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Spectroscopic Studies on Alumino Alkali Zirconia Silicate Glasses Mixed with Tiatanium ions for Optoelectronic Device Application

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Abstract: $Li_2O–Al_2O_3–ZrO_2–SiO_2$ glasses mixed with different concentrations of TiO_2 have been synthesized by melt quenching method. The properties like optical absorption, ESR and photoluminescence were investigated. The optical absorption and ESR studies indicated that a proportion of titanium ions exist in the Ti^{3+} state in addition to the Ti^{4+}state in these samples. Photoluminescence spectra exhibit a broad emission band in the visible region. The luminescence band is attributed to radiative recombination of self-trapped excitons localized on substitutionally positioned octahedral Ti^{4+} ions. The luminescence efficiency is found to increase with the content of TiO_2.
Keywords: $Li_2O–Al_2O_3–ZrO_2–SiO_2$ glasses, melt quenching, optical absorption, ESR and photoluminescence.

Introduction:

Alumino alkali silicate glasses are well known for the variety of their applications, which include low cost-optical connectors, actinide immobilization, implantlogy medical prostheses), and dielectric and sealant materials for solid oxide fuel cells [1]. Addition of zirconia (ZrO_2) gives good mechanical properties in terms of hardness. For certain specific concentration ratios of ZrO_2/Al_2O_3, the material possess a negative thermal expansion (NTE), which is highly useful for extending the range of applications of these materials. The presence of ZrO_2 in alumino alkali silicate glasses is expected to increase the electrical resistivity and chemical inertness and to improve the transparency over a wide range of wavelengths (300 nm to 8 ▪ m). The inclusion of ZrO_2 in alumino alkali silicate glasses causes a substantial increase in the refractive index, a decrease in the cut-off wavelength for absorption and a reduction in photochromism. Such changes in physical properties make these glasses a good host for rare-earth ions, which induce luminescence emission with high efficiency. In view of these qualities, ZrO_2 containing glasses find a variety of applications, such as thermal barrier coatings, optical filters, laser mirrors and gate dielectrics in microelectronics [2].

The range of applications of aluminio alkali zirconium silicate glasses can further be widened by mixing a small quantity of TiO_2 to these high transmitting glasses. The TiO_2 containing glasses are being used in optoelectronic devices, integrated circuits and low-loss optical waveguides [3]. The objective of the present presentation is to obtain a comprehensive understanding on the topology and valence states of titanium ions in the aluminio alkali zirconia silicate glasses mixed with tiatanium ions as a function of concentration of TiO_2 through a systematic study of spectroscopic properties

Experimental:

The glass samples are prepared by melt quenching method and optical polished. The density of the glasses was determined by the principle of Archimedes' using o–xylene as the buoyant liquid. The mass of the samples was measured to an accuracy of 0.0001 g using Ohaus digital balance Model AR2140 for evaluating the density. The optical absorption spectra of the glasses were recorded to a resolution of 1 nm at room temperature in the spectral wavelength range covering 300–1000 nm using JASCO Model V-670 UV–vis–NIR spectrophotometer. The ESR spectra of finely ground powders of the samples were recorded at room temperature with an E11Z Varian X-band (• • = 9.5 GHz) ESR spectrometer. The luminescence spectra of the samples were recorded at room temperature with a Photon Technology International fluorescence spectrophotometer.

Results and Discussion:

The table represents the physical parameters of $Li_2O–Al_2O_3–ZrO_2–SiO_2$: TiO_2 glasses.

