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Optical Properties of Fluoroborate glasses doped with Samarium(Sm^{3+})

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Abstract

By doping rare earth ions, the structural and optical properties of borate glasses can be improved and obtaining optimized concentrations is challenging in laser glass research. Borate glasses among others are promising due to their excellent optical performance and enhanced response suitable for photonic devices. 0.5, 1.0, 1.5, 2.0 mol% concentration of rare earth ion Samarium (Sm^{3+}) doped Sodium Magnesium Zinc Floro Borate (NaMgZnFB) glasses were prepared by conventional melting procedure. Optical absorption, excitation, luminescence spectra and life time have been measured at room temperature. The studies on spectroscopic properties were carried. Sm^{3+} glasses has shown about eight absorption bands at 402, 471, 943, 1078, 1225, 1368,1467 and 1520 nm respectively. Their reddish orange emission is observed at 598nm with 401nm excitation wavelength. The decay curves have been plotted to evaluate their lifetimes and emission mechanism that arise in the glasses have been explained. Raman studies suggested that Sm_2O_3 could modify the properties of glass. Scanning Electron Microscopy (SEM) of the sample indicates the amorphous nature of the glass matrix and Energy Dispersive X-ray Analysis (EDAX) gives information about the elements which are present in the investigated glass samples. These glasses are expected to give interesting application in the field of optics. Notable improvements of optical and structural properties due to the doping samarium ions are evidenced. Excellent features of our results suggest that these glasses are promising for lasers and other device applications. Predominant emission feature has been observed at 0.5 mol% concentration of Sm^{3+} in doped Sodium Magnesium Zinc Fluoro Borate glass sample when compared to other

prepared Sm^{3+} doped glasses. From the photoluminescence analysis, 0.5 mol% Sm^{3+} contained glass sample has been suggested as a potential orange luminescent glass matrix for several photonic device applications.

Keywords: Glasses, Samarium, Absorption, Luminescence, Emission, Life decay.

1. INTRODUCTION

Glasses doped with rare earth ions find important applications in various electronic and optical devices like optical fibers, fluorescent displays, optical detectors, and wave guides [1-3]. Glasses host with low phonon energy and stability are ideal for doping rare earth ions as they reduce multi phonon relaxation, de-excitation between rare earth ions energy levels and favor the observation of same transitions between levels which are closely spaced in addition to enhancing the quantum efficiency of luminescent transitions. Such materials find numerous applications in the field of photonic devices [4]. Of the different glasses, fluoroborates have low melting point, low phonon energy and higher emission cross sections [5]. It was observed that glass former B_2O_3 is capable of forming glass at medium temperatures. An extensive work has been carried out on alkali borate glasses [6-12]. Because there are changes in their properties as more alkali is added and that are quite different from the changes in corresponding alkali silicates. The effects of changes in NaF content of sodium fluoroborate glasses studied by Shelby et.al [13]. Among trivalent rare earth (RE) ion series, Samarium (Sm^{3+}) has chosen as luminescence center as it exhibit fluorescence in reddish- orange emission in the visible spectral region. In the present work, synthesis of floroborate glasses doped with samarium ions are reported as a function of the nominal doping of Sm_2O_3 and their spectroscopic properties were studied.

2. EXPERIMENTAL DETAILS

Sodium Magnesium Zinc Fluoro Borate (NaMgZnFB) glasses (G1,G2,G3,G4) doped with 0.5, 1.0, 1.5, 2.0 mol% of Samarium (Sm^{3+}) were prepared by conventional melt quenching technique. The molar composition of glasses investigated in this work is 65 H_3BO_3+ MgF_2 (20-X) + 10NaF+5ZnO + X Sm_2O_3 where (X= 0.5, 1.0, 1.5, and 2.0). High purity chemicals of H_3BO_3, NaF, MgF_2, ZnO and Sm_2O_3 were used as starting materials. All the starting chemicals were weighed in the above mol % ratio, well mixed, grinded and heated for 60 min in a platinum crucible at 1050 ^{O}C in an electric furnace, then cooled quickly to 350^{o}C and annealed at this temperature for 5 hours to eliminate mechanical and thermal strains. The optical absorption spectrum in the wavelength region from 300 nm to 2000 nm was

