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# Spectroscopic studies of $Sm^{3+}$ ions doped alkaline-earth chloro borate glasses for visible photonic applications

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## ABSTRACT

A new series of $Sm^{3+}$ ions doped Alkaline-Earth Chloro Borate (AECB) glasses with compositions (25-x)CaO-5SrO-10BaCl$_2$-60B$_2$O$_3$-xSm$_2$O$_3$ (x = 0.1 mol%–2.5 mol%) were prepared by a conventional melt quenching technique and characterized with XRD, absorption, excitation, photoluminescence (PL) and fluorescence decay spectral measurements. From the absorption spectra, Judd-Ofelt (J-O) intensity parameters ($\Omega_2$, $\Omega_4$, $\Omega_6$) have been measured. The PL spectra under 402 nm excitation show bright reddish-orange emission at 602 nm. The decay spectral profiles of $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (602 nm) luminescence transition used to measure experimental lifetimes ($\tau_R$). The Inokuti-Hirayama model used to understand the predominant energy transfer mechanism involved in the prepared glasses. The evaluated emission cross-sections ($\sigma_{se}$), branching ratios ($\beta_R$) and quantum efficiency (η) allows us to contemplate that the $Sm^{3+}$ ions doped AECB glasses are aptly suitable as potential gain mediums for visible reddish orange lasers pumped directly by commercially available 405 nm laser diodes.

## 1. Introduction

Inorganic luminescent materials doped with rare earth (RE) and transitional metal (TM) ions have attracted much attention due to their wide range of applications, such as field emission displays (FEDs), white light emitting diodes (w-LEDs), plasma display panels (PDPs), lasers, up-converters, stimulated phosphors, energy storage materials, solar photovoltaic materials and optical amplifiers and so on [1–8]. Glasses are suitable hosts for the RE ions as they can provide a long composition range, good RE ion solubility and are cost-effective. The luminescence and absorption properties of RE ions in glasses depend on the chemical composition, structure and nature of bonds of the host glass [9]. Because of the unique properties of glasses doped with RE ions, they are quite suitable for point-to-point communication in space where atmospheric attenuation does not interfere with the propagation of radiation, surgical eyes and biological applications. Recently, glass lasers have achieved wide attention because they have high gain, long fluorescence lifetimes and can be simply made in a variety of geometries [10–13].

Lanthanide ions like $Eu^{3+}$, $Tb^{3+}$, $Pr^{3+}$, $Sm^{3+}$ provide the most efficient options for visible lasers, since they have a multitude of energy levels in the UV–vis part of the spectrum. Also these RE ions have partially filled 4f shell that is well shielded by $5s^2$ and $5p^6$ orbitals. The f-f emission transitions in lanthanides yield sharp lines in the optical spectra. The use of RE element is based on 'line type' spectra corresponding to f-f transitions which can give luminescence in the visible region with high luminescence efficiency [14]. However, activators like $Eu^{3+}$, $Tb^{3+}$, $Pr^{3+}$ have problems related to the excitation bands as they are less capable in absorbing the ultraviolet light, when compared to $Sm^{3+}$ to produce emissions in the red region. Among the lanthanide ions, $Sm^{3+}$ is one of the most frequently used RE ion to give orange/red luminescence with strong fluorescence intensity, large emission cross-sections and high quantum efficiency [15]. Orange/Red luminescence of $Sm^{3+}$ originates from its partially forbidden f-f transitions. $Sm^{3+}$ has a four level laser transition emitting from orange to far red region [16]. These four level emission transitions occur between the meta-stable level $^4G_{5/2}$ and $^6H_{j/2}$ (j = 5, 7, 9, 11) respectively [17,18]. Among them, the emission $^4G_{5/2} \rightarrow {}^6H_{7/2}$ at 602 nm is the most strong with large emission cross-section compared to other transitions. Apart from $^4G_{5/2} \rightarrow {}^6H_{7/2}$ emission, laser action may also occur from the metastable level to the other $^6H_J$ levels, but are less efficient than the main transition. $Sm^{3+}$ ions doped ceramics and glasses have been found to be particularly attractive lasing mediums by virtue of the long metastable lifetime combined with the high branching ratio and narrow line-width of the radiative transition [19]. These properties are the main characteristics of RE ions in an amorphous host material.

