TechnoChem

International Journal of TechnoChem Research
ISSN: 2395-4248 www.technochemsai.com
Vol.01, No.01, pp 66-69, 2015

Non-linear Optical Studies on CuO Doped Lithium Zirconium Silicate Glass Ceramics for Laser Application

Ch. Srinivasa Rao, T. Srikumar, S. Shantkriti and M.C. Rao*

Department of Physics, Andhra Loyola College, Vijayawada - 520008, A.P., India
PG & Research Department of Biotechnology, National College (Autonomous), Dindigul Road, Tiruchirapalli- 620001, Tamilnadu, India

Abstract: $Li_2O–ZrO_2–SiO_2$ glasses have been synthesized and subsequently crystallized with different concentrations of CuO (0 to 0.3 mol % in the steps of 0.05) as nucleating agent. The ESR, optical absorption and photo induced second order susceptibility studies have been carried out to explore the influence of copper valence states and their coordination with oxygen on structural and optoelectronic aspects of the samples. The photo induced second harmonic generation studies with 10 ns Er: glass laser were carried out to examine the suitability of these materials for optically operated devices. The quantitative analysis of the results of non linear optical studies have shown that 0.2 mol % of CuO is the optimal concentration for getting the highest values of second order susceptibility coefficients.

Keywords: $Li_2O–ZrO_2–SiO_2$ glasses, melt quenching, optical absorption, ESR and photo induced second order susceptibility.

Introduction:

Lithium zirconium silicate glass ceramics mixed with transition metal ions are useful as optical filters, laser mirrors, and alternative gate dielectrics in microelectronics in a number of nonlinear devices [1, 2]. Among various transition metal ions, copper ion is a very interesting ion to probe in the glass ceramic material. In the silicate glass matrices copper ions are expected to exist as metallic Cu, cuprous Cu^+ or cupric Cu^{2+} ions. 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 [3]. Due to the crystallization, there is a possibility for the formation of copper nanoclusters in glasses; such nanocrystals are expected to exhibit absorption bands at characteristic surface plasmon resonance in the visible region and optical nonlinearity. In the present investigation we have synthesized $Li_2O–ZrO_2–SiO_2$ glasses crystallized with different concentrations of CuO as nucleating agent and characterized by variety of techniques viz., ESR, optical absorption and photo induced second order susceptibility studies with a view to have some understanding over the influence of copper valence states and their coordination with oxygen on structural aspects of the samples. In present work we are compared the optical absorption, ESR and photo induced second order susceptibility studies on $Li_2O–ZrO_2–SiO_2$ glasses doped with 0.2 mol % of CuO before and after crystallization.

Experimental:

The samples are prepared by melt quenching method as reported in our earlier papers. The optical absorption spectra of the glasses were recorded at a resolution of 0.1 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 the fine powder of the samples were recorded at room temperature on E11Z Varian X-band (□

= 9.5 GHz) ESR spectrometer. The non linear optical effects (controlled by the output of SHG) were recorded after the achievement of maximal poling; the incident beam of the 10 ns Er: glass laser.

Results and Discussion:

Fig. 1 represents the optical absorption spectra of $Li_2O–ZrO_2–SiO_2$ glasses doped with 0.2 mol % of CuO recorded at room temperature in the wavelength region 200 –1200 nm before and after crystallization. The absorption spectra of these samples exhibited a broad band with a meta center between 800-850 nm [4]. Due to crystallization, the half width at full maximum and peak height of this broad band is observed to increase. It may be noted here that in the spectra of the pre-crystallized sample a weak band at about same wavelength could be visualized. However the optical band gap is found to be considerably higher for the pre-crystallized samples.

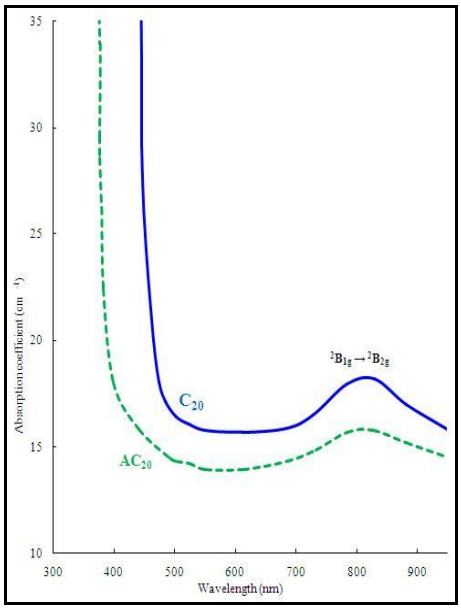

Fig. 1 Optical absorption spectra of $Li_2O–ZrO_2–SiO_2$ glasses doped with 0.20 mol % of CuO recorded at room temperature before and after crystallization

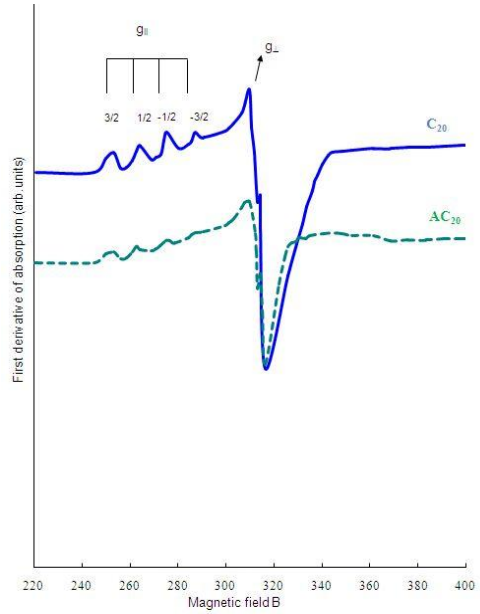

Fig. 2 ESR spectra of $Li_2O–ZrO_2–SiO_2$ glasses doped with 0.20 mol % of CuO recorded at room temperature before and after crystallization