recorded using UV-VIS-NIR (UV-3600 plus) Spectrophotometer. The excitation and photoluminescence (PL) spectra in the range of 350-700nm of the Sm^{3+} doped glass matrices were recorded with FL920 Edinburg Fluorolog fluorimetre using Xenon flash lamp as exciting source. Life decay spectra were recorded by Fluorolog-3 spectrophotometer. Raman spectrum was performed by Raman Spectrophotometer (LabRAM HR800). The SEM with EDS images were recorded with Carl Zeiss EVO MA15 with EDAX (Oxford INCA Penta FETX3) has been employed to investigate the morphological studies of the prepared glass samples. All the measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

3.1 Optical absorption

The absorption spectra of Sm^{3+} ions doped NaMgZnFB glasses in Visible and Near IR regions with varied concentration of 0.5, 1.0, 1.5 and 2.0 mol% is shown in figure-1. It contains two absorption bands related to the transitions $^6H_{5/2} \rightarrow {}^4F_{5/2}, {}^4M_{15/2}$ in visible region at 402 nm,471 nm and six absorption bands related to the transitions from $^6H_{5/2} \rightarrow {}^6F_{11/2}, {}^6F_{9/2}, {}^6F_{7/2}, {}^6F_{5/2}$ $^6F_{3/2}$ and $^6F_{1/2}$ in Near IR region at 943,1078,1225,1368, 1467 and1520 nm respectively. The absorbance intensities are considerably enhanced with the increase of Sm^{3+} ions concentration. The majority of the transitions in the spectra originate from the induced electric dipole interactions with the selection rule $\Delta j \leq 6$. Certain transitions also contain magnetic dipole contribution with selection rule $\Delta J=0, \pm 1$. In the visible region, all the other transitions are spin forbidden and hence some of the absorption intensity bands are weak[14].

