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Spectroscopic studies on $Li_2O–Nb_2O_5–SiO_2:V_2O_5$ glass ceramics embeded with nano ferroelectric crystals

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Abstract: In this study we have investigated some physical properties of $Li_2O–Nb_2O_5–SiO_2:V_2O_5$ glass ceramics containing nano ferroelectric crystal phases. The glasses were synthesized by melt quenching technique and subsequently crystallized. The samples were characterized by XRD, SEM and DTA techniques. The SEM pictures indicated that the samples contain well defined and randomly distributed crystal grains of the size ~50-100nm. The X-ray diffraction studies have revealed the presence of LiV_3O_8, $Li_2V_2O_5$, $LiVO_3$, $NbVO_5$, $LiNbO_3$, $Nb_6V_2O_{19}$, $Nb_2V_2O_9$ and Li_2SiO_3 crystalline phases in these samples. The ESR spectra of glass are observed to be complex made up of resolved hyperfine components arising from unpaired $3d^1$ electron of ^{51}V isotope. The optical absorption spectra of glass ceramic exhibited two broad absorption bands with the meta-centers at 634 and 1040 nm attributed to $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2E$ transitions of VO^{2+} ions.The photoluminescence spectra of these glass ceramics exhibited a broad emission band in the region 750-850 nm; due to $^2E \rightarrow {}^2T_2$ transition of vanadyl ion. The analysis of the results of optical absorption, ESR and photoluminescence spectra of the studied glass ceramics have indicated that a considerable proportion of vanadium ions do exist in V^{4+} state in addition to V^{5+} state, and the redox ratio increases with increase in the concentration of crystallizing agent V_2O_5. Such studies are helpful for considering these materials for the applications in electro-optical and non linear optical devices.
Keywords: Ferroelectric nano crystal phases, Optical absorption, Photoluminescence.

Introduction:

Lithium niobium silicate glasses ceramics containing transition metal ions find a wide range of applications, such as glass fibers and optical lenses as electrodes and as glass planar optical waveguides [1] due to their electro chromic and electro-optical properties. In these glass ceramics there is a possibility for the formation of $LiNbO_3$ nano sized crystal phases which exhibit ferroelectric properties and makes the material for the potential applications in optoelectronics, acousto-optics [2]. The $Li_2O–Nb_2O_5–SiO_2$ glasses ceramics with V_2O_5 is an added advantage for the simple reason that the presence of vanadium ions makes the material to exhibit semiconducting behavior due to electron hopping between V^{4+} to V^{5+} ions[3]. The formation of $Li_2V_2O_5$ crystal grains facilitate to accelerate the rate of hopping of electron between V^{4+} and V^{5+} ions which ultimately lead to the enhancement of conductivity.

In this study we have investigated some physical properties of $Li_2O–Nb_2O_5–SiO_2:V_2O_5$ glass ceramics containing nano ferroelectric crystal phases to have a comprehensive understanding over the topology and valence states of vanadium ions in glass ceramic network in the light of variable oxidation states of vanadium ions.

Experimental:

The glasses were synthesized by melt quenching technique and subsequently crystallized. The samples were characterized by XRD, SEM and DTA techniques. The optical absorption, photoluminescence spectra and ESR of these glass ceramics have been recorded.

Results and Discussion:

The SEM pictures (Fig.1) of crystallized $Li_2O–Nb_2O_5–SiO_2$: V_2O_5 glass samples exhibited well defined, randomly distributed crystals (of the size~50 nm) ingrained in glassy matrix. The formation of $Li_2V_2O_5$, $Nb_6V_2O_{19}$, $Nb_2V_2O_9$ crystalline phases detected from the XRD studies (Fig. 2) emphasizes the presence of vanadium ions in V^{4+} state in addition to V^{5+} state in these glass ceramics. X-ray diffraction studies indicate the formation of LiV_3O_8, $Li_2V_2O_5$, $LiVO_3$, $NbVO_5$, $LiNbO_3$, $Nb_6V_2O_{19}$, $Nb_2V_2O_9$ and Li_2SiO_3 crystalline phases in these samples. All DTA traces exhibit typical glass transitions with the inflection point between 560–600 ^oC; it is interesting that glass transitions temperature (T_g) shows decreasing trend with increase in the content of nucleating agent. At about 950 ^oC, the thermogram of each glass ceramic exhibits well-defined principal exothermic effect along with weak multiple steps due to crystallization. The appearance of peaks due to multiple exothermic effects in the DTA pattern advocates the presence of different phases of crystallization in the samples.

The optical absorption spectra of $Li_2O–Nb_2O_5–SiO_2$: V_2O_5 glass ceramics (Fig. 3) recorded at room temperature in the wavelength region 400−1200 nm. The spectra of the glass ceramics exhibited two broad absorption bands with the meta-centers at 634 and 1040 nm attributed to $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2E$ transitions of VO^{2+} ions. As the content of the nucleating agent V_2O_5 continues to increase, a gradual growth of these bands with a slight shift of the meta-centre towards higher wavelength could clearly be seen; this observation is an evocative of increase in the rate of reduction of V^{5+} ions to VO^{2+} ions in the glass ceramics. Excitation of $Li_2O–Nb_2O_5–SiO_2$: V_2O_5 glass ceramic samples with the wavelength corresponding to $^2B_2 \rightarrow {}^2B_1$, resulted a broad emission band (Fig. 4). Since the wavelength of this band is close to the maximum of the band $^2B_2 \rightarrow {}^2E$, this band is attributed to $^2E \rightarrow {}^2T_2$ transition of V^{4+} ions; the emission band is relatively broad and structures less. With increase in the concentration of V_2O_5, the intensity of the peak is observed to increase with a red shift.

