission characteristics for device applications, the characteristic features of host material as well as the concentration dependent studies of Sm³⁺ ions are very much essential. In this direction an extensive research has been carried out to identify the new glasses doped with Sm³⁺ ions.

In the present study, the optical and structural properties of Sm³⁺ ions in potassium niobate silicate glasses are investigated through the Raman, absorption, excitation and photoluminescence spectra. The Judd-Ofelt intensity parameters (λ₁, λ₂ and λ₃) have been derived from absorption spectra, which is in turn used to calculate radiative properties of the excited luminescent levels of Sm³⁺ ions. The decay times of the 4G5/2 excited level for different concentration of Sm³⁺ ions have been measured. The non-exponential behavior of decay curves has been analyzed through Inokuti-Hirayama model. The characteristic emission and the radiative parameters obtained for the 4G5/2 → 6H7/2 transition indicate that the KNbSiSm glass could be very much useful for the development of lasers and photonic device applications in the visible region.

2. Experimental details

2.1. Materials and methods

Sm³⁺-doped potassium niobate silicate glasses (KNbSiSm) with a chemical composition of 30 K₂O-25 Nb₂O₅- (44.95-x)SiO₂-xSmO₃, where x = 0.05, 0.1, 0.5, 1.0 and 2.0 mol %, were prepared by conventional melt quenching technique [6] and referred as KNbSiSm005, KNbSiSm01, KNbSiSm05, KNbSiSm10, KNbSiSm10 and KNbSiSm20 respectively. The compositions of the batch materials (~15 g) were melted in a platinum crucible at 1350°C for about 2-3 h. The melts were then poured onto a preheated brass mould at a temperature of 450°C and then the glass samples were annealed for 12 h to remove the thermal stress and strains and polished carefully for spectral measurements.

2.2. Physical and spectroscopic measurements

For 1.0 mol % Sm³⁺-doped KNbSiSm10 glass, the physical parameters such as density (d = 3.37 g cm⁻³), concentration (C = 1.47X10²¹ ions/cm³), optical path length (l = 0.396 cm) and the refractive index (n = 1.81) were determined. The Raman spectrum of the undoped sample was measured by Renishaw invia Raman microscope using 785 nm diode laser. The optical absorption spectrum of KNbSiSm10 glass was recorded using a Perkin Elmer Lambda-950 UV-Vis-NIR spectrophotometer in the wavelength range of 350-2200 nm. The excitation and photoluminescence spectra were obtained by
Exciting the samples at 404 nm and the decay measurements were done using Jobin Yvon Fluorolog-3 spectrophotometer using xenon arc lamp as an excitation source.

3. Results and discussion

3.1. Analysis of Raman spectrum

![Fig. 1. Raman spectrum of undoped KNbSi glass with 785 nm laser excitation](image)

