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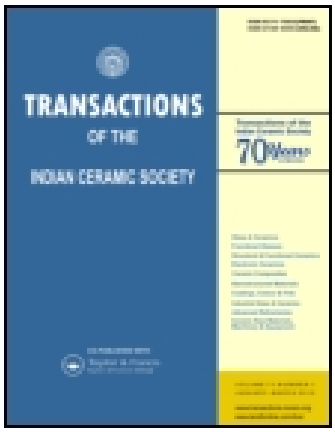

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Ionic to Electronic Conductivity Studies of Lithium-Borate Ruby-Glass-Ceramics Containing Gold Nano Particles

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Glass-ceramics containing Au nanoparticles have been synthesized in the glass composition $30Li_2O$-$70B_2O_3$ with $HAuCl_4.3H_2O$ as dopant. The characteristic ruby colour has been observed which is attributed to the surface plasmon resonance of the Au nanoparticles, uniformly embedded in the glass matrix. The imparted red colour due to the presence of gold nanoparticles has been confirmed by studying the optical absorption spectra using UV-VIS spectrometer in the visible range (400-1000 nm) which show a characteristic absorption peak at ~560 nm. In order to check the crystallization/ amorphous nature, the samples were powdered and characterized using X-ray diffraction (XRD). The microstructural modifications in the samples due to the addition of Au have been recorded using scanning electron microscopy (SEM). Further, the electron spin resonance (ESR) studies reveal that the electronic state of gold is either Au^0 or Au^+. AC conductivity studies have been performed at room temperature over a frequency range 100 to 10 MHz. The ac conductivity data is fitted by Almond-West law with power exponent 's'. The dc conductivity is found to be increasing with the increase of temperature for a typical ruby glass, but almost constant with dopant concentration.

[Keywords : Ruby-glass, Gold nanoparticles, Optical absorption, SPR, Transport properties]

Introduction

Ruby glasses containing gold nanoparticles or other noble metal nanoparticles have been extensively investigated for the past decades because of their excellent properties such as ultrafast optical response and large third order non-linear susceptibility.[1–4] This kind of glasses are expected to be promising materials for ultrafast optical switches and optical circuits with micrometer size. Hence, preparation and characterization of materials containing noble metal nanoparticles is the most challenging task for researchers in the area of materials science. Glasses containing metal nanoparticles look very distinctive with different colours. Since the quantum size effects and enhanced surface effects are expected to influence the electronic and optical properties at much smaller particle sizes, it leads to more interest for researchers to fabricate the metal nanoparticles in glasses.[5, 6] Such investigated gold-ruby glasses are used not only as decorative glasswares but also for many technological applications in the field of electrical and optical communications. Silicate ruby glasses are synthesized mainly by using $HAuCl_4.3H_2O$ along with a reducing agent, such as tin based compounds, and then annealing the glass for several hours at a particular temperature.[7, 8] Metal nanoparticles in glasses are also precipitated using electron beam and laser irradiation. In these methods the metal ions are reduced but need thermal treatment.[9]

In this paper, we report precise dopoing of gold nanoparticles in borate matrix, viz. "lithium-borate ruby-glass-ceramics" without thermal treatment and addition of any reducing agent. The samples have been characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), electron spin resonance (ESR), optical absorption, and the ac conductivity at various temperatures over a wide frequency range 100-10 MHz has been studied.

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Experimental

Borate glasses with the composition $30Li_2O$-$70B_2O_3$-$xHAuCl_4.3H_2O$ (LBA) (where x = 0.01, 0.04 and 0.06 wt%) were prepared by melt quenching technique. The powders were thoroughly mixed and then melted at 1000°C. The melt was stirred well and kept again in the furnace at the melting temperature for about 10 min. Then the melt was quenched between two brass plates at room temperature. The quenched glass samples so obtained were found to be ruby-red in colour. The deepness of the colour was found to be increasing with increase in concentration of gold dopant. The samples were optically polished for optical measurements. Optical absorption spectra were recorded using UV-VIS spectrometer (USB2000, Ocean Optics, USA) in the visible range (400-1000 nm). For XRD (XPERT PRO, Philips), SEM (440I, LEO UK) and ESR (Expand, Brooker) samples were powered and examined at room temperature. Flat and random pieces of samples with thickness ~1 mm coated with silver paste on either side were used for the study of ac conductivity at room temperature using an impendence analyzer (Agilent 4294A, 40-110 MHz).

Results and Discussion

The absorption spectra of the prepared glass $30Li_2O$-$70B_2O_3$ (LB) and respective ruby-glass-ceramics containing gold nanoparticles (LBA) are shown in Fig. 1.

