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Non linear optical effects in nano-crystallized lithium silicate glass ceramics mixed with small concentrations of CuO.

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Abstract: Lithium niobium silicate glasses are synthesized and crystallized with different concentrations of CuO (0.0 to 0.2 mol% in the steps of 0.05). The sample then characterized by SEM. The Optical absorption, ESR and Photo-induced second order susceptibility studies are carried out. have indicated that major proportion of copper ions exist only in Cu^{2+} state in the samples crystallized up to 0.2 mol% CuO. Photo induced second order susceptibility studies have indicated that 0.2 mol% of CuO is the optimal concentration for getting the highest values of second order susceptibility coefficients.
Keywords: silicate glass ceramics, second order susceptibility.

Introduction:

Lithium Niobium silicate glass ceramics mixed with transition metal ions is well known due to their electro chromic and non-linear optical properties [1]. Transition metal ions like copper ions are generally being used as crystal stimulators for controlled crystallization processes, giving rise to enormous numbers of nucleation centers in the original glass. In the silicate glass matrices copper ion is expected to exist as metallic Cu, cuprous Cu^{+}, or cupric Cu^{2+} ions. Due to the crystallization, there is a possibility for the formation of copper nanoclusters in glasses; such nano crystals are expected to exhibit absorption bands at characteristic surface plasma resonance in the visible region and optical nonlinearity [2]. The glass ceramics containing copper ions in different oxidation states are highly useful for consideration of the materials to use in electrical memory switching devices. There are also reports suggesting that copper ions in some glass ceramics containing alkali ions like lithium do exist in Cu^{3+} state and form $LiCuO_2$ crystal phases with Li-layered structures. Li–Cu–O containing systems have attracted great interest as cathode material for an advanced lithium ion batteries [3].

In the present investigation we have synthesized Li_2O–Nb_2O_5–SiO_2 glasses, crystallized them with different concentrations of CuO as nucleating agent and characterized them by variety of techniques like SEM. Later, we have studied ESR, optical absorption properties with a view to have some understanding over the influence of copper valance states and their coordination with oxygen on structural aspects of the samples. Finally, we have undertaken photo induced second order susceptibility studies to examine the suitability of these materials for optically operated devices.

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 and ESR of these glass ceramics have been recorded. The photo-induced second order susceptibility of the glass ceramics was measured using standard nano-second (ns) photoinduced technique (Fig. 2.20). A Er: Glass laser operated at 10 Hz with the pulse duration of 10 ns was used as a fundamental laser light source.

Results and Discussion:

The scanning microscopy pictures of some of the samples are shown in Fig.1. The pictures clearly indicate that the samples contain well defined, randomly distributed crystals of different sizes (varying from 100 to 500 nm) ingrained in glassy matrix.Fig.2 represents the optical absorption spectra of Li_2O-Nb_2O_5-SiO_2: CuO glass ceramics recorded at room temperature in the wavelength region 200-1200 nm. The absorption spectra of all the glasses exhibited a broad band with a meta center between 800-850 nm. With increase in the concentration of CuO the half width at full maximum and peak height of this broad band is observed to increase. the optical absorption in the glass ceramic samples is dominated by polaronic transfer between the Cu^+ and Cu^{2+} species.With the increase in concentration of Cu^{2+} ions in the glass ceramic network, a large number of donor centers are created, and subsequently, the excited states of localized electrons originally trapped on Cu^+ sites begin to overlap with the empty 3d states on the neighboring Cu^{2+} sites, and as a result, the impurity or polaron band becomes more extended into the main band gap.

The ESR spectra (Fig. 3) of Li_2O–Nb_2O_5–SiO_2: CuO glass ceramics recorded at room temperature have exhibited a strong asymmetric signal with a hyperfine structure partially resolved at $g_\perp \sim 2.08$ and a shallow quadruplet at about $g_{ll} \sim 2.4$.

Copper ions are expected to exist mainly in Cu^{2+} state in Li_2O–Nb_2O_5–SiO_2: CuO glass network. However, the oxidation or reduction of copper ions from Cu^{2+} to Cu^{3+} and Cu^+ appears to be possible during melting, annealing and crystallization processes. Cu^{2+} ions occupy octahedral positions where as Cu^+ and Cu^{3+} ions are expected to occupy tetrahedral positions in the glass network [5].The broad absorption band observed in the optical absorption spectra (fig.2) of Li_2O–Nb_2O_5–SiO_2:CuO glass ceramics is assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ transition of Cu^{2+} ions [6]. The broadening of this band may be attributed to the super position of three electron transition in d orbitals corresponding to $^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ transitions. Fig. 4 represents the comparison plot of second-order susceptibility versus applied dc field at a temperature of 270 ^oC for the glass ceramic samples; the figure indicates substantial increase of the second-order susceptibility with the increase of the field for all the samples. The highest value of $\chi^{(2)}$; incidentally we have observed the lowest optical band gap for Li_2O–Nb_2O_5–SiO_2 glasses crystallized with 0.2 mol% of CuO.