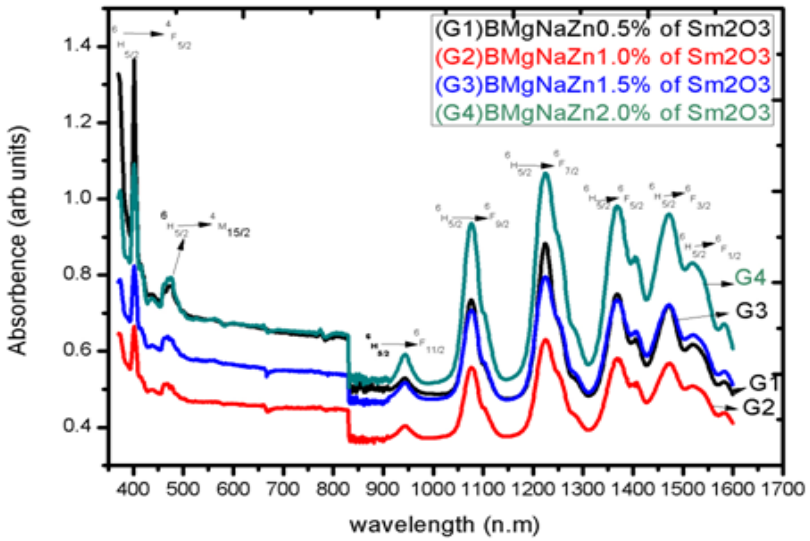

Figure 1: Absorption spectrum of Sm^{3+} doped NaMgZnFB glasses

3.2 Excitation spectra

Excitation spectra of NaMgZnFB: Sm^{3+} glass matrix recorded at the emission wavelength 598 nm is depicted as figure2. The excitation spectra consists of 11 peaks corresponding to the transitions from the ground state $^6H_{5/2}$ to the various excited states $^4D_{7/2}$,$^4D_{3/2}$,$^6P_{7/2}$, $^4L_{15/2}$, $^6P_{3/2}$,$^6P_{5/2}$, $^4G_{9/2}$,$^4F_{5/2}$,$^4I_{13/2}$,$^4I_{11/2}$ and $^4F_{3/2}$ at the wavelengths of 342, 360, 374, 388, 401, 415, 436, 447, 460, 470 and 525 nm respectively. The optical absorption spectrum of MgNaZnFB: Sm^{3+}glass in the UV-Vis region shown in figure 2 is compared with this excitation spectrum and it is confirmed that these transitions of Sm^{3+} ions are similar.

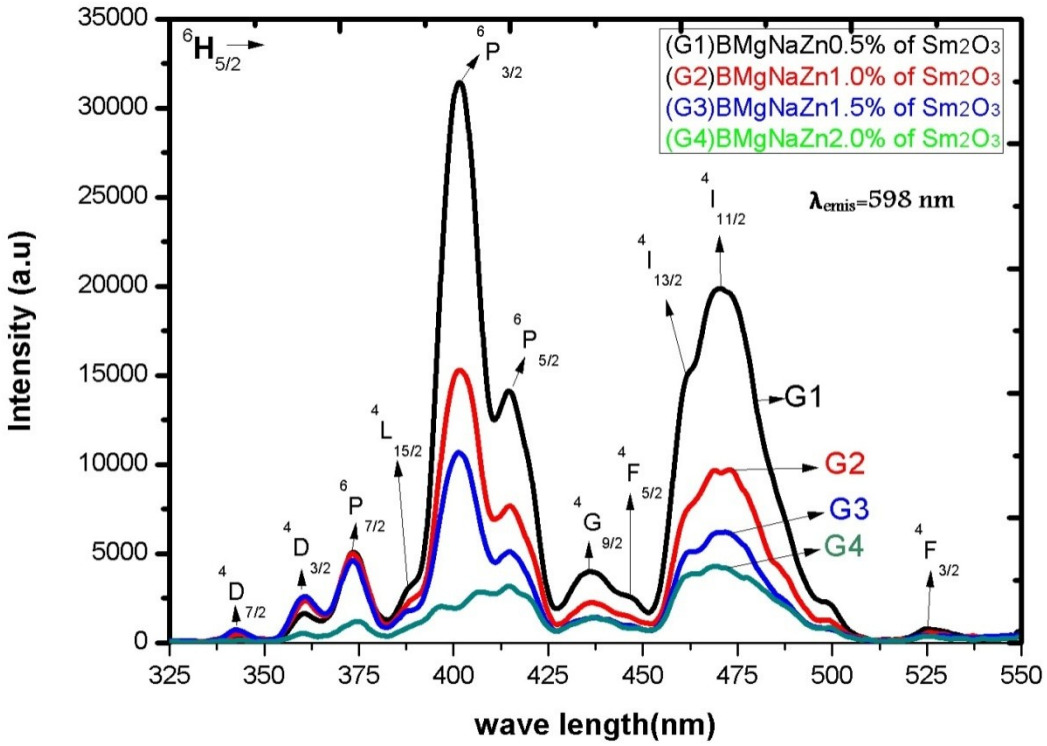

Figure 2: Excitation spectrum of Sm^{3+} doped NaMgZnFB glasses

3.3 Fluorescence properties

The emission spectra of NaMgZnFB: Sm^{3+} glass is shown in fig 3. It exhibits four emission bands at 562, 598, 645 and 705 nm which are assigned to $^4G_{5/2}\rightarrow{}^6H_{5/2}$,$^6H_{7/2}$,$^6H_{9/2}$ and $^6H_{11/2}$ transitions, respectively[15]. The highest intensity obtained at wavelength of 598 nm corresponding to $^4G_{5/2}\rightarrow{}^6H_{7/2}$ transition. As the concentration of samarium increases, the emission intensity decreases from 0.5 mol % to 2.0 mol %. In the present work, 0.5 mol% of samarium is optimized concentration. It is likely to be effect of concentration quenching. From the emission spectra, it is

observed that the main visible emission intensity of Sm^{3+} ion is in the reddish-orange part of spectra and corresponds to $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition located at 598 nm. From the absorption, excitation and emission spectra of NaMgZnFB:Sm^{3+} glasses, the energy level diagram of Sm^{3+} in Fluoro borate glass was defined in the figure 4.

