ORIGINAL RESEARCH PAPER
Volume - 12 | Issue - 03 | March - 2023 | PRINT ISSN No. 2277 - 8179 | DOI : 10.36106/ijsr
INTERNATIONAL JOURNAL OF SCIENTIFIC RESEARCH

IONIC TO ELECTRONIC TRANSITION CONDUCTIVITY STUDIES OF LITHIUM-BORATE RUBY-GLASS-CERAMICS CONTAINING GOLD-NANO-PARTICLES

Physics

Dr. Shivapraksh Y* Dept. of Physics, Government First Grade College, Devanahalli-562110, Karnataka, India. *Corresponding Author

Dr. Satish M Dept. of Physics, Government First Grade College, Doddaballapura-561203, Karnataka, India.

Dr. Dinesh C. M Dept. of Physics, Government First Grade College and PG Center, Chinthamani-563125, Karnataka, India.

ABSTRACT

Glass-ceramics containing Au nanoparticles have been synthesized by selecting the base glass with specific composition 30Li2O–70B2O3 - x HAuCl4.3H2O [LBA] (x=0.01-0.06) all in wt % have been prepared by conventional melt quenching technique. The characteristic ruby color has been observed which is attributed due to the surface plasmon resonance of the Au nanoparticles uniformly embedded in the glass matrix. The imparted red color due to the presence of gold nanoparticles has been confirmed by studying the optical absorption spectra using UV-VIS spectrometer in the visible range (400-1000nm) which show a characteristic absorption peak at ~560nm. In order to check the crystallization/amorphous nature, the samples were powdered and characterized using XRD. The microstructural modifications in the samples due to the addition of Au have been recorded using SEM. Further, the ESR studies reveal that the electronic state of gold is either Au0 or Au+. AC conductivity studies have been performed at RT over a frequency range 100 to 10MHz. 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, surface plasmon resonance, transport properties.

1. INTRODUCTION

The investigations on ruby glasses containing gold nanoparticles or other noble metal nanoparticles has been extensively investigated for the past decades because of their excellent properties such as an ultrafast optical response and large third order non-linear susceptibility [1-3]. These kinds 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 colors. Since the quantum size effects and enhanced surface effects are expected to influence the electronic and optical properties at much smaller particle sizes leads more interest for researchers to fabricate the metal nanoparticles in glasses [5, 6]. Such investigated gold-ruby glasses are mainly used not only for decorative glassware but also for many technological applications in the field of electrical and optical communications. Silicate ruby glasses were synthesized mainly by using $HAuCl_4.3H_2O$ along with 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 needs thermal treatment [9].

In this communication, we report fabrication of gold nanoparticles in borate matrix namely, "lithium-borate ruby-glass" without thermal treatment and addition of any reducing agents. The samples have been characterized using X-ray diffraction, Scanning electron microscopy, Electron spin resonance, Optical absorption and studied the ac conductivity at various temperatures over a wide frequency range 100-10MHz.

2. Experimental

Borate glasses with the composition $30Li_2O–70B_2O_3$ - x $HAuCl_4.3H_2O$ [LBA] (where x=0.01, 0.04 and 0.06 wt %) have been prepared by melt quenching technique. The powders were thoroughly mixed and then melted at 1000°C respectively. The melt was stirred well and kept again in the furnace at the melting temperature for about 10 min. The melt was quenched between two brass plates at room temperature. The quenched glass samples so obtained were found to be ruby-red in color. The deepness of the color was found to be increasing with the 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 (U.K)] and ESR (Expand, Brooker) samples were powered and examined at room temperature. The flat and random pieces of the samples with the thickness ~1mm 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).

3. 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 figure 1. It is clearly seen that the broad absorption peak of each sample centered at 550-580nm [Fig. 1 (b-d)]. 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 figure 1(a). In addition to the peak ~550 nm, there is 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].

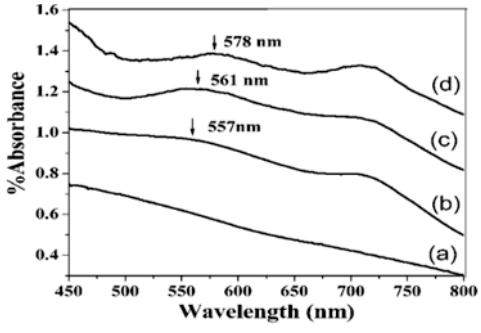

Fig 1. Absorption spectra of LB and LBA samples: (a) Sample without Au, (b) Sample with 0.01 wt% of Au, (c) Sample with 0.04 wt % of Au ,(d) Sample with 0.06 wt% of Au.