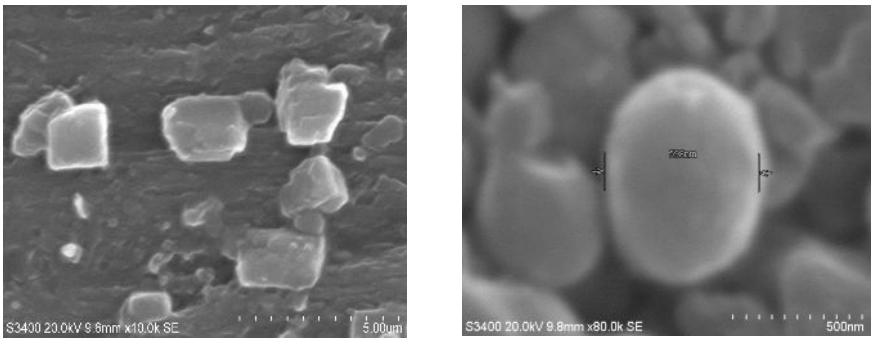

Fig 1. SEM photographs of Li_2O–Nb_2O_5–SiO_2 crystallized sample doped with 0.2 mol% of CuO.

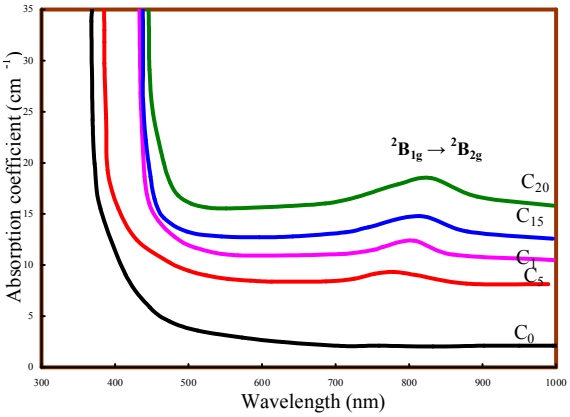

Fig 2. Optical absorption spectra of Li_2O-Nb_2O_5-SiO_2 glass ceramics doped with different concentrations of CuO recorded at room temperature

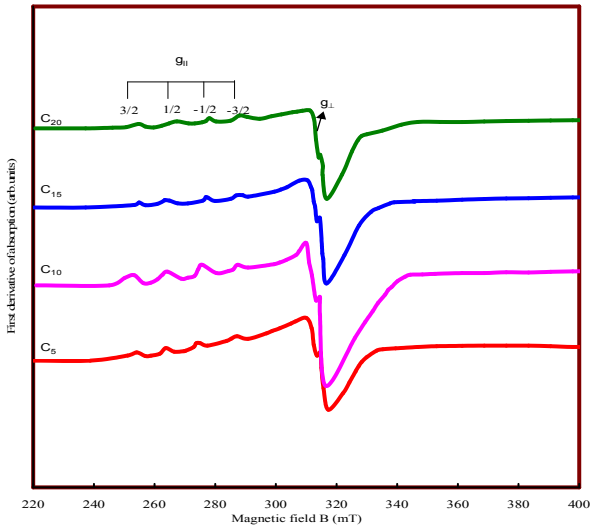

Fig. 3 .ESR spectra of Li2O-Nb2O5-ZrO2-SiO2: CuO glass ceramics recorded at room temperature.

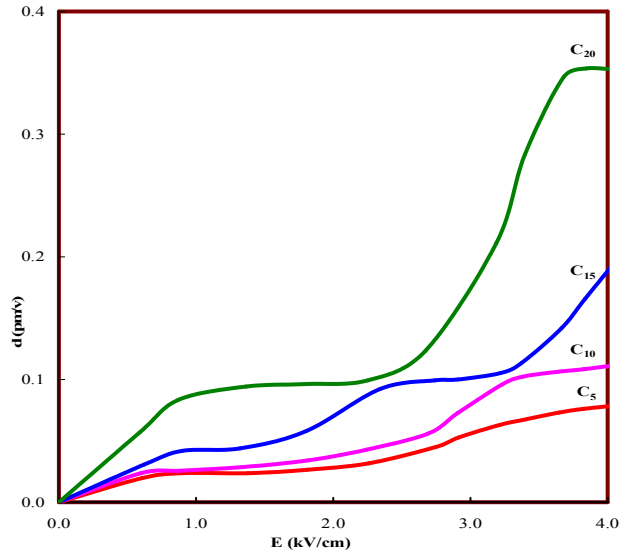

Fig.4 Dc-field dependence of the effective second-order susceptibility for the Li2O-Nb_2O_5-SiO_2 crystallized samples doped by different amount of CuO. (A fundamental 20 ns laser Er: glass laser at wavelength 1540 nm was applied)

Conclusions:

The analysis of the results of optical absorption, ESR and IR spectra of the studied glass ceramics have indicated that major proportion of copper ions exist only in Cu^{2+} state in the samples crystallized up to 0.2 mol% CuO. Photo induced second order susceptibility studies have indicated that 0.2 mol% of CuO is the optimal concentration for getting the highest values of second order susceptibility coefficients.

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