Chemical Concepts

International Journal of Chemical Concepts
ISSN:2395-4256 www.chemconsai.com
Vol.01, No.01, pp 05-08, 2015

Spectroscopic Studies on CuO Doped Li_2O-ZrO_2-SiO_2 Glass Ceramics

Ch. Srinivasa Rao[1], T. Srikumar[1], S. Shantkriti[2] and M.C. Rao[1]*

[1]Department of Physics, Andhra Loyola College, Vijayawada - 520008, A.P., India
[2]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 X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) 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 and to examine the suitability of these materials for optically operated devices. XRD pattern revealed the presence of clear peaks at $2\theta = 31.34^o$ and 36.59^o corresponding to $LiCuO_2$ orthorhombic crystal phase. SEM indicated that the samples contain well defined, randomly distributed crystals of different sizes ingrained in glassy matrix. FTIR revealed the presence of various bands due to bridging of oxygen perpendicular to Si–Si axis within the Si−O−Si plane.

Keywords: $Li_2O–ZrO_2–SiO_2$ glasses, melt quenching, XRD, SEM and FTIR.

Introduction:

A considerable effort has been spent to obtain high performance glass ceramics for several potential applications in medical, automotive, and telecommunication fields [1]. Low-temperature co-fired ceramics (LTCCs) have created good perspective for these applications with special attention to glass ceramic materials. The glass ceramic materials are mainly produced via two controlled stages of nucleation and crystallization. These materials have some advantages, such as minimal or even zero porosity and homogeneous microstructure, over the ceramics that are produced via powder metallurgy [2]. These advantageous properties are achieved by precipitating a large percentage of desired crystal phases (at least 50 % vol.) in glass ceramics [3]. LZSA glass ceramics (Li_2O-ZrO_2-SiO_2-Al_2O_3) have been studied because of their beneficial mechanical and thermal properties [4], among other interesting features. 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 [5, 6]. 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 [7]. Due to 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

various techniques viz., XRD, SEM and FTIR studies with a view to have some understanding about the influence of copper valence states and their coordination with oxygen on structural aspects of the samples. In this paper we present the XRD, SEM and FTIR studies on CuO doped $Li_2O–ZrO_2–SiO_2$ glass ceramics.

Experimental:

The samples were prepared by melt quenching method as reported in our earlier papers. The crystalline phases in the heat treated samples were identified using Rigaku D/Max ULTIMA III X-ray diffractometer with CuK_α radiation. Scanning electron microscopy studies were carried out on these samples to observe the crystallinity using HITACHI S-3400N Scanning Electron Microscope. 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.

Results and Discussion:

X-ray diffraction pattern of the Li_2O-ZrO_2-SiO_2 glass ceramic doped with 0.2 mol % of CuO is shown in Fig. 1. The pattern exhibited peaks due to variety of crystal phases; some of them are Li_6CuO_4, $CuSiO_3$, $Li_6Si_2O_7$, $Li_2Si_3O_5$, Li8SiO6, $Li_2Si_2O_5$, Li_4SiO_4, Li_2SiO_3, $Li_2Si_3O_7$; the details of JCPDS card numbers of these crystalline phases can be found in the reference [8]. From the XRD pattern of the crystallized glass ceramic, we have also observed diffraction peak with significant intensity and full width at half maximum due to LiCuO crystal phase at about $2\theta = 25.59^o$. The presence of such phase clearly suggests that a fraction of the copper ions do exist in Cu^+ state. However, as the concentration of CuO increased, no considerable hike in the intensity of this peak is observed. Another interesting feature of XRD pattern is the presence of clear peaks at $2\theta = 31.34^o$ and 36.59^o corresponding to $LiCuO_2$ orthorhombic crystal phases; this observation points out that there is a possibility for the copper ions to exist in Cu^{3+} state and participate in the network forming with square planar CuO_4 structural units connected linearly along the c - axis. The formation of LiCuO and $LiCuO_2$ crystalline phases detected from the XRD studies along with the other conventional crystalline phases emphasizes that copper ions do exist in Cu^+ and Cu^{3+} state in addition to Cu^{2+} state in these glass ceramics [9].