Structural details of the undoped KNbSi glass have been studied using Raman spectroscopy. The unpolarized Raman scattering spectrum measured using the 785 nm laser excitation exhibits four bands at 241, 882, 1379 and 3281 cm\(^{-1}\) as shown in Fig. 1. It is noticed from Fig. 1 that the high intensity phonon band at 882 cm\(^{-1}\) possesses lesser energy than that of pure SiO\(_2\) glass, which has a maximum phonon band around 1100 cm\(^{-1}\) [9]. The stretching modes of the Si-O-Si bands of SiO\(_4\) tetrahedral with non-bridging oxygen atoms occur are active in the region 800-1300 cm\(^{-1}\) [10, 11] and the stretching modes of the Nb-O bonds in the NbO\(_6\) octahedral occur in the 300-900 cm\(^{-1}\) region [12-14]. Particularly, the bands of SiO\(_2\) occur at 1200, 1100, 950, 900, 850 cm\(^{-1}\), while for the Nb-O in octahedral symmetry occurs at 870, 730, 625, and 340 cm\(^{-1}\). The structural role of NbO\(_5\) in silicate, borate, germanate and gallate glasses has been investigated and found that NbO\(_5\) groups exist in the glass network [15, 16]. Fukumi et al.[14] investigated the structural position of NbO\(_6\) - groups in K$_2$O- Nb$_2$O$_5$- SiO$_2$ glass systems and noticed the Raman band in the 800- 900 cm\(^{-1}\) region, which is attributed to NbO\(_6\) octahedral with non-bridging oxygen and with much distortion. The broad bands in the 600- 800 cm\(^{-1}\) region are attributed to less distorted NbO\(_6\) octahedra in non-bridging oxygen’s. The bands at 815- 870 cm\(^{-1}\) are related to the Nb-O stretching modes of distorted NbO\(_6\) octahedral sharing a corner with SiO\(_4\) tetrahedral. As the Nb content increases, the NbO\(_6\) octahedral as well as cluster start to appear, while the tetrahedral disappear. The characteristic intense band at 882 cm\(^{-1}\) is attributed to the presence of Si- O- Si and the band at 241 cm\(^{-1}\) is assigned to the presence of Nb- O. The characteristic bands around 1379 cm\(^{-1}\) and 3281 cm\(^{-1}\) are assigned to H- O- H vibration mode.

3.2. Absorption spectrum and Judd-Ofelt parameters

![Fig. 2. Optical absorption spectra of KNbSiSm10 glass (a) UV-Vis (b) NIR regions.](image)

Optical absorption spectra of Sm\(^{3+}\)-doped KNbSiSm10 glass recorded in the ultraviolet (UV) - visible (Vis) and near infrared (NIR) regions are shown in Fig. 2(a) and 2(b) respectively. The shape and peak positions of Sm\(^{3+}\)- doped glasses [6, 17]. The spectra revealed sixteen absorption bands corresponding to the transition from the 6H\(_{5/2}\) ground state to the higher energy levels $^4H_{15/2}$, $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^4F_{9/2}$, $^4F_{11/2}$, $^4G_{5/2}$, $^4G_{9/2}$, $^4I_{11/2}$, $^4G_{13/2}$, $^4G_{15/2}$, $^4I_{15/2}$, $^4G_{17/2}$, $^4I_{17/2}$, $^4G_{19/2}$, $^4I_{19/2}$, $^6P_{5/2}$, $^6P_{3/2}$, $^6P_{7/2}$ and $^4D_{3/2}$. The assignment of absorption levels is done by comparing with energy levels of Sm\(^{3+}\): aquo-ion [18]. The experimental oscillator strengths ($\phi_{\text{exp}}$) of absorption bands determined from absorption spectrum are used to evaluate the JO parameters, $\Omega_i (i=2, 4, 6)$ by the least-square fit, which gives the best fit between the experimental ($\phi_{\text{exp}}$) and calculated oscillator strength ($\phi_{\text{Cal}}$) as listed in Table 1.

| Transition | Energy (cm\(^{-1}\)) | $\phi_{\text{Cal}}$ | $\phi_{\text{exp}}$ |
|------------|---------------------|-------------------|-------------------|
| $^4I_{15/2}$ | 21097 | 1.42 | 2.12 |
| $^4G_{9/2}$ | 22727 | 0.12 | 0.28 |
| $^4P_{5/2}$ | 23809 | 1.08 | 0.85 |
| $^4P_{3/2}$ | 24752 | 7.16 | 7.17 |
| $^4P_{1/2}$ | 26595 | 2.67 | 1.18 |
| $^4D_{3/2}$ | 27624 | 1.19 | 2.20 |

