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An Investigation of Two Distinct Borate-Based Reddish Ruby Glasses Containing Gold Nanoparticles

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Abstract

Objective: To overcome the limitation seen in the method of synthesis of Gold (Au) Nano Particles (AuNPs) in the ruby glasses by choosing the special binary borate-based glass composition without the need of adding any reducing agents and to produce reddish-ruby color in the glasses containing AuNPs. **Methods:** Two distinct binary borate glass compositions 30BaO-70B_2O_3 and 30Li_2O–70B_2O_3 with $HAuCl_4.3H_2O$ (gold chloride) as a dopant are used to prepare ruby glasses by the melt quenching synthesis method. Without adding any reducing agents and heat treatment, the samples are formed in reddish ruby color containing AuNPs. The samples have been characterized by advanced techniques such as Optical absorption, XRD-analysis, SEM, and ESR analysis. **Findings:** Ruby-reddish color has been observed in both distinct binary borate-based glasses due to the Surface Plasmon Resonance (SPR) of the AuNPs homogeneously embedded in the glass matrix. The deepness of the color increases with the increase of Au dopant concentration. The characteristic absorption peak seen at around ~560nm in the spectral observation of optical absorption studies gives strong evidence for the existence of AuNPs in the prepared glasses. The average gold particles size was found to be around 20-30 nm from the characteristic Bragg's reflection sharp peaks in XRD of lithium-borate. SEM studies confirm that the addition of Au dopant increases the kinetics of growth and crystallization partially in both binary glass samples. The ESR analysis reveals that the electronic state of gold in the glass samples is either Au^0 or Au^+. **Novelty:** For the first time, the investigation of reddish-ruby colored binary borate-based glasses embedded with AuNPs is achieved without the aid of heat treatment and the need to add any reducing agents.

Keywords: XRD; SEM; Gold Nanoparticles; Borate Glass; Optical Absorption; ESR

1 Introduction

Since ancient times, glass has been regarded as a fascinating material due to its distinct physical and chemical properties. Particularly colored glasses find potential usage in more expensive decorative articles due to their retention of transparent properties under visible light. Synthesis of colored glasses with the aid of Metal Nano Particles (MNPs) such as Au, Ag, Pt, Cu, Pd, Re, Zn, Ru, Co, Cd, Al, Ni, and Fe within glass matrix has been investigated over the past decades not only for their potential usages in decorative purpose but also to make use their remarkable characteristic properties such as ultrafast optical response and significant third-order non-linear susceptibility in advanced technological applications [1–3]. Because such glasses are also found to be promising materials for micrometer sized optical circuitry and ultrafast optical switches [4,5]. Thus, even today the fabrication of colored glasses containing MNPs is the most advanced research work in the field of material science with the expectation that quantum size effects and improved surface effects could affect the electrical and optical characteristics at much smaller particle sizes [6–8]. The investigation of a unique ruby glass containing Gold (Au) Nano Particles (AuNPs) is the subject of one such study. In past reports, it has been observed that in the fabrication of typical ruby glasses, gold chloride is used as a dopant along with oxidation reducing agents such as tin-based compounds for instance and then the striking ruby color is achieved by a systematic heat treatment program for several hours [9–12]. However, as per the detailed literature survey, none of the reports presented the investigation of ruby glasses without redox mechanisms and heat-treatment or annealing technique as these procedures are inevitable to agglomerate the AuNPs in the glasses and impart the reddish ruby or crimson red color to the samples. The general observation of this small gap seen in the reported research work may be due to the lack of selection of the appropriate composition of glass formers (SiO_2, BaO, PbO) and glass network modifiers (alkalis and alkaline earth for instance) with whatever the proportions tried to form a specific glass whose network can support for the accommodation of AuNPs without adding reducing agents. This minor limitation is over overcome in the present study by researching two distinct and unique binary borate-based glasses in which the AuNPs are easily synthesized without the need to add any reducing agents and a characteristic reddish-ruby color in the samples is also achieved by avoiding the prolonged traditional heat-treatment on the samples [11,12]. The prepared glass samples have been thoroughly characterized by UV-Visible Optical absorption, X-Ray-Diffraction (XRD), Scanning Electron Microscopy (SEM) and Electron Spin Resonance (ESR) studies to confirm the presence of AuNPs and the microscopic modification in the prepared glass samples series with the increase of gold dopant concentration.