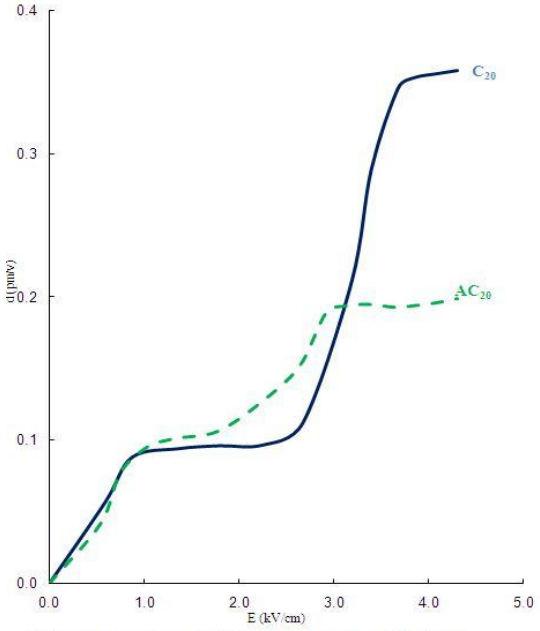

Fig. 3 Dc-field dependence of the effective second order susceptibility for the $Li_2O–ZrO_2–SiO_2$ glasses doped with 0.20 mol % of CuO before and after crystallization

The ESR spectra (Fig. 2) of $Li_2O–ZrO_2–SiO_2$ glasses doped with 0.2 mol % of CuO recorded at room temperature before and after crystallization have exhibited a strong asymmetric signal with a hyperfine structure partially resolved at $g_{\perp}$ ~ 2.08 and a shallow quadruplet at about g_{ll} ~ 2.4. The line width of parallel and perpendicular hyperfine peak is observed to be more for crystallized sample than pre-crystallized sample. Fig. 3 represents the comparison plot of second-order susceptibility versus applied dc field at a temperature of 270 ^{0}C for $Li_2O–ZrO_2–SiO_2$ glasses doped with 0.2 mol % of CuO before and after crystallization; the figure indicates that the second-order susceptibility is more for crystallized sample than pre-crystallized sample.

The broad absorption band observed in the optical absorption spectra of $Li_2O–ZrO_2–SiO_2$: CuO glass ceramics is assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ transition of Cu^{2+} ions [5]. Further, the optical activation energy associated with $^2B_{2g} \rightarrow {}^2B_{1g}$ is 1.54 eV for sample C_{20}; this is clearly a characteristic signal of inter valence transfer or a polaronic type of absorption. The ESR and optical absorption spectral data can be correlated to understand the environment of Cu^{2+} ions in $Li_2O—ZrO_2–SiO_2$ glass ceramics. Under the application of high dc field, the electrical forces form orientation file which align the corresponding state dipole moments and form the macroscopic non-centrosymmetry. The coupling of this acentric field with the third order susceptibility, χ^3, gives rise to effective second-order susceptibility through the Eq.

$$\chi^{(2)} = 3\chi^{(3)} \; E_{dc} \text{ ---- --------- (1)}$$

The induced polarizability is quadratically dependent on the pump electromagnetic wave and the induced coefficient is an effective optical second order nonlinear coefficient $\chi^{(2)}$. This one is commonly believed to arise from the symmetry breaking recorded dc-electric field acting on the third-order nonlinear susceptibility as per the Eq. (1). [6, 7] In the present investigation we have observed the highest value of $\chi^{2)}$; for $Li_2O–Nb_2O_5–ZrO_2–SiO_2$ glass crystallized with 0.2 mol % of CuO than precrystallized sample. The maximal NLO effects for the amorphous sample were observed only after heat treatment at higher temperatures (320 ^{0}C). Such an observation suggests that the degree of depolymerization that causes the induced dipole moment is less in the sample.

Conclusions:

We have synthesized $Li_2O–ZrO_2–SiO_2$ glass and subsequently crystallized with 0.2 mol % of CuO as nucleating agent and characterized it. The analysis of the results of optical absorption and ESR of the studied glass and glass ceramic have indicated that a considerable proportion of copper ions do exist in Cu^+ state in addition to Cu^{2+} state especially in the precrystallized sample than crystallized sample. Photo induced second order susceptibility 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) have indicated that $Li_2O–ZrO_2–SiO_2$ glass doped with 0.2 mol % of CuO after crystallization is the best candidate for getting the highest values of second order susceptibility coefficients.

References:

1. Sigaev V.N., Ryzhenkov V.S., Lotarev S.V., Golubev N.V., Yu S. Stefanovich A. O., J. Non-Cryst. Solids 356 (2010) 958-965.
2. Sawa N., Nakanishi K. and Hanada T., Thin Solid Films 516 (2008) 4665-4672.
3. Cattaruzza E., Battaglin G., Gonella F., Polloni R., Scremin B.F., Mattei G., Mazzoldi P.and Sada C., Appl. Surface Sci. 254 (2007) 1017-1021.
4. Di Bartolo B. (Ed.), Spectroscopy of Solid-State Laser – Type Materials, Plenum Publishing Corporation, New York, (1987) 238.
5. Srinivasa Rao L., Srinivasa Reddy M., Krishna Rao D. and Veeraiah N., Solid State Sci. 11(2009) 578-587.
6. Kityk I. V., Marciniak B., Sahraoui B., Cryst. Res. Technol. 37 (2002) 477-484.
7. Williams M., Hunter D., Pradhan A. K. and Kityk I. V., Appl. Phys. Lett. 89 (2006) 043116.

*****

www.technochemsai.com