Table: The physical parameters of $Li_2O–Al_2O_3–ZrO_2–SiO_2$: TiO_2 glasses

Sample	Density (g/cm^3)	Avg. mol. wt.	Dopant ion conc. N_i ($\times 10^{20}$ ions/cm^3)	Interionic distance (Å)	Polaron radius Å	Molar volume cm^3/mol	Refractive index
T_0	2.5024	58.37	–	–	–	23.33	1.784
T_1	2.5265	58.87	2.62	15.62	6.29	23.30	1.785
T_2	2.5491	59.36	5.20	12.43	5.01	23.29	1.786
T_3	2.5712	59.86	7.79	10.86	4.38	23.28	1.786
T_4	2.5935	60.36	10.35	9.88	3.98	23.27	1.787
T_5	2.6191	60.86	12.94	9.18	3.70	23.24	1.788

Fig. 1 presents optical absorption spectra for the $Li_2O–Al_2O_3–ZrO_2–SiO_2$: TiO_2 glass samples recorded at room temperature in the wavelength region 300–900 nm. The absorption edge, observed at 376.6 nm for the glass sample T_2, exhibited a blue shift with increasing TiO_2 concentration. Additionally, the spectrum of glass T_2 exhibited two clearly resolved absorption bands at 544 and 700 nm. As the concentration of TiO_2 is increased further, the half width and intensity of these two bands was observed to decrease with a slight shift in the peak positions towards lower wavelength.

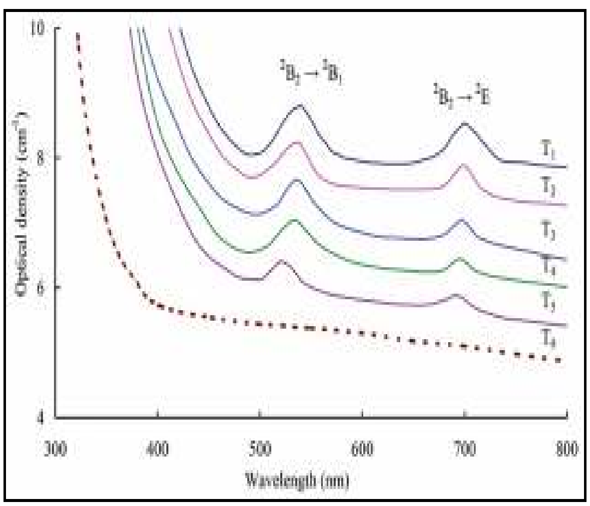

Fig. 1 Optical absorption spectra for the $Li_2O–Al_2O_3–ZrO_2–SiO_2$: TiO_2 glasses

ESR spectra of $Li_2O–Al_2O_3–ZrO_2–SiO_2$ glasses doped with different concentrations of TiO_2 recorded at room temperature are shown in Fig. 2. The spectrum of glass T_2 sample consists of an intense asymmetric spectral line centered at about g =1.990. The half width and the intensity of this signal exhibited a gradual decrease with the concentration of TiO_2.

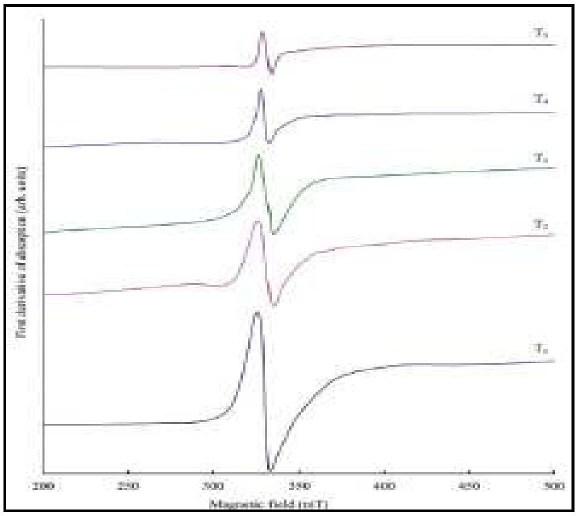

Fig. 2 ESR spectra of Li_2O–Al_2O_3–ZrO_2–SiO_2 glasses doped with different concentrations of TiO_2 recorded at room temperature

