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# Photostimulated optical effects and some related features of CuO mixed $Li_2O$–$Nb_2O_5$–$ZrO_2$–$SiO_2$ glass ceramics

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**Abstract**

We have synthesized $Li_2O$–$Nb_2O_5$–$ZrO_2$–$SiO_2$ glasses and subsequently crystallized them with different CuO contents (0–0.3 mol% in the steps of 0.05) as nucleating agents and characterized them by XRD, SEM and DSC. We have also studied IR, Raman, ESR, optical absorption photoluminescence and dielectric properties to explore the influence of copper valance states and their coordination with oxygen on structural and optoelectronic aspects of the samples. These studies have indicated that there is a possibility for the copper ions to exist in $Cu^{+}$ and $Cu^{3+}$ states (in addition to $Cu^{2+}$ state) in these glass ceramics and participate in the glass network forming. Finally, we have undertaken photoinduced second harmonic generation studies (after the samples were dc field treated at elevated temperatures) with 10 ns Er:glass laser (of wavelength 1540 nm with power densities up to 1.5 $GW/cm^2$) to examine the suitability of these materials for optically operated devices. The analysis of the results of non-linear optical studies has shown that 0.2 mol% of CuO is the optimal concentration for getting the highest values of second order susceptibility coefficients.


*Keywords:* B. Spectroscopy; C. Dielectric properties; D. Glass ceramics; D. Silicate

## 1. Introduction

Niobium silicate glasses and glass ceramics mixed with transition metal ions are well known due to their electro chromic and non-linear optical properties [1–4]. The addition of $ZrO_2$ to these glasses makes them to be more electrical, chemical and thermal resistant; the presence of zirconium oxide in oxide glasses also causes to increase the mechanical strength and is found to widen the range of transparency (300 nm to 8 μm) of the glasses [5–7]. In view of these qualities, the $ZrO_2$ mixed niobium silicate glasses are expected to be useful as optical filters, laser mirrors, and alternative gate dielectrics in microelectronics and in a number of nonlinear devices [8,9].

Partial crystallization of the glasses is expected to have profound influence on several physical properties viz., optical, mechanical, electrical, thermal and chemical durability of the material. Recently, transparent crystallized glasses, i.e., composites of crystalline and glassy phases, consisting of nonlinear optical or ferroelectric crystals have received much attention and there have been many reports on the fabrication and characterization of such transparent crystallized glasses [10]. Transparency of glass ceramics can be retained by controlling the crystallization of a glass precursor with appropriate chemical compositions and appropriate nucleating agent. The general conditions for the retention of transparency of glass even after the crystallization include small refractive index difference between the crystalline and residual glass phases, a small birefringence of the crystallites and smaller wavelength of the incident light when compared with the size of crystallites. Investigations along these lines have been carried out on several glass systems including some silicate, fluoride or oxyfluoride matrices, polymers and thin films [11–15].

Transition metal ions are generally being used as crystal stimulators for controlled crystallization processes, giving rise

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to enormous numbers of nucleation centers in the original glass. Among various transition metal ions, copper ion is a very interesting ion to probe in the glass ceramic material. In the silicate glass matrices this ion is expected to exist as metallic Cu, cuprous $Cu^{+}$, or cupric $Cu^{2+}$ ions as per the following redox reaction

$$4Cu^{2+} + 2O_2^{-} \leftrightarrow 4Cu^{+} + O_2$$

It is known that the valence state in copper affects not only optical, chemical, electrical and mechanical properties but also the glass-forming ability of the system [16,17]. 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 [18–20]. In view of these qualities, 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 materials for advanced lithium ion batteries [21].

Further, thermally poled silica based glasses and glass ceramics under electrical fields are the materials of choice for applications in optoelectronics because of their excellent optical properties; recently for some of the silicate based glasses, the value of $\chi^{(2)}$ is reported to be ~0.30 pm/V [22]. For applications like modulators, routers or switches, the amplitude of the electric field $E_{dc}$ recorded in the material has to be strong and stable at the place of the optical waveguides. The stability of the electric field in the poled glasses is, thus, an important factor in determining the nonlinear optical properties produced during the poling process.