Over the years, the studies of borate based glasses have gained interest due to their structural and optical properties. Boron trioxide

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($B_2O_3$) is the main constituent in borate glasses. Being a good glass former, $B_2O_3$ can form glass alone with relatively good transparency, chemical durability, thermal stability and good RE ion solubility [20–23]. Borate glasses have several merits like low softening point and easy processing. But these glasses possess high phonon energies [24], which may hamper their luminescence efficiency through multiphonon relaxation. Earlier reports suggest that, alkali or alkaline earth cations added to a borate glass can improve their optical properties such that they acts as good laser hosts with high gain, high energy storage capacity and low optical losses [25]. Alkali and alkaline earth metals affects the network connectivity, arrangement of modifier cations and modifier chain bonding in glasses by substituting the bridging oxygens with non-bridging oxygens [26,27]. Among the alkaline earth metals, SrO being a very good network modifier destroys or modifies the local symmetry (bridging and non-bridging oxygens) around the borate (glass former) network [28–30]. This normally transforms the $BO_3$ units into $BO_4$ units resulting decrease in the number of non-bridging oxygens. This leads to a strong and well connected closely packed glass structure [31]. $Sr^{2+}$ ions also create bonding defects by breaking the borate bonds (B—O—B) which creates empty space and easy path ways for the other doped ions. The presence of SrO in glasses also increases the reticulation and rigidity of the network due to large field strength values of $Sr^{2+}$ ions which restrict the accumulation of oxygen ions around borates.The presence of SrO in glasses make the glasses more resistant toward moisture [32]. Another alkali metal CaO added to a borate glass also acts as a network modifier and reduces the tendency of crystallization due to its large cation size. Addition of CaO to a borate glass breaks the B—O—B bonds and creates more number of non-bridging oxygens which can transforms the coordination number around the boron ion. Due to low diffusion rates, Ca has strong binding with the network. From the literature it is evident that, $BaCl_2$ added to a glass can enhance the glass formation tendency [33]. In addition to this, glasses containing $BaCl_2$ are more transparent in IR region [33]. Also they can bring significant changes in the glass properties due to the difference in ligand field symmetry between mixed anions [34]. Addition of alkaline earth metals like CaO, SrO and $BaCl_2$ provides the strong network linkages at the alkaline earth sites and are tightly bounded into the structure. The sites where the modifier ions are relatively immobile, can improve the chemical durability by reducing the ionic contribution to the electrical conductivity of glasses [35]. Addition of chloride ($BaCl_2$) to the glasses can decrease the phonon energies which in turn help to improve the stimulated emission cross section and efficiency of the glasses [34]. All the aforementioned scientific patronages offered by SrO, CaO, $BaCl_2$ and $B_2O_3$ prompted us to prepare a glassy system namely alkaline earth chloro borate (AECB) glasses and doped them with $Sm^{3+}$ ions to understand their luminescence efficiency in reddish-orange visible region. In borate glasses, it is evident that substitution of halides like fluoride, bromide, chloride, iodide, etc., brings interesting changes in physical and optical properties like melting point, glass transition temperature, density and shear modulii, rigidity, net charge and distribution of interconnected interstices, etc. [36–39]. Although, there are many reports available in literature pertaining to structural, physical and optical characterization of RE doped alkali based borates, fluoro borates, chloro borates, to the best of our knowledge there are no reports related to AECB glasses.