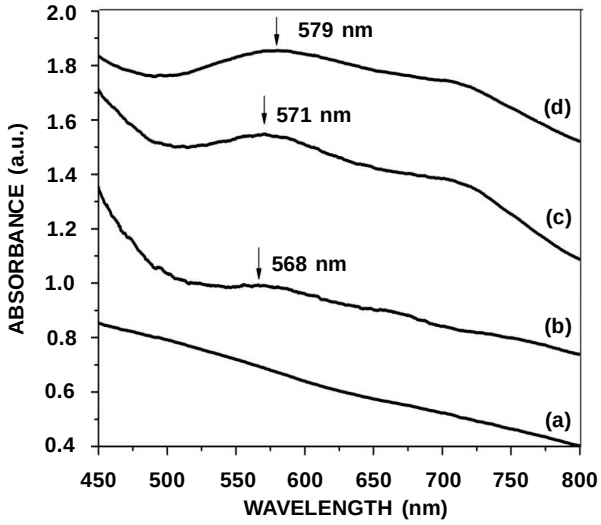

Fig. 1 – Absorption spectra of LB and LBA samples containing Au: (a) 0 wt%, (b) 0.01 wt%, (c) 0.04 wt% and (d) 0.06 wt%

It is clearly seen that the broad absorption peak of each sample is centered at 550-580 nm (Figs. 1b-1d). This peak is attributed to the surface plasmon resonance (SPR) due to the metallic gold nanoparticles embedded in the glass matrix.[10, 11] There is no such absorption peak as seen in Fig. 1a. In addition to the peak at ~550 nm, there is a weak peak centered around ~700 nm attributed to inter-band transition from the d-band to empty state in the conduction band of the metallic gold particles.[6]

X-ray diffraction patterns of LB and LBA (Fig. 2) clearly shows sharp peaks at 38.71°, 44.87° and 64.95°. These prominent peaks correspond to reflections from the planes (111), (200) and (220) of gold respectively.[12, 13] The average gold particle size (*D*) in the LBA sample with 0.06 wt% gold dopant was calculated using the standard Debye-Scherrer equation, mentioned below, and found to be ~28 nm.

$$D = K\lambda / \beta\cos\theta \qquad ..(1)$$

where *K* is the particle shape factor (generally taken as 0.9), λ is the wavelength of CuKα radiation, β is the integral breadth of a reflection (FWHM in radian), and θ is the Bragg angle at the peak position.

SEM images of lithium-borate glass series are presented in Figs. 3a-3d. The image of sample LB with

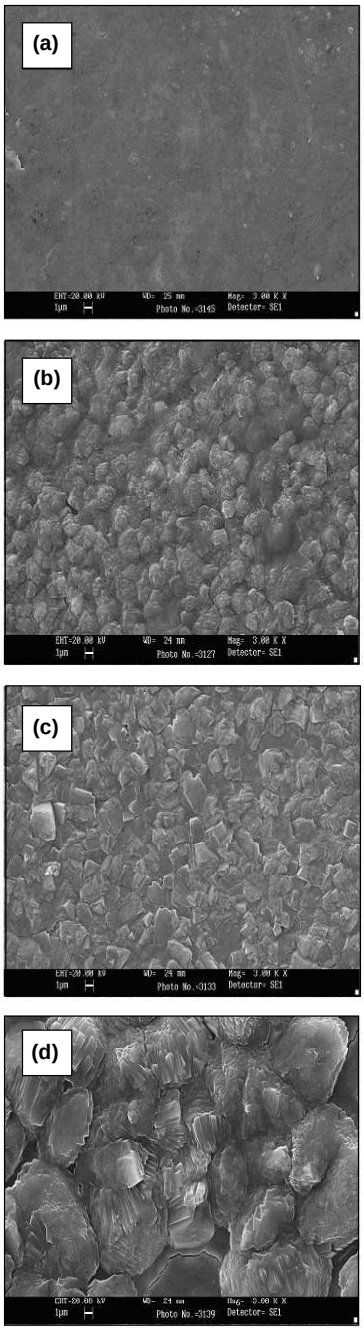

Fig. 3 – SEM images of LB and LBA samples containing Au: (a) 0 wt%, (b) 0.01 wt%, (c) 0.04 wt% and (d) 0.06 wt%