2 Methodology

Two distinct binary glasses with unique compositions, $30BaO\text{-}70B_2O\text{-}xHAuCl_{4.}3H_2O$ [Ba-B-Au] and $30Li_2O–70B_2O_3$ – $xAuCl_3$ [Li-B-Au] [where x = 0.01, 0.04 and 0.06 wt.% is the dopant available in the form $HAuCl_4.3H_2O$ (Auro chloric acid) which is highly hygroscopic in the open atmosphere] have been synthesized by melt-quenching technique [9–12]. In the synthesis process, highly purified chemical powders of analytical grade were thoroughly mixed in porcelain crucibles separately and then heated in the muffle furnace at 850°C for a few minutes till the mixer in the crucible homogenized the melt and then raised the temperature to 1100°C for Ba-B-Au batch of glasses and

1000°C for Li-B-Au batch of glasses. Then both melts were poured on heavy brass blocks and quickly quenched by keeping another heavy brass block at room temperature. This method of quenching is unique compared to other methods of synthesis in terms of rate of cooling as seen in the reports [10–12]. The base glasses without the gold dopant became quite transparent, while the glass samples with the dopant added were found to be reddish ruby in color with no phase separation. The reddish ruby hue was found to be increasing with the increase of dopant concentration in both Ba-B-Au and Li-B-Au glass samples series as shown in Figure 1 and Figure 2. Well-polished shiny flat samples were used for Optical absorption studies using a UV-Vis Spectrometer [Instrument model: USB-2000, Ocean Optics (USA)] to confirm the presence of AuNPs in the samples. The fine powdered form of the prepared samples was used for X-Ray-Diffraction (XRD) [Instrument Model: XPERT PRO, Philips], Scanning Electron Microscopy (SEM) [Instrument Model: 440I, LEO (U.K)] and ESR (Instrument Model: Expand, Brooker) studies at room temperature.

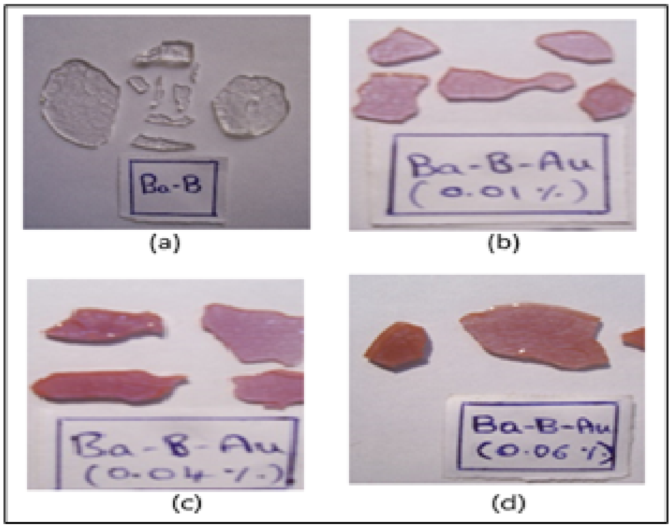

Fig 1. Synthesized glass samples (a) B

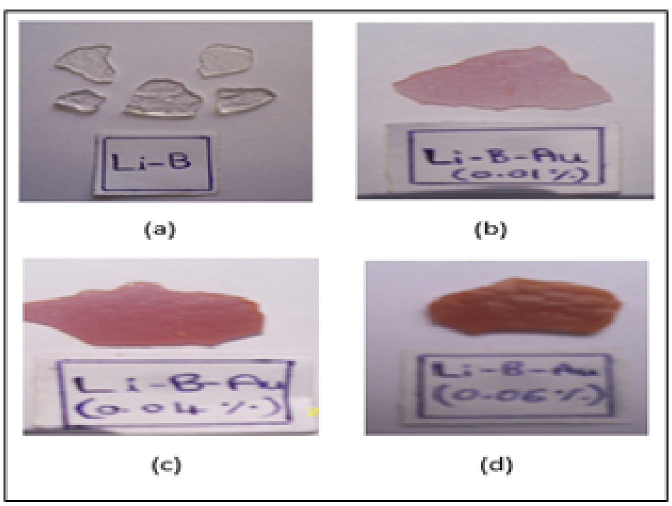

Fig 2. Synthesized glass samples (a) Li-B base glass, (b) Li-B-Au1 ruby glass, (c) Li-B-Au2 ruby glass, (d) Li-B-Au3 ruby glass

3 Results and Discussion

3.1 Optical absorption studies

The optical absorption spectra for the prepared base glasses (Ba-B and Li-B) and the gold doped ruby glasses series (Ba-B-Au and Li-B-Au) are presented in Figures 3 and 4. One can see a clear broad absorption peak at 550-580nm for the Ba-B-Au and Li-B-Au ruby glass samples, but no such peak is observed for the base glasses without gold dopant is the fundamental confirmation of the presence of Au particles in the samples [13]. Creation of such a peak is anticipated and could be attributed to the surface plasmon resonance (SPR) mechanism [13,14]. As explained in the Mie theory, the mechanism of SPR is attributed to the polarization of the free electrons with respect to the heavier ionic core of the AuNPs in the presence of electromagnetic waves in the visible range [15]. Further, Figure 1**(b)**-**(d)** and Figure 2 **(b)**-**(d)** show the gradual shift of the peak position towards the higher wavelength side confirming that the size of the AuNPs in the samples could increase with the increase of gold dopant concentration in both Ba-B-Au and Li-B-Au ruby glasses.