X-ray diffraction pattern of LB and LBA are shown in figure 2 in which one can clearly see the sharp peaks at 38.71°, 44.87° and 64.95°. These prominent peaks corresponds to reflections from the planes (111), (200) and (220) of gold respectively [12,13]. The average gold particle size in the LBA sample with 0.06 wt% of gold dopant was calculated using the standard Debye-Scherer 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.

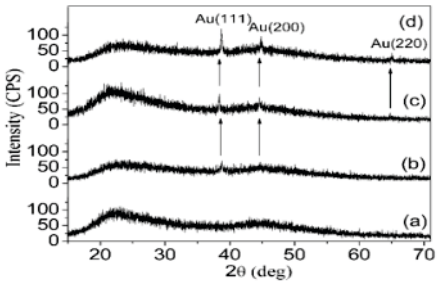

Fig 2. XRD Pattern of LB and LBA samples: (a) Sample without Au, (b) Sample with 0.01 wt% of Au, (c) Sample with 0.04 wt % of Au, (d) Sample with 0.06 wt% of Au.

SEM images of lithium-borate glass series are presented in figure 3 (a-d). One can notice in figure 3(a) that the image of the sample (LB) with 0 % of gold dopant shows homogeneous phase, on the other hand the samples with different concentration of gold dopant (LBA) [Figs 3(b) to 3(d)] clearly show the growth of small particles/crystallites of different size. 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 the growth of particular phase seems to be layered structure in LBA samples and hence the formation of glass-ceramic.

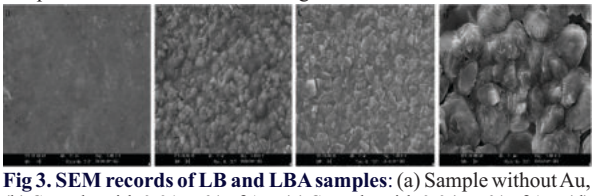

Fig 3. SEM records of LB and LBA samples: (a) Sample without Au, (b) Sample with 0.01 wt% of Au, (c) Sample with 0.04 wt % of Au, (d) Sample with 0.06 wt% of Au.

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 the figure 4. It is clearly seen that there is neither sharp signal nor hyperfine split in the entire spectrum, which is indicating 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 color without reducing agent and heat treatment, the mechanism of Au^+ to Au^0 appears to be complicated [14].

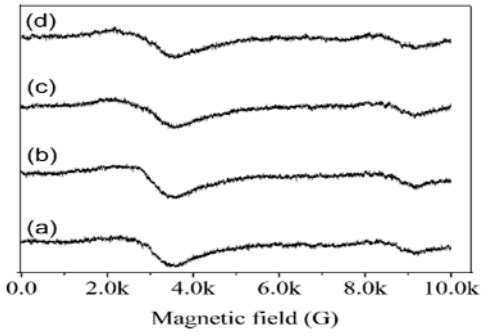

Fig 4. ESR spectrum of LB and LBA samples: (a) Sample without Au, (b) Sample with 0.01 wt% of Au, (c) Sample with 0.04 wt % of Au, (d) Sample with 0.06 wt% of Au.

The ac conductivity of the glasses investigated was found to increase up to ~10^{-6} S/cm 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.

$$\sigma(\omega) = \sigma_o + A\omega^s \quad (2)$$

where σ_o is frequency independent and it is determined as dc conductivity. The power law exponent 's' is obtained from the computer fits on the non-linear curves shown in figure 5 and found to be almost constant and lie between 0.1 to 0.2. The dc conductivity in LB and LBA samples found to be almost same with the increase of the gold concentration. Both the values of 's' and the dc conductivity values obtained from Almond-West type power law fit are listed in Table 1. Since the concentration of Li^+ ions is fixed, one may conclude that the Li^+ ion movement responsible for the observed conductivity may be assisted by the Au particles without dominating over the ionic conductivity at room temperature [17]. Further, the variation of frequency dependent ac conductivity is studied upon heating for one of the Au doped sample (LBA with x = 0.06 wt%) and it is shown in figure 6. Again the values of power law exponent 's' is determined from the computer fitted conductivity data to the Eq.2 shown in the figure 6 and listed in Table 2.

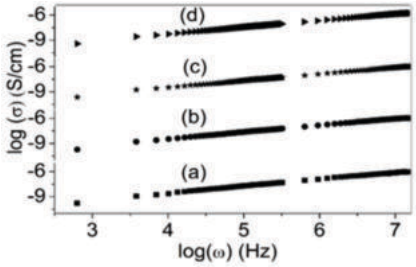

Fig 5. AC conductivity of LB and LBA samples at RT: (a) Sample without Au, (b) Sample with 0.01 wt% of Au, (c) Sample with 0.04 wt % of Au, (d) Sample with 0.06 wt% of Au.