The magnitudes of JO parameters ($\Omega_i$) are important for...
the investigation of glass structure and the excited state dynamics of lanthanide (Ln³⁺) ions. Generally, the Ω parameter is sensitive to the symmetry of the rare earth ion site and strongly affected by covalence between rare earth ions and ligand anions, where as Ω₁ and Ω₂ are related to the rigidity of the host medium in which the ions are situated [19]. The magnitudes of Ω₁, Ω₂, and Ω₃ their trends and radiative lifetimes (τₑ, ms) for KNbSiSm10 glass are tabulated in Table 2 along with the other reported systems [19- 20]. In the present investigation the trend of JO parameters have been observed as Ω₁ > Ω₄ > Ω₆. Similar observation has been found for LSFB10 [19], tellurite [20], Pb(PO₃)₂ [21], LBTA [22], PbO-PbF₂ [23] and Calibo [25] glasses. Using these JO parameters, several radiative properties have been calculated as given in Table 3.

Table 2. Comparison of JO parameters (Ω, x10⁻²⁰ cm²), their trend and radiative lifetimes (τₑ, ms) of 4G₅/₂ excited level in different Sm³⁺ doped glasses.

| Glass         | Ω₁    | Ω₄    | Ω₆    | Trend          | τₑ    | Reference  |
|---------------|-------|-------|-------|----------------|-------|------------|
| KNbSiSm10     | 2.08  | 5.56  | 4.22  | Ω₆ > Ω₄ > Ω₂  | 1.6   | Present work|
| L5FBS10       | 2.34  | 7.54  | 5.40  | Ω₄ > Ω₆ > Ω₂  | 2.15  | [19]       |
| Tellurite     | 0.06  | 0.34  | 0.24  | Ω₆ > Ω₄ > Ω₂  | 0.21  | [20]       |
| Pb(PO₃)₂      | 1.70  | 4.00  | 2.20  | Ω₆ > Ω₄ > Ω₂  | 2.75  | [21]       |
| LBTA          | 0.27  | 2.52  | 2.47  | Ω₆ > Ω₄ > Ω₂  | 4.88  | [22]       |
| PbO-PbF₂      | 1.16  | 2.60  | 1.40  | Ω₆ > Ω₄ > Ω₂  | 4.46  | [23]       |
| BLNS          | 3.92  | 8.17  | 5.82  | Ω₆ > Ω₄ > Ω₂  | 2.88  | [24]       |
| Calibo        | 0.98  | 5.04  | 4.73  | Ω₆ > Ω₄ > Ω₂  | 3.97  | [25]       |

Table 3. Comparison emission peak positions (λₑ, nm), effective linewidths (Δλₑ, nm), radiative transition probabilities (A, s⁻¹), peak stimulated emission cross-sections (σₑ, x10⁻²⁰ cm²) calculated branching ratios (βₑ) and experimental (βₑ) for KNbSiSm10 glass with different Sm³⁺ doped systems [6,17,20].

| Transition | Parameters | KNbSiSm (present work) | Fluorophosphate [8] | Phosphosilicate [17] | Telurelite [20] |
|------------|------------|------------------------|---------------------|---------------------|----------------|
| 🟢G₄→H₁₀   | λₑ         | 567                    | 562                 | 563                 | 563            |
|           | Δλₑ        | 15.60                  | 10.5                | 10.4                | 3.64           |
|           | A          | 37                     | 24                  | 28                  | 2              |
|           | σ (λₑ)     | 1.10                   | 1.27                | 1.21                | 5.50           |
|           | βₑ         | 0.066                  | 0.06                | 0.09                | --             |
|           | βₑ(Exp)    | 0.236                  | 0.07                | 0.16                | 0.02           |
| 🟢G₅→H₁₀   | λₑ         | 604                    | 598                 | 598                 | 598            |
|           | Δλₑ        | 15.86                  | 12.3                | 10.4                | 6.04           |
|           | A          | 285                    | 159                 | 123                 | 44             |
|           | σ (λₑ)     | 9.7                    | 9.10                | 6.76                | 6.76           |
|           | βₑ         | 0.505                  | 0.41                | 0.40                | --             |
|           | βₑ(Exp)    | 0.457                  | 0.39                | 0.52                | 0.49           |
| 🟢G₆→H₁₂   | λₑ         | 651                    | 645                 | 645                 | 643            |
|           | Δλₑ        | 16.41                  | 14.8                | 13.9                | 16.92          |
|           | A          | 171                    | 124                 | 126                 | 19             |
|           | σ (λₑ)     | 7.574                  | 8.01                | 7.06                | 2.57           |
|           | βₑ         | 0.302                  | 0.32                | 0.41                | --             |
|           | βₑ(Exp)    | 0.317                  | 0.42                | 0.30                | 0.22           |