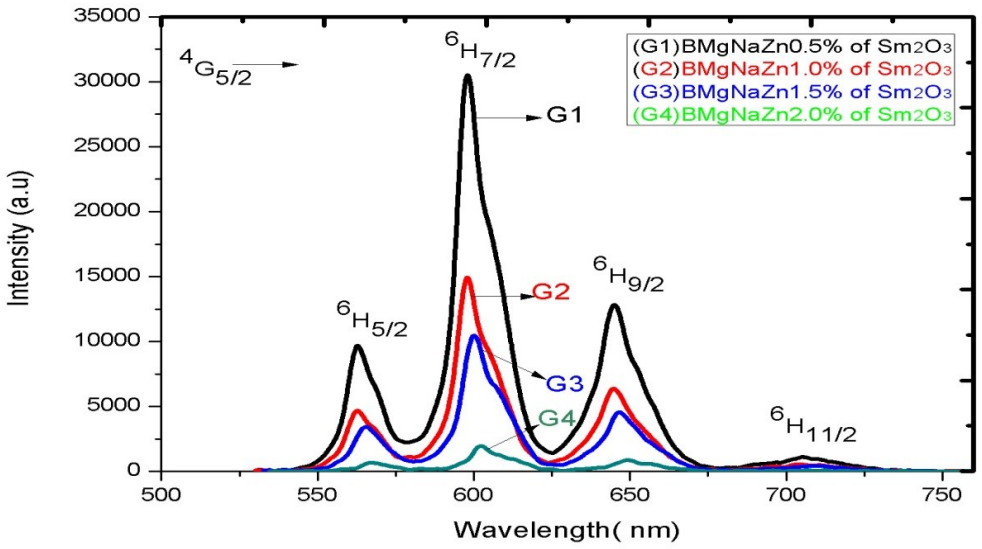

Figure 3: Fluorescence spectrum of Sm^{3+} doped NaMgZnFB glasses

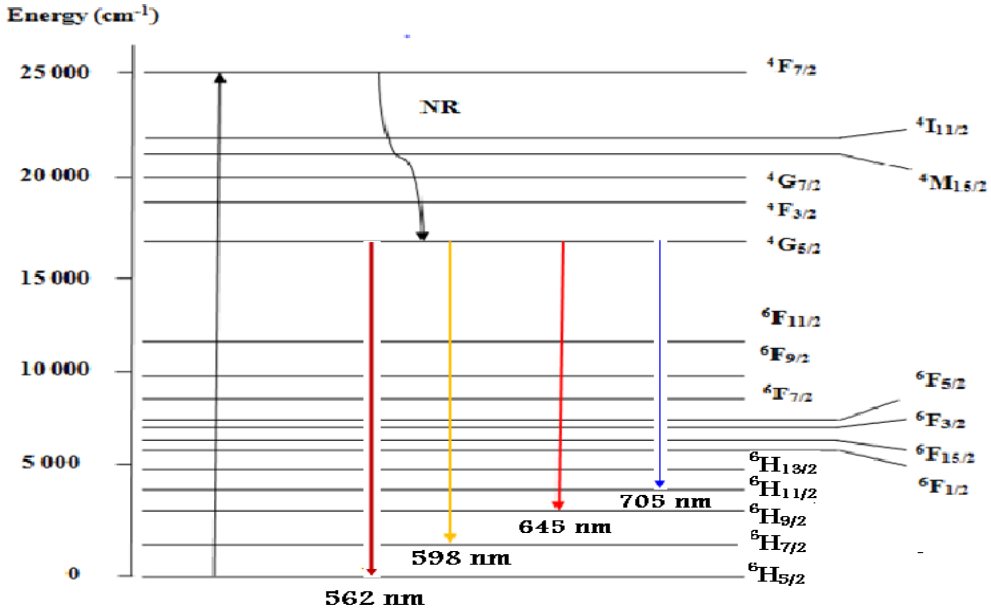

Figure 4: Partial energy level diagram of samarium ion NaMgZnFB glasses

3.4 Decay lifetime

The lifetime of the $^4G_{5/2}$ level, for all the glass samples with different concentrations of Sm^{3+} ions was measured by monitoring the florescence decay of $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition under the excitation of 401 nm at room temperature. The characteristic decay curves have been obtained particularly for glass samples with 0.5, 1.0, 1.5, and 2.0 mol% of Sm^{3+} concentrations are displayed in fig. 5. There are two important mechanisms to explain energy transfer process resulting in luminescence quenching. The first one is due to cross-relaxation between pairs of Sm^{3+} ions and another one is connected with the migration of excitation energy which can