In the present work, we have prepared AECB glasses doped with varying concentration of $Sm^{3+}$ ions and studied their absorption, excitation, emission and decay spectral features. In the process of understanding their luminescence efficiency and to optimize the concentration of $Sm^{3+}$ ion concentration in AECB glasses, we have evaluated radiative transition probabilities, radiative lifetimes, stimulated emission cross-sections and quantum efficiencies.

## 2. Experimental techniques

### 2.1. Preparation

$Sm^{3+}$ ions doped AECB glasses, with composition (25-x)CaO–5SrO–10$BaCl_2$–60$B_2O_3$–x$Sm_2O_3$ (x = 0.1 mol%–2.5 mol%) were prepared by the conventional melt-quenching technique. For our convenience these glass samples are abbreviated as AECB_0.1, AECB_0.5, AECB_1.0, AECB_1.5, AECB_2.0 and AECB_2.5 depending on RE ion concentration from 0.1 mol% to 2.5 mol% respectively. All the starting materials viz. CaO, $SrCO_3$, $H_3BO_3$, $BaCl_2.2H_2O$ and $Sm_2O_3$ were of analytical reagent grade (Make - Merck). Prior to melting and quenching process, the reagents were weighed according to the stoichiometric proportions. The weighed materials then homogeneously mixed in an agate mortar and the mixture was transferred into silica crucibles. The silica crucibles were then placed in an electric furnace and heated at 1100 °C for 30 min to get homogeneous melt. The melts were then quenched between pre-heated brass plates to get glass samples of uniform thickness. The obtained glass samples were annealed for 2 h at 400 °C to attain thermal and structural stability. The obtained glass samples are transparent, non-hygroscopic and chemically stable.

### 2.2. Apparatus

The X-ray diffraction (XRD) patterns were recorded on XPERT-PRO diffractometer using Cu $K_\alpha$ ($\lambda$ = 1.54059 Å) radiation. The densities of the glasses were measured by Archimedes' method, using water as an immersion liquid. Refractive indices have been measured using Brewester's angle method (He–Ne laser with a wavelength 650 nm line). The optical absorption spectra of the samples were recorded at room temperature (RT) in the spectral wavelength range covering 320–2000 nm with a spectral resolution of 0.1 nm using a JASCO model V-670 UV–vis-NIR spectrophotometer. The excitation, UV–vis PL spectra and PL decay measurements were measured by using a Hitachi-F7000 fluorescence spectrophotometer with 150 W Xenon lamp as the radiation source. All the measurements were carried out at RT.

## 3. Results and discussion

### 3.1. XRD spectral analysis

In order to check the amorphous nature of the prepared glass, the XRD pattern was recorded for an un-doped AECB glass and is shown in Fig. 1. The absence of sharp peaks in Fig. 1 indicates the amorphous nature of the prepared glass.

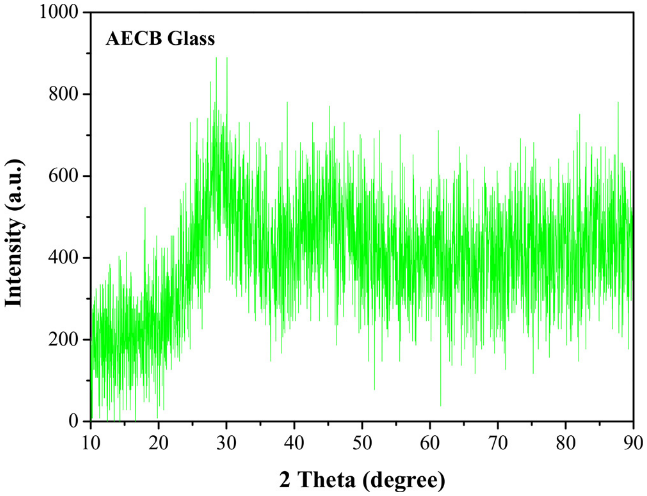

**Fig. 1.** XRD pattern of an undoped AECB glass.