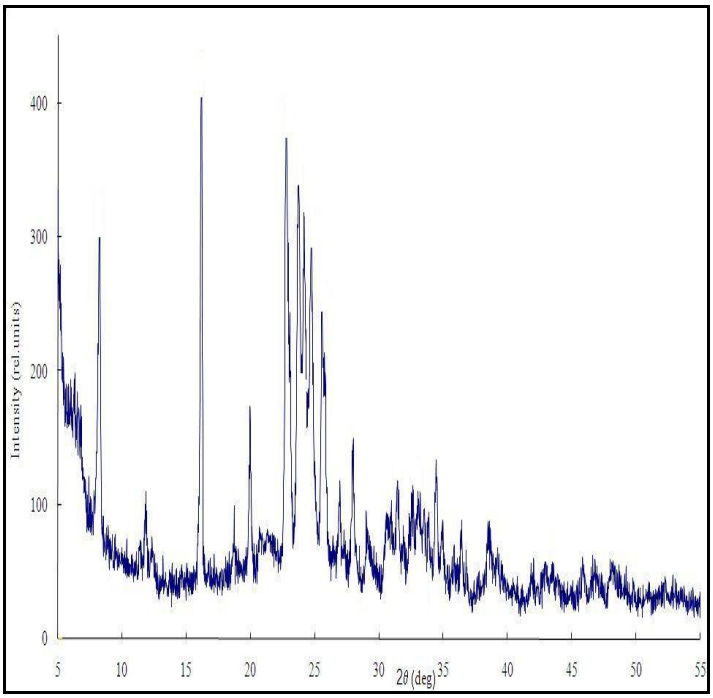

Fig. 1 XRD pattern of $Li_2O–ZrO_2–SiO_2$ glass ceramic doped with 0.2 mol % of CuO showing different possible crystal phases

Fig.2 represents the SEM photograph of the crystallized sample of $Li_2O–ZrO_2–SiO_2$ glass ceramic doped with 0.2 mol % of CuO. The picture clearly indicated that the sample contains well defined, randomly distributed crystals of different sizes (varying from 100 to 500 nm) ingrained in glassy matrix. The residual glass phase is acting as an interconnecting zone among the crystallized areas making the samples free of voids and cracks.

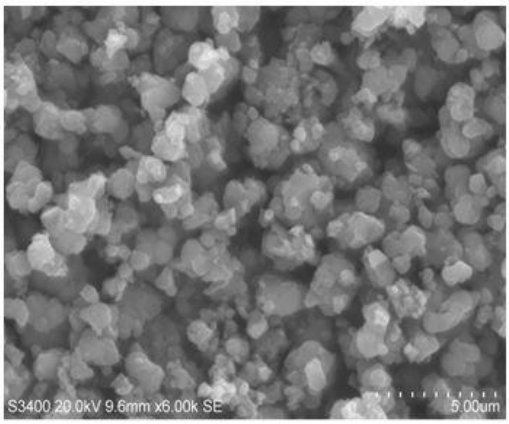

Fig. 2 SEM photograph of the crystallized sample of $Li_2O–ZrO_2–SiO_2$ glass ceramic doped with 0.2 mol % of CuO

Fig. 3 represents the IR spectra of CuO free $Li_2O–ZrO_2–SiO_2$ glass ceramic. The spectra exhibited the bands viz. at 1050 cm^{-1} due to Si−O−Si asymmetric vibrations; 800 cm^{-1} due to bending mode of bridging oxygen perpendicular to Si–Si axis within the Si−O−Si plane (symmetrical vibration band); 980 cm^{-1} due to Si–O–Zr linkages; 530 and 700 cm^{-1} due to Zr–O–Zr vibrations of ZrO_4; 475 cm^{-1} due to Si−O−Si / O−Si−O bending modes [10].