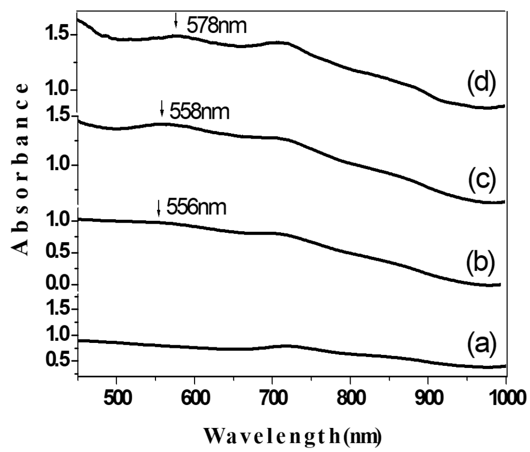

Fig 3. Optical absorption spectra

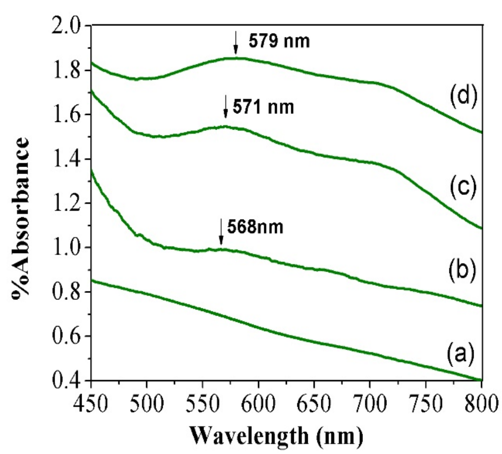

Fig 4. Optical absorption spectra of (a) Li-B base glass sample, (b) Li-B-Au1 glass sample, (c) Li-B-Au2 glass sample, (d) Li-B-Au3 sample

3.2 XRD Analysis

X-ray diffraction graphical pattern of all barium-borate samples presented in Figure 5 shows no sharp peaks indicating that samples retain the amorphous nature even with the presence of gold nanoparticles. This result is attributed to the dominant nature of Ba-B glass network in highly amorphous form and could not give the reflection from the existing gold as well. Whereas in XRD of lithium-borate glasses (Figure 6) shows the prominent Bragg's reflection peaks at 38.71°, 44.87° and 64.95°. These are the standard peaks of the gold formed from the crystal planes (111), (200) and (220) [16,17]. The intensities of these peaks increase with the increase of gold concentration in the samples confirming the gradual crystallization growth in the samples. Hence these glass samples could be considered as partially glass-ceramics also. Using the Deby-Scherer equation, as shown below, the average size of the AuNPs was calculated and found to be approximately 28 nm.

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

where λ is the incident monochromatic wavelength of CuKα radiation, β is the integral breadth of a reflection (Full Width Half Maximum), and θ is the Bragg angle at the peak position. K is the particle shape factor.