accelerate the decay by energy transfer to the structural defects acting as energy sinks [16]. The life time has been found to be 505.9 ns for 0.5 mol%, 680.93 ns for 1.0 mol%, 917.87 ns for 1.5 mol%, and 1284.64 ns for 2.0 mol% Sm^{3+} doped NaMgZnFB glasses.

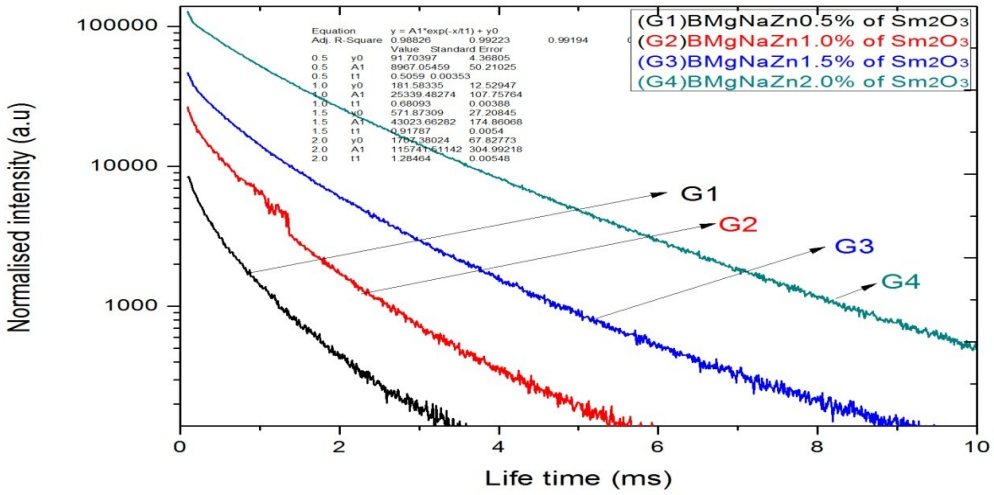

Figure 5: Decay life time of Sm^{3+}: NaMgZnFB glasses

3.5 Raman spectra

The Raman spectrum of the prepared glass exhibited broad peaks in the range studied 900 to 3500 cm^{-1} as shown in figure 6. In this spectrum, the broadening of peaks arises due to disorders in the glass matrix. In the present spectrum, the peak at 2080 cm^{-1} is high intense, due to symmetric stretching mode and while others are less intense compared to this. The less intensity peaks happens due to asymmetric stretching vibration. Hence it can be concluded that Samarium oxide contributes broad peaks around 2080 cm^{-1} due to Sm^{3+}-O- Sm^{3+} vibrations.