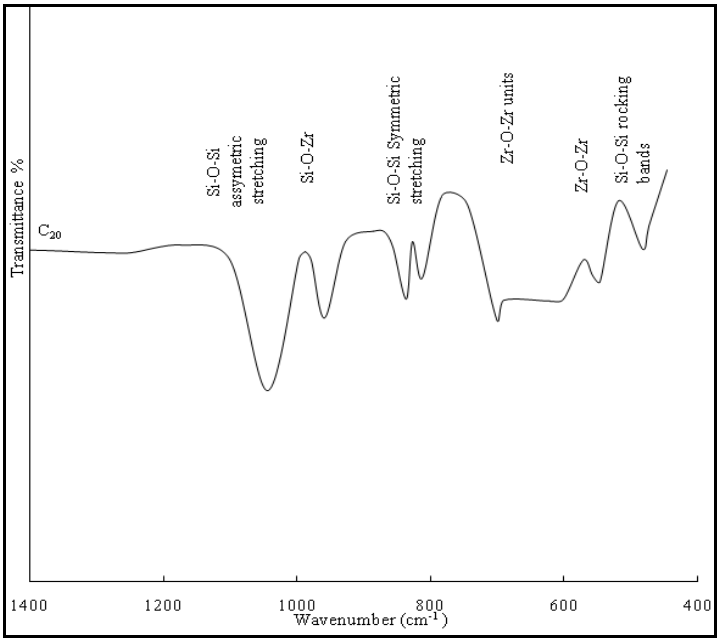

Fig. 3 FTIR spectra of $Li_2O–ZrO_2–SiO_2$ glass ceramic doped with 0.2 mol % of CuO

Conclusions:

We have synthesized $Li_2O–ZrO_2–SiO_2$ glass ceramics subsequently crystallized with 0.2 mol % of CuO as nucleating agent and characterized it. The analysis of results of XRD revealed the presence of clear peaks at $2\theta = 31.34^o$ and 36.59^o corresponding to $LiCuO_2$ orthorhombic crystal phase. The formation of LiCuO and $LiCuO_2$ crystalline phases detected by the XRD studies along with other conventional crystalline phases emphasizes that copper ions do exist in Cu^+ and Cu^{3+} state in addition to Cu^{2+} state in these glass ceramics. SEM indicated that the sample contains well defined, randomly distributed crystals of different sizes ingrained in glassy matrix. FTIR revealed the presence of various bands due to bridging of oxygen perpendicular to Si–Si axis within the Si−O−Si plane.

References:

1. Tummala R. R., J. Amer. Cera. Soc. 74 (1991) 895–908.
2. McMillan P. W. Glass-ceramics. 2nd ed. Non-metallic solids. London; New York: Academic Press; 1979.
3. Strnad Z. E., Glass-ceramic materials: liquid phase separation, nucleation, andcrystallization in glasses. Glass science and technology-8 Amsterdam; New York: Elsevier; 1986.
4. Montedo O. R. K., Bertan F. M., Piccoli R., Hotza D., Klein A. N. and de Oliveira A. P. N., Amer. Cera. Soc. Bull., 87 (2008) 34–40.
5. 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.
6. Sawa N., Nakanishi K. and Hanada T., Thin Solid Films 516 (2008) 4665-4672.
7. 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.
8. Powder Diffraction File, Alphabetical Index, Inorganic Compounds 2003, Published byJCPDS – International Centre for Diffraction Data, Newtown Square, PA. 19073–3273.
9. Klassen V. H. and Hopper R., Z. Anorg. Allg. Chem. 486 (1982) 101-114.
10. Nakamura M., Mochizuki Y., Usami K., Itoh Y. and Nozaki T., Solid State Commun. 501984) 1079-1081.

*****