Fig. 3 shows luminescence emission spectra of Li_2O–Al_2O_3–ZrO_2–SiO_2: TiO_2 glasses recorded at room temperature and excited at a wavelength corresponding to their absorption edge. The spectrum of the sample T_2 exhibited a broad emission band with a large Stokes shift with the meta-centre at about 508 nm. As the concentration of TiO_2 is increased, the luminescence intensity is observed to increase. The optical absorption and ESR spectra of these glasses are due to existence of Ti^{3+} ions in octahedral coordination with tetrahedral compression. For d^1 ions in tetragonally compressed octahedron, the ground state is $B_2|xy>$. Hence, the bands observed in the optical absorption spectra at about 540 and 690 nm of the studied glass are assigned to $^2B_{2g}\rightarrow{}^2B_{1g}$ and $^2B_{2g}\rightarrow{}^2A_{1g}$ transitions of the Ti^{3+} ions respectively [4, 5]. With an increase in concentration of TiO_2, a gradual decay of these bands could clearly be seen; an observation indicating that there is a decreasing fraction of Ti^{4+} ions that have been reduced in to Ti^{3+} ions. The analysis of the ESR spectral results also supports this fact. In the ESR spectra, the asymmetric intense line observed at g=1.990 is due to tetragonally compressed octahedral sites of Ti^{3+} ions in the ground state $B_2|xy>$.

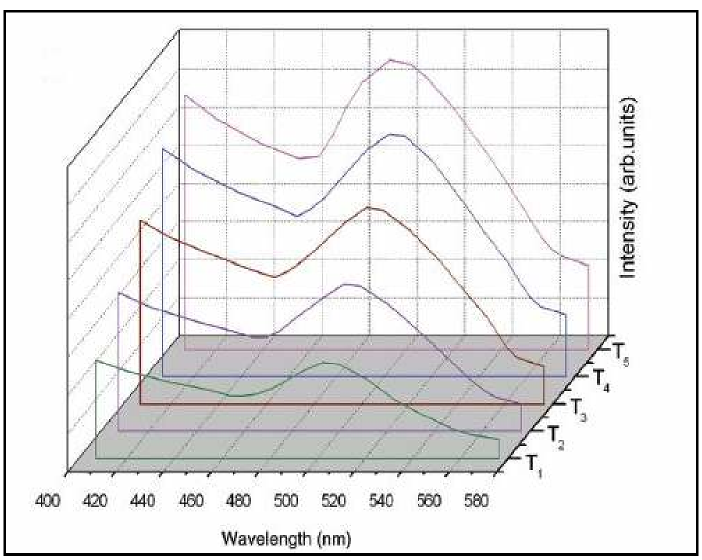

Fig. 3 shows luminescence emission spectra of Li_2O–Al_2O_3–ZrO_2–SiO_2: TiO_2 glasses recorded at room temperature

The luminescence band is attributed to radiative recombination of self-trapped excitons (STEs) localized on a substitutionally positioned octahedral Ti^{4+} ions.

Conclusions:

$Li_2O–Al_2O_3–ZrO_2–SiO_2$ glasses mixed with different concentrations of TiO_2 (ranging from 0 to 5.0 mol %) has been synthesized and a variety of properties optical absorption, ESR and photoluminescence were investigated. The optical absorption and ESR studies indicated that a proportion of titanium ions exist in the Ti^{3+} state in addition to the Ti^{4+}state in these samples. However, the reduction factor appears to decrease with increasing content of TiO_2. Photoluminescence spectra of thee samples excited at wavelengths corresponding to their absorption edges exhibit a broad emission band in the visible region. The excitation of substitutionally positioned octahedral Ti^{4+} ions is identified to be responsible for the observed luminescence emission. The luminescence efficiency is found to increase with the content of TiO_2. Finally it is concluded that there is an increasing electrical rigidity (or insulating strength) of $Li_2O–Al_2O_3–ZrO_2–SiO_2$ glass samples with the addition and increasing content of TiO_2.

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