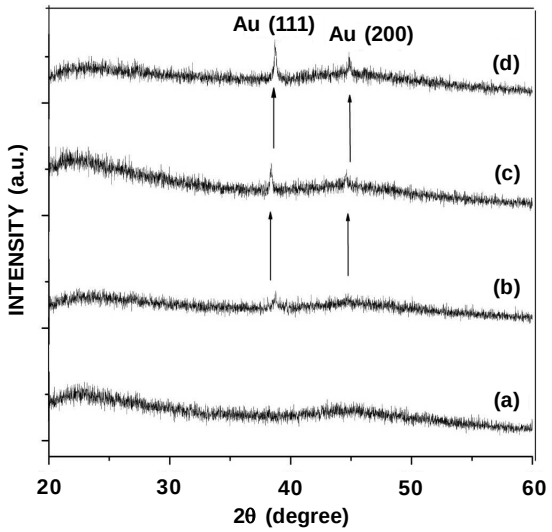

Fig. 2 – XRD pattern of LB and LBA samples containing Au: (a) 0 wt%, (b) 0.01 wt%, (c) 0.04 wt% and (d) 0.06 wt%

0% gold dopant (Fig. 3a) shows homogeneous phase, whereas the samples with different concentrations of gold dopant (LBA) (Figs. 3b-3d) clearly show the growth of small particles / crystallites of different sizes. It is extremely difficult to realize the presence of gold particles in the nano range from these images. However, one can conclude that the addition of gold dopant induces kinetics of growth of the particular phase, seems to be layered structure in LBA samples, and hence the formation of glass-ceramics.

Electron spin resonance (ESR) studies have been performed to understand the electronic state of the Au in LBA samples. It is well known that Au^{2+} are paramagnetic and ESR active. They can form several interesting complexes.[14] On the other hand, Au^0 and Au^+ are ESR inactive.[14, 15] The ESR spectra of all the samples under investigation are shown in Fig. 4. It is clearly seen that there is neither sharp signal nor hyperfine split in the entire spectrum, which indicates that the samples have neither paramagnetic ions nor unpaired electrons. Hence the electronic state of the gold must be either Au^0 or Au^+.[16] In the present study, ruby colour is observed without adding any reducing agent and heat treatment, and hence, the mechanism of transformation from Au^+ to Au^0 appears to be complicated.[14]

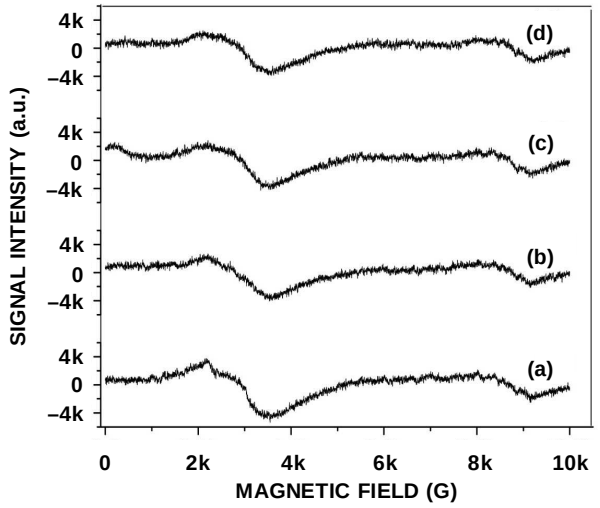

Fig. 4 – ESR spectra of LB and LBA samples containing Au: (a) 0 wt%, (b) 0.01 wt%, (c) 0.04 wt% and (d) 0.06 wt%

The ac conductivity of the glasses investigated has been found to increase up to ~10^{-6} S.cm^{-1} with the increase of frequency (Fig. 5). Non linear exponent variation of the ac conductivity has been analyzed using Almond-West type power law with a single exponent as shown below.

$$\sigma(\omega) = \sigma(0) + A\omega^s \qquad ..(2)$$

where σ is the total electrical conductivity, $\sigma(0)$ is the dc conductivity which is frequency independent part of the σ versus ω plot, ω is the angular velocity, A is a constant

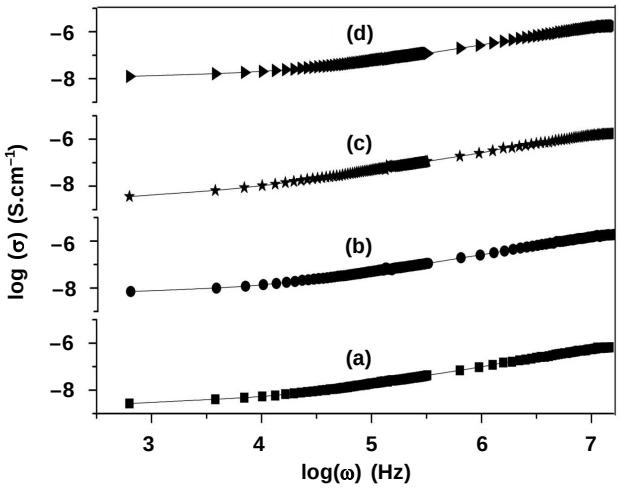

Fig. 5 – AC conductivity of LB and LBA samples at room temperature containing Au: (a) 0 wt%, (b) 0.01 wt%, (c) 0.04 wt% and (d) 0.06 wt%