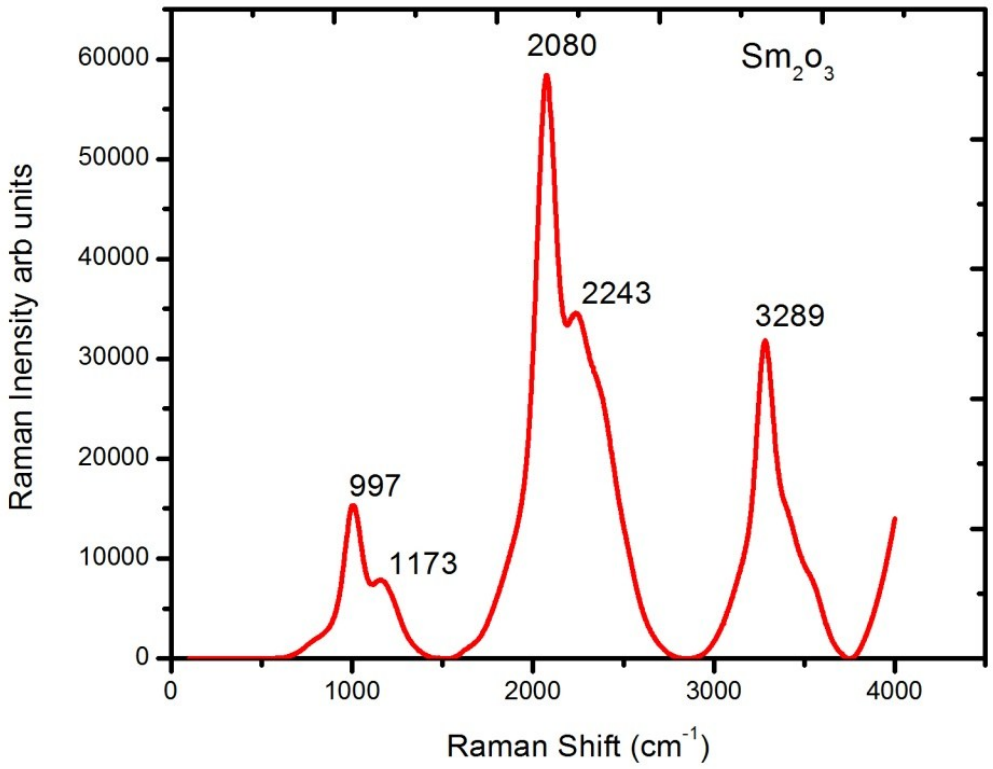

Figure 6: Raman spectra of Sm^{3+}: NaMgZnFB glasses

3.6 SEM and EDAX

SEM image explores the smooth surface of the sample. This smooth surface indicates that the amorphous nature of the glass matrix [17] and also we couldn't identify any grain boundaries from the surface morphological image of the Sm^{3+} doped NaMgZnFB for 0.5 mol% glass sample as shown in Figure 7.The elemental analysis has been carried out from the EDAX spectral profile as shown in Figure 8. The deficiency of F may be due to its low melting temperature and there by evaporating after 250°C which is clearly visible in the EDAX spectrum in figure 8. The spectrum gives the information about the elements which are present in the investigated glass samples.