Table 1

Sample	σ_{dc} (S/cm) at RT	s
LB	0.33 x 10^{-8}	0.10
LBA (0.01 wt %)	0.41 x 10^{-8}	0.22
LBA (0.04 wt %)	0.61 x 10^{-8}	0.17
LBA (0.06 wt %)	1.54 x 10^{-8}	0.18

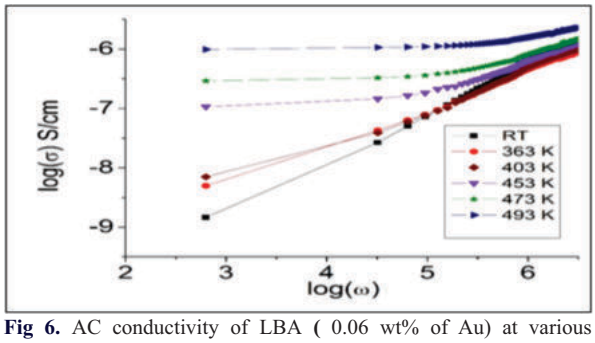

Fig 6. AC conductivity of LBA (0.06 wt% of Au) at various temperatures.

Table 2

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

The 's' value is found to increase from 0.02 to 0.73 as the temperature increase from RT to 493K, 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 fit and found to be varied from the order 10^{-12} to 10^{-6} S. The mechanism of conductivity may partially by the hopping of small polaran formed by the 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 [18].

4. CONCLUSIONS

Gold nanoparticles have been fabricated in a borated based glass to obtain the "lithium-borate ruby-glass-ceramic". The characteristic ruby color 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 the 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 the presence of partially ionized Au atoms.

5. Acknowledgements.
The authors acknowledge and thank the Department of Physics, Indian Institute of Science, Bangalore for providing the experimental facilities (XRD, ESR).

6. Source of Funding:
The authors acknowledge the UGC (COSIST/DRS) for financial assistance for the research work.

7. REFERENCES

[1] R.West, Y. Wang and T. Goodson III, J Phys Chem B 2003;107:3419-26.
[2] Jun Sasia and Kazuyuki Hirao, J App Phy 2001;89(8):4548-53.
[3] N.Venkataram, R. Sai Santosh Kumar, D. Narayana Rao, S.K. Medda, Sucheta De and Goutam de., J Nanoscience and Nanotechnology, 2006;8:1990-94.
[4] Stephan Link and Mostafa A El-Sayed., Rev Phy Chem, 2000;19(3):409-53.
[5] B. Balamurugan and Toshiro Mayuyama, App Phy Lett-5; 87:143105 (11 pp).
[6] S. Haslbeck, K.P. Martinek, L. Stievano and F.E.Wagner, Hyperfine Interact, 2005;165:89-94.
[7] F.E. Wagner, S. Haslbeck, L. Stievano, S.C. Alogero, Q.A. Pankhurst and K.P. Martinek, Nature 2000;407:691-92.
[8] Jongho shin, Kyungsik Hang, Ki-Soo Lim, Ik-Bu Sohn, Young-Chul Noh and Jongmin Lee, Appl Phys A 2008;93:923- 27.
[9] Collen L. Nehl and Jaspn H. Hafner, J Mater Chem 2008;18:2415-19.
[10] Jeremy Vosburgh, Robert H. Doremus, J Non-Cryst Solids. 2004;349:309-14.
[11] Jianqiang Hu, Zhouping Wang and Jinghoung Li, Sensors 2007;7:3299- 311.
[12] Hongbo Liao, Weixinn Lu, Shengwen Yu, Weijja Wen and Georg, K.L.Wang, Opt Soc Am B 2005;22(9):1923-26.
[13] Z. Qu and E. Roduner, J Chem Eng.,2009;4:602-6.
[14] T. Vanngard, S. Akerstrom, Nature 1959;184:183-4.
[15] J.W Orton, ILIFFE BOOKS LTD., LONDON. 1968.
[16] Ahmed Issa, Rajan V Anavekar, Reiner Kuchler, Rolan Bohmer, Otmar Kanert and Himanshu Jain, J Phys Chem. 2009;223:1273-84.
[17] Himanshu Jain, Ahmed Issa, Rajan V. Anavekar, Ronald Bohmer, Otmar Kanert and Reiner Kuchler, App Phy Lett 2009;95:142908(3pp).