In the present investigation we have synthesized $Li_2O$–$Nb_2O_5$–$ZrO_2$–$SiO_2$ glasses, crystallized them with different concentrations of CuO as nucleating agents and characterized them by a variety of techniques viz., XRD, SEM and DSC. Later, we have studied IR, Raman, ESR, optical absorption photoluminescence and dielectric 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 photoinduced second order susceptibility studies (after the samples were dc field treated at elevated temperatures) to examine the suitability of these materials for optically operated devices.

## 2. Experimental

The detailed compositions of the glasses used in the present study are as follows:

$C_0$: $30.00Li_2O-10Nb_2O_5-5ZrO_2-55SiO_2$

$C_5$: $29.95Li_2O-10Nb_2O_5-5ZrO_2-55SiO_2$: 0.05CuO

$C_{10}$: $29.90Li_2O-10Nb_2O_5-5ZrO_2-55SiO_2$: 0.10CuO

$C_{15}$: $29.85Li_2O-10Nb_2O_5-5ZrO_2-55SiO_2$: 0.15CuO

$C_{20}$: $29.80Li_2O-10Nb_2O_5-5ZrO_2-55SiO_2$: 0.20CuO

$C_{25}$: $29.75Li_2O-10Nb_2O_5-5ZrO_2-55SiO_2$: 0.25CuO

$C_{30}$: $29.70Li_2O-10Nb_2O_5-5ZrO_2-55SiO_2$: 0.30CuO

Analytical grade reagents of $Li_2CO_3$, $Nb_2O_5$, $ZrO_2$, $SiO_2$ and CuO powders in appropriate amounts (all in mol%) were thoroughly mixed in an agate mortar and melted in a platinum crucible in the temperature range of 1450–1500 °C in an automatic temperature controlled furnace for about 30 min. The resultant bubble free melt was then poured in a brass mould and subsequently annealed at 400 °C. For the crystallization, the glass specimens were first heated up to crystallization temperature 900–950 °C (identified from DSC traces) at the rate of 3 °C/min and then were held at 900 °C for 72 h; samples were cooled slowly (for about 3 h) to the off-set temperature of the crystallization peak (to avoid cracks, voids due to subsequent sudden cooling) and then chilled in air to room temperature.

The samples prepared were mechanically ground and polished to a mirror finish with cerium oxide powder; the final dimensions of the samples used for the measurements are about 1 cm × 1 cm × 0.2 cm. Scanning electron microscopy studies were carried out on these samples to observe the crystallinity using HITACHI S-3400N Scanning Electron Microscope. The crystalline phases in the heat treated samples were identified using Rigaku D/Max ULTIMA III X-ray diffractometer with $CuK_{\alpha}$ radiation. Differential thermal analysis was carried out by Netzsch Simultaneous DSC/TG Thermal Analyzer STA409C with 32-bit controller to determine the glass transition temperature and crystalline peaks. High temperature furnace together with a sample carrier suitable for $C_p$ measurements and $Al_2O_3$ crucibles was used. Apparatus was calibrated both for temperature and for sensitivity with melting temperatures and melting enthalpies of the pure metals: Ga, In, Sn, Zn, Al, Ag, and Au. All the recordings were carried out in argon (5 N pure) atmosphere to prevent samples from oxidation. Heating rate was 10 °C/min in the temperature range 32–1300 °C.

The density of the glasses was determined to an accuracy of (±0.0001) by the standard principle of Archimedes' using o-xylene (99.99% pure) as the buoyant liquid. The mass of the samples was measured to an accuracy of 0.1 mg using Ohaus digital balance Model AR2140 for evaluating the density. The refractive index ($n$) of the samples was measured at $\lambda = 589.3$ nm using Abbe refractometer with monobromo naphthalene as the contact layer between the glass and the refractometer prism to an accuracy of 0.001. Infrared transmission spectra were recorded on a JASCO-FT/IR-5300 spectrophotometer that can record spectrum up to a resolution of 0.1 $cm^{-1}$ in the spectral range 400–2000 $cm^{-1}$ using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). These pellets were pressed in a vacuum die at ~680 MPa. The Raman spectra were recorded with an NIR excitation line (1064 nm) using a Bio-Rad spectrometer FTS