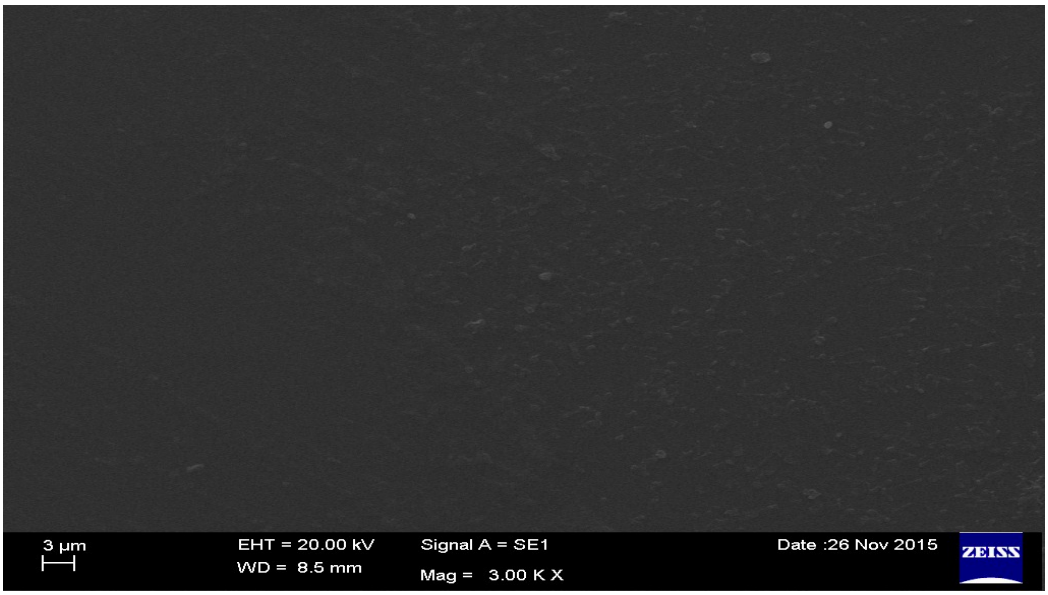

Figure 7: SEM image of Sm^{3+} doped NaMgZnFB glasses

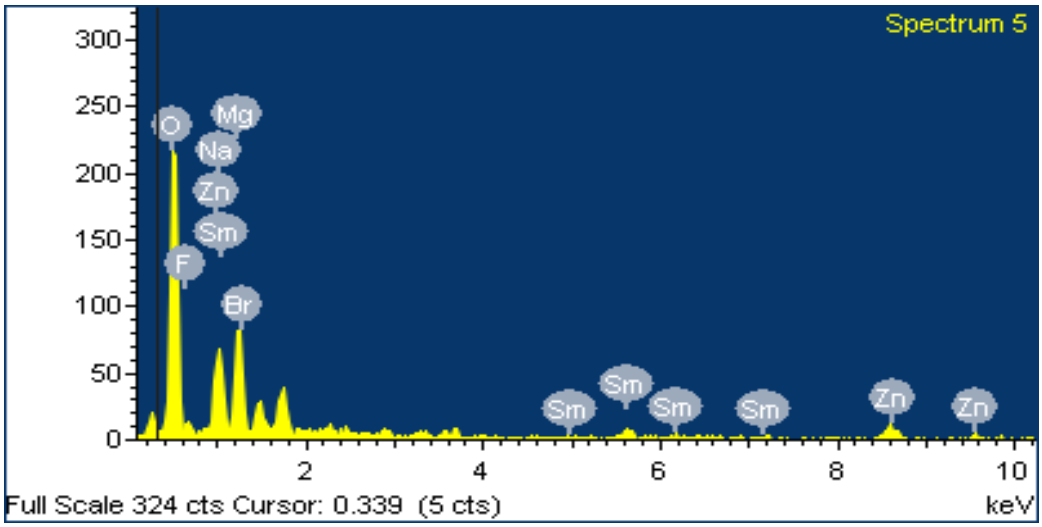

Figure 8: EDAX of Sm^{3+} doped NaMgZnFB glasses

4. CONCLUSIONS

From the absorption spectra, various absorption transitions are assigned. From these transitions, one transition is chosen for excitation of samarium ions and emission spectra are recorded. From emission spectra, four luminescence transitions are observed. Among these transitions, emission transition at 598 nm has high in

intensity. With the increases of content of samarium, concentration quenching is observed. Decay curves of the visible emissions have been plotted to measure life times. The structural, morphological and compositional analysis of host glass has been demonstrated by RAMAN shift, SEM and EDAX studies. From the results of these investigations, it is concluded that the 0.5 mol% of Sm^{3+} doped fluoroborate glass is more useful for reddish-orange luminescent photonic device applications. It was found suitable for wide application in the field of spectral hole burning process, photovoltaic cells and other laser applications.

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