and s is the power law exponent, which is obtained from the computer fits on the non linear curves shown in Fig. 5. The value of exponent is found to be almost constant and lie between 0.1 and 0.2.

The dc conductivities in LB and LBA samples have been found to remain almost constant with the increase of gold concentration. Both the values of 's' and dc conductivity obtained from Almond-West type power law fit are listed in Table I. Since the concentration of Li^+ ions is fixed, one may conclude that Li^+ ion movement responsible for the observed conductivity may be assisted by Au particles without dominating over the ionic conductivity at room temperature.[17]

Table I : σ(0) and *s* values obtained for all the samples at room temperature

Sample	σ(0) (S.cm^{-1}) × 10^{-8}	s
LB	0.33	0.10
LBA (0.01 wt% Au)	0.41	0.22
LBA (0.04 wt% Au)	0.61	0.17
LBA (0.06 wt% Au)	1.54	0.18

Further, the variation of frequency dependent ac conductivity is studied upon heating one of the Au doped samples (LBA with x = 0.06 wt%) and is shown in Fig. 6. The value of power law exponent, *s*, is determined from the computer fitted conductivity data of Fig. 6 by applying Eqn 2. The value is found to increase from 0.02 to 0.73 as the temperature increases from RT to 493 K (Table II), which shows that the ac conductivity is strongly dependent on temperature. The values of dc conductivity at various temperatures are determined from the same computerized

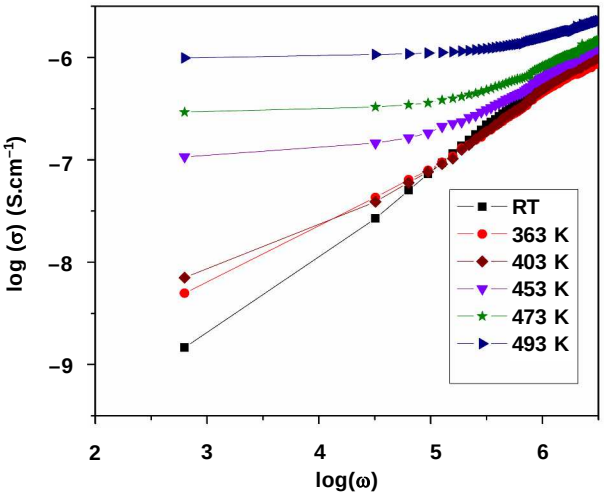

Fig. 6 – AC conductivity of LBA (0.06 wt% Au) at various temperatures

Table II : σ(0) and *s* values obtained for a typical LBA glass containing gold nanoparticles at various temperatures

Sample	Temperature (K)	σ(0) (S.cm^{-1})	s
LBA (0.06 wt% Au)	300 (RT)	5.7×10^{-12}	0.02
	363	3.5×10^{-11}	0.06
	403	6.2×10^{-10}	0.14
	453	9.6×10^{-8}	0.43
	473	2.8×10^{-7}	0.62
	493	1.0×10^{-6}	0.73

fit and found to vary from the order 10^{-12} to 10^{-6} S.cm^{-1}. The mechanism of conductivity may be partially the hopping of small polaron formed by the free electrons that are trapped at partially ionized or quasineutral gold atoms. These traps are present within the interfacial region between the gold nanoparticles and the oxide glass.[17]

Conclusions

Gold nanoparticles have been incorporated in a borated based glass to obtain the "lithium-borate ruby-glass-ceramics". The characteristic ruby colour has been observed in all the glasses without adding any reducing agent and heat-treatment. Presence of gold nanoparticles has been confirmed by studying the optical absorption spectra. XRD analysis of LBA glasses shows the reflection due to the presence of gold. SEM studies show that addition of gold increases the kinetics of growth. ESR studies reveal that the electronic state of gold is either Au^0 or Au^+. The ac conductivity of ionically conducting lithium-borate glass is assisted by the Au atoms and it seems that there is a partial transition from ionic to electronic conduction in the sample due to the presence of partially ionized Au atoms.

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