



Study on Tb³⁺ containing high silica and low silica calcium aluminate glasses: Impact of optical basicity

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ARTICLE INFO

Article history:

Received 21 November 2011

Received in revised form 14 February 2012

Accepted 22 March 2012

Keywords:

Glass

Infrared spectroscopy

Optical spectroscopy

Optical basicity

Luminescent materials

ABSTRACT

Two series of glasses based on high silica (CAS) and low silica calcium aluminates (LSCA) have been investigated for their structural, optical and Tb³⁺ luminescence properties. The compositional modification reduces host phonon energy in LSCA glasses. Still, LSCA glasses exhibit Tb³⁺ green luminescence quenching, whereas no quenching observed in CAS glasses. Material property influence on this behaviour has been discussed with an insight into the redox state of active ions.

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1. Introduction

The extensive ability of property tailoring by compositional modifications makes glasses most preferable engineered material for numerous applications. Its revolutionary role in optical communication and solid-state lasers attracted tremendous attention in the last five decades resulting in significant exploration of glass science to achieve desired properties [1,2]. Host phonon energy is one of such intrinsic property of glass which plays key role in favouring the luminescence performance of active ions by limiting or allowing the multi-phonon relaxation of excited levels [3,4]. Among several glasses, silicates in general and high silica calcium-alumino-silicate (CAS) in particular are of special interest with great industrial and scientific importance [5–7]. These glasses exhibit maximum phonon energy of about 1000–1100 cm⁻¹, which limits their suitability for infra-red as well as up-conversion luminescence applications. It is possible to reduce the phonon energy of these glasses by partially substituting silica contents with alumina. Thus the maximum phonon energy of such low silica calcium aluminate (LSCA) glasses comes down to 750–800 cm⁻¹ [8]. Further, the comparatively high mechanical strength, better chemical durability and non-toxicity of LSCA glasses over heavy metal oxides and other low phonon energy host glasses makes them favourable for infrared luminescence and visible up-conversion applications.

Nevertheless, such alterations in chemical composition of glasses may develop adverse effects on other constructive properties. Usually the compositional changes bring about structural rearrangements and modify the optical basicity of glass [9]. Basicity defines the metal–ligand interactions in terms of electron density carried by the ligand and affects the oxidation state of dopant metal ions, which reflects on their optical as well as spectroscopic properties [10]. Such consequences of optical basicity can be well studied experimentally by using multi-valence ions as probe, since their redox equilibrium is highly sensitive to optical basicity of glass. In the present work, CAS and LSCA glasses doped with varied concentration of Tb₂O₃ have been prepared and studied for the effect of compositional variations on their structural, optical and luminescence properties. Terbium has been selected as an active ion owing to its ability to exhibit multi-valence (Tb³⁺ and Tb⁴⁺) states. In addition to this, the blue emission of Tb³⁺ from ⁵D₃ excited level is sensitive to host phonon energy; whereas, that of green emission from ⁵D₄ level has negligible dependence making it an ideal ion to study the host effect.

2. Experimental

Two series of glasses having chemical compositions (Series 1, CAS: 23CaO–5Al₂O₃–58SiO₂–4MgO–10NaF and Series 2, LSCA: 57.3CaO–28.7Al₂O₃–10SiO₂–4MgO in mol%) with varied Tb₂O₃ concentration of 0.25, 0.5, 1, 2, 4, 8, 16, 24, 32 and 40 in excess wt% were prepared by conventional melt quenching technique. For both series, glass melting was carried out in a pure platinum crucible in 1450–1600 °C temperature range for one to one and half hours followed by annealing at 590–750 °C depending upon their

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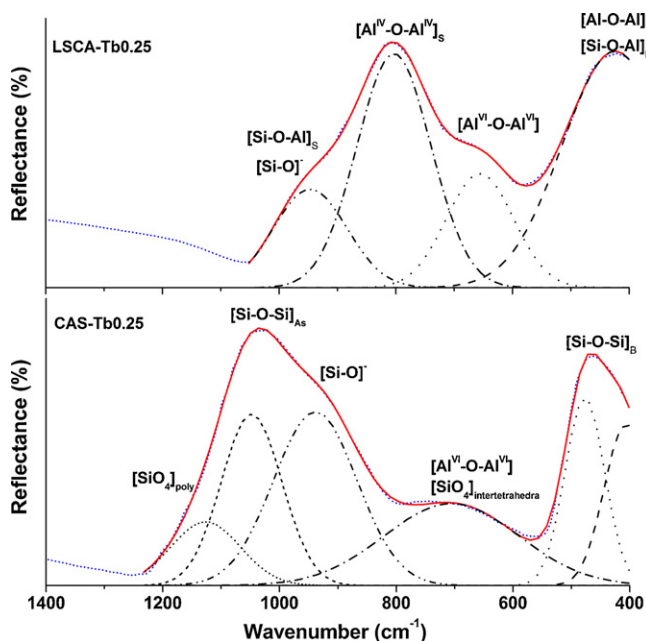


Fig. 1. FTIR reflectance spectra of CAS and LSCA glasses.

composition. The obtained glasses were labelled on the basis of dopant ion concentrations. The infrared reflectance spectra were recorded in 400–1500 cm^{-1} range to study the structural properties of glasses using Fourier Transform Infrared (FTIR) spectrometer (Perkin-Elmer, Model: 1615 series). The density of well annealed glasses was measured by Archimedes' buoyancy principle using water as immersion liquid on Mettler-Tollado digital balance fitted with a density measurement kit. Refractive indices were recorded with an accuracy of 10^{-5} on a Prism Coupler refractometer (Model Metricon M-2010, Pennington, NJ) built-in with five different lasers as illuminating sources. The optical absorption spectral measurements were carried out on a UV-Vis-NIR spectrophotometer (Perkin-Elmer, Model: Lambda-20) in the 200–1100 nm wavelength range. The luminescence spectra of Tb^{3+} ions were recorded on a fluorescence spectrophotometer (Model: Quantum Master-enhanced NIR, from Photon Technologies International, USA).