3.3. Excitation spectrum

Fig. 3. Excitation spectrum of KNbSiSm10 glass by monitoring the emission at 604 nm.

The excitation spectrum of KNbSiSm10 glass by monitoring emission at 604 nm shows three observations (4G₅/₂) have been determined as listed in Table 3.

3.4. Emission spectrum

The emission spectra for different concentrations of Sm³⁺ doped KNbSiSm glasses under 404 nm excitation are shown in Fig. 4. The observed four emission peaks at 567, 604, 651 and 709 nm are assigned to 4G₅/₂ → 6H₇/₂, 6H₅/₂, 6H₃/₂ and 6H₁₁/₂ transitions respectively [27]. These transitions are useful in high density optical storage, for the measurement of emission spectra of different concentration of Sm³⁺ ion doped glasses.

Fig. 4. Photoluminescence spectra for different concentration of Sm³⁺ ions in KNbSiSm glasses under 404 nm excitation.
These evaluated radiative parameters are compared with those of Sm³⁺-doped fluorophosphates [6], phosphate [17] and tellurite [20] glasses. It is observed that the transition probabilities (A_R, s⁻¹) and peak stimulated emission cross-sections (σ_p) are high for all the emission transitions in the (KnbSiSm) glass. These results indicate that the \(^{4}G_{5/2} \rightarrow ^{6}H_{7/2}\) transition in KnbSiSm glass could be very much useful for the development of lasers and photonic devices in the visible region.

3.5. Decay curve analysis

Fig. 5 shows the decay curves of \(^{4}G_{5/2}\) excited level for different concentrations of Sm³⁺-doped KnbSiSm glasses.

Fig. 5. Decay curves for the \(^{4}G_{5/2}\) level in for different concentrations of Sm³⁺-ions in KnbSiSm glasses.

Fig. 6. Partial energy level diagram of Sm³⁺-ions in KnbSiSm10 glass showing excitation, radiative, non-radiative decays and possible cross-relaxation channels.

Table 4. The experimental lifetime (\(\tau_{\text{exp}}\), ms) of \(^{4}G_{5/2}\) level, energy transfer parameters (Q), critical transfer distances (\(R_0, \text{Å}\)) and donor-acceptor interaction parameters (C_DA, X10⁻⁴¹ cm⁻⁶ s⁻¹) for different Sm³⁺- concentrations in KnbSiSm glasses.

4. Conclusions

Potassium niobate silicate glasses with different concentrations of Sm³⁺-ions were prepared and characterized for their structural and optical properties through Raman, absorption, excitation, emission and decay measurements at room temperature. The Raman spectrum revealed the basic structural units related to the presence of Si-O-Si and Nb-O bands which are attributed to NbO\(_6\) octahedral with non-bridging oxygen’s. Judd-Ofelt (JO) parameters (\(\Omega_i, (i=2, 4, 6)\) have been evaluated from the oscillator strengths of absorption bands in UV-Vis/NIR regions. Various radiative parameters like radiative transition probabilities (A_R, s⁻¹), peak stimulated emission cross-sections (σ_p), experimental (\(\lambda_{\text{exp}}\)) and calculated (\(\lambda_\text{cal}\)) branching ratios for the emission transitions of Sm³⁺-ion in KnbSiSm10 glass. From these results it is suggested that Sm³⁺-doped potassium niobate silicate glasses are more efficient luminescent materials for the development of lasers and photonic devices in the visible region.

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