The ESR spectra of $Li_2O–Nb_2O_5–SiO_2$: V_2O_5 glass ceramics recorded at room temperature are shown in Fig. 5; are observed to be complex made up of resolved hyperfine components arising from unpaired $3d^1$ electron of ^{51}V isotope. As the concentration of nucleating agent V_2O_5 is increased, an increasing degree of resolution and the intensity, of the signal have been observed. The change in the V^{4+}/V_{tot} ratio seems to be one of the reasons for the variations in the line-shape.

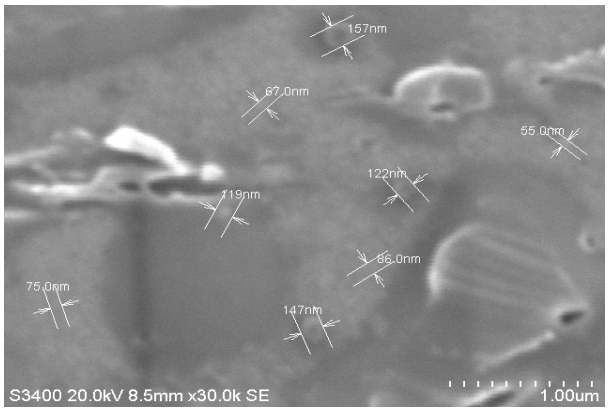

Fig.1 SEM photographs of $Li_2O–Nb_2O_5–SiO_2$ glasses crystallized with 0.8 mol% of V_2O_5

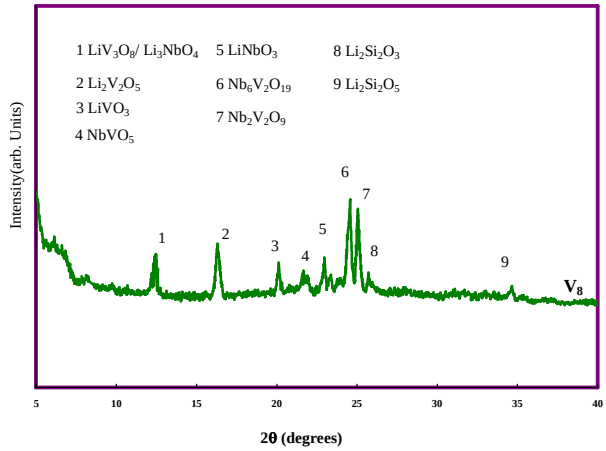

Fig. 2. XRD pattern of $Li_2O–Nb_2O_5–SiO_2$: glass ceramic doped with 0.8 mol% of V_2O_5.

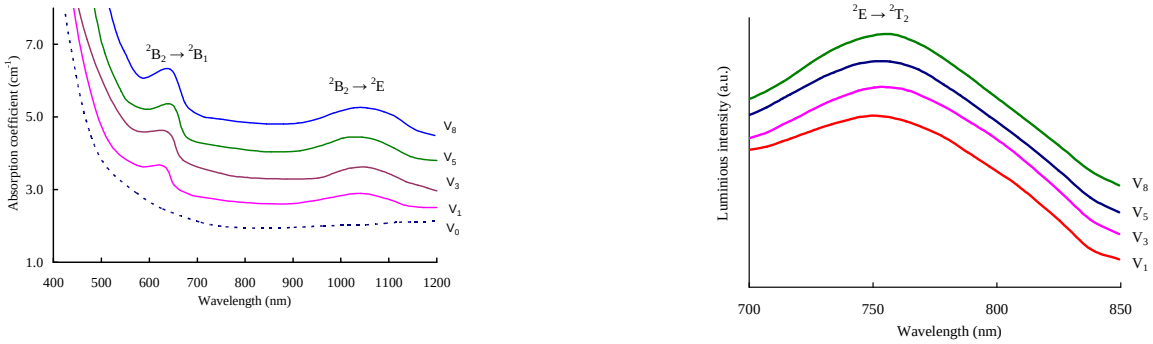

Fig.3 Optical absorption spectra of $Li_2O–Nb_2O_5–SiO_2$: V_2O_5 glass ceramics recorded at room temperature and **Fig.4** Photoluminescence spectra of $Li_2O–Nb_2O_5–SiO_2$: V_2O_5 glass ceramics excited at wavelength corresponding to the transition $^2B_2 \rightarrow {}^2B_1$ recorded at room temperature.

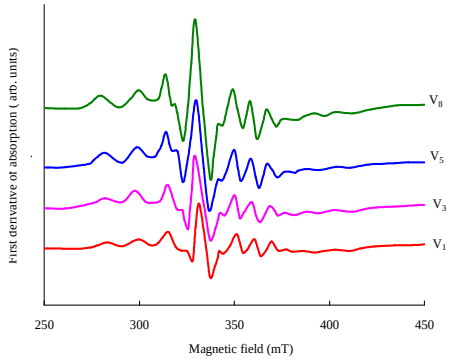

Fig.5 ESR spectra of $Li_2O–Nb_2O_5–SiO_2$: V_2O_5 glass ceramics recorded at room temperature.

Conclusions:

The characterization of the samples by SEM, XRD and DTA techniques have indicated that the samples contain well defined and randomly distributed grains of different crystalline phases.The analysis of the results of optical absorption, ESR and photoluminescence spectra of the studied glass ceramics have indicated that a considerable proportion of vanadium ions do exist in V^{4+} state in addition to V^{5+} state, and the redox ratio increases with increase in the concentration of crystallizing agent V_2O_5.

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