3. Results and discussion

3.1. Glass structure

Fig. 1 presents the recorded FTIR reflectance spectra of CAS-Tb0.25 and LSCA-Tb0.25 glasses, which demonstrate significant structural differences as evidenced from the deconvoluted components for individual glasses. For CAS-Tb0.25 glass, the most intense band is observed at around 1040 cm^{-1} due to asymmetric stretching vibration of Si–O–Si bond of $[\text{SiO}_4]$ tetrahedral units, with a shoulder at around 940 cm^{-1} due to non bridging Si–O $^-$ vibrations [7]. In addition to this, a broad hump has been observed at around 550–780 cm^{-1} due to the vibrations of Al–O bond in $[\text{AlO}_6]$ octahedral unit, which coexists with two inter-tetrahedral Si–O–Si vibrations in the region of 600–800 cm^{-1} . The Si–O–Si bending vibration is found at around 430–470 cm^{-1} region. At 1130 cm^{-1} , a weak band is observed due to stretching vibrations of $[\text{SiO}_4]_{\text{poly}}$ units indicating the presence of polymerized silicate network in CAS glasses [7]. For LSCA glasses, four major absorption bands have been observed with most intense band centred at around 790 cm^{-1} , which has been identified as due to the symmetric stretching vibrational transitions of Al–O–Al bond in $[\text{AlO}_4]$ tetrahedra [11]. Similarly, the bands at around 950 cm^{-1} , 650 cm^{-1}

and 560–400 cm^{-1} are attributed to the vibrational transitions of Al–O–Si and Si–O $^-$ stretchings, symmetric stretching of Al–O in $[\text{AlO}_6]$ octahedral unit and bending modes of Al–O–Al and Si–O–Al respectively [7,11].

The comparison of overall spectral appearance in both LSCA and CAS glasses suggests that the majority of Al^{3+} ions are tetrahedrally coordinated in LSCA glasses, whereas they have octahedral coordination in CAS glasses. That is, in CAS glass network, $[\text{AlO}_6]$ unit represents the role of Al^{3+} ion as network modifier; while at high Al_2O_3 content, Al^{3+} ions forms $[\text{AlO}_4]$ tetrahedral units with the aid of Ca^{2+} ions and act as network formers as in the present LSCA glasses which contain only 10 mol% of SiO_2 [12]. Such replacement of $[\text{SiO}_4]$ structural units by $[\text{AlO}_4]^-$ in LSCA glasses results in the reduction of effective glass phonon energy from 1040 cm^{-1} in CAS glasses to 790 cm^{-1} in LSCA glasses.

3.2. Physical properties and glass optical basicity

The complete change of glass network from CAS to LSCA glasses as discussed in earlier section has significantly affected their physical and optical characteristics. The measured density and refractive indices of both series of glasses have been listed in Table 1. It is observed that the LSCA glasses exhibit higher values of density and refractive index over CAS series of glasses. In general, the Al–O bond length (~ 1.75 Å) is higher than Si–O bond length (~ 1.6 Å) in tetrahedral network [13,14] indicating more volume fraction for $[\text{AlO}_4]$ tetrahedron over $[\text{SiO}_4]$ tetrahedron. However, the formation of $[\text{AlO}_4]^-$ tetrahedral units reduces the non-bridging oxygen (NBO) in LSCA glass matrix to compensate extra charge on aluminium ion giving rise to a denser network. Table 1 also enlists the optical basicity of present glasses along with their molecular electronic polarizability. The optical basicity has been calculated from the chemical composition of glasses using the relation [15],

$$\Lambda_{\text{glass}} = \sum_i \frac{X_i(\text{O})}{\gamma_i} \quad (1)$$

where $X_i(\text{O})$ is the fraction of oxygen atoms carried by the individual M_xO_y oxide to the total number of oxygen atoms in glass and γ_i is the basicity moderating parameter. The basicity moderating parameter, γ_i can be evaluated from the Pauling's electronegativity of cation (χ_{Mi}) using the relation $\gamma_i = 1.36(\chi_{\text{Mi}} - 0.26)$. The LSCA glasses are found to exhibit higher values of basicity than that of CAS glasses. In case of oxide materials, the basicity shows direct dependence on polarization state of oxygen ions as well as metal–oxygen bond ionicity [10,15]. Thus the bonding type between metal ion and anion and in turn the corresponding bond strength is vital in defining the basicity of glasses. As the basicity increases, the ionic characteristics of the glass also increase as can be seen from the glass ionicity (I_{glass}) values of present glasses listed in Table 1, which have been calculated using the relation [15,16],

$$I_{\text{glass}} = \sum_i \left\{ 1 - \exp \left[-\frac{1}{4} (\chi_{\text{O}} - \chi_{\text{Mi}})^2 \right] \right\} \quad (2)$$

where χ_{O} and χ_{Mi} are Pauling's electronegativity for oxygen and metal ions respectively. This enhanced ionicity results in the reduced bond strength, which thereby reduces the effective phonon energy as observed in present study. The Al^{3+} ions owing to their lower field strength over Si^{4+} , form less covalent bonding with oxygen leading to the higher ionicity of Al–O bond than that of Si–O bond. Further, the optical basicity is increasing continuously with the increase of Tb_2O_3 concentration in both series of glasses. As the rare earth oxides (as network modifiers) are comparatively basic in nature, they contribute to increase the overall optical basicity of glasses.

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