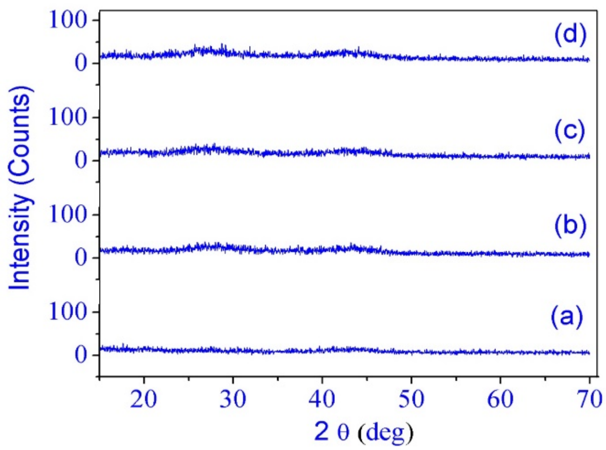

Fig 5. XRD pattern of (a) Ba-B, (b) Ba-B-Au1, (c) Ba-B-Au2, (d) Ba-B-Au3 samples

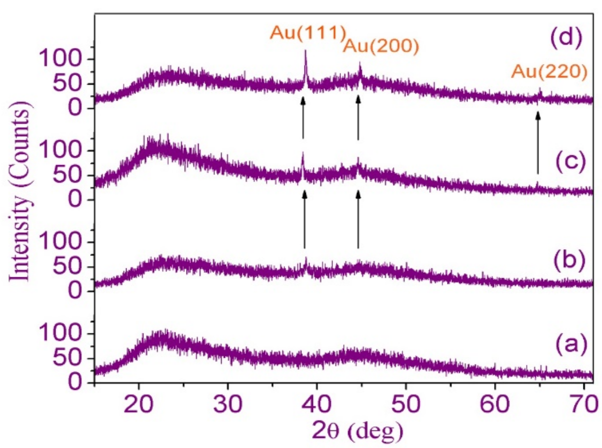

Fig 6. XRD pattern of (a) Li-B, (b) Li-B-Au1, (c) Li-B-Au2, (d) Li-B-Au3 samples

3.3 SEM Analysis

SEM images of barium-borate and lithium-borate glass series are presented in Figure 9 and Figure 10 respectively. One can notice in Figure 5**(a)** and Figure 6**(a)** that the images of both the base glass samples (Ba-B and Li-B) show a clear homogeneous phase with 100% transparency. Figure 9**(b)** to Figure 9**(d)** and Figure 10**(b)** to Figure 10 **(d)** clearly show the growth of small particles/crystallites of different sizes with almost all spherical shaped structures in Ba-B-Au samples and layered structures in Li-B-Au samples. However the embedded AuNPs in such a range could not be realized in any of the SEM images. However, it is evident from the SEM pictures that the amorphous matrix undergoes partial crystallization development upon the addition of gold dopant to the resulting borate glass samples.

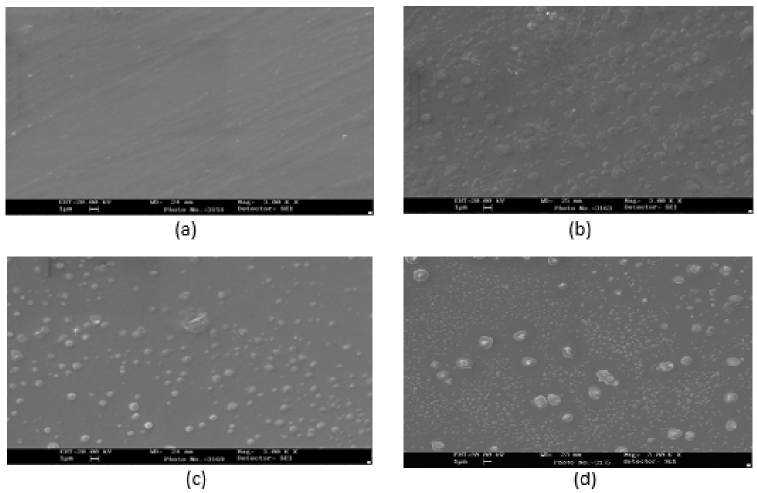

Fig 7. SEM images of (a) Ba-B, (b) Ba-B-Au1, (c) Ba-B-Au2, (d) Ba-B-Au3 samples

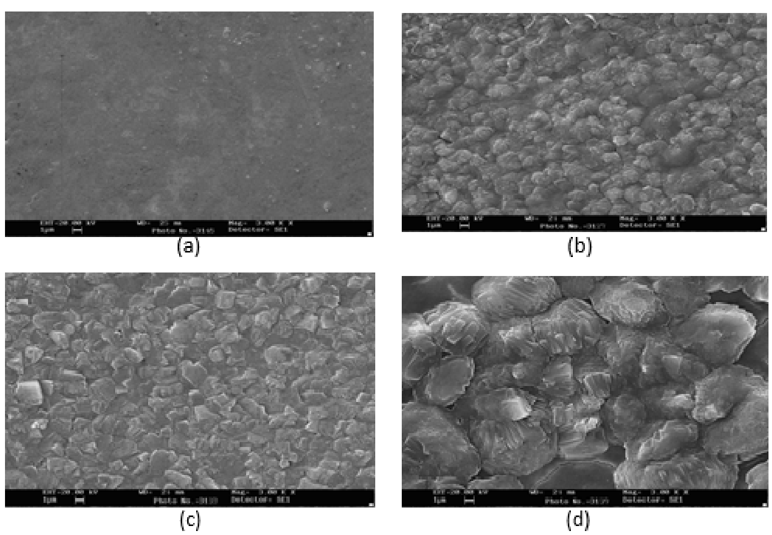

Fig 8. SEM images of (a) Li-B, (b) Li-B-Au1, (c) Li-B-Au2, (d) L-B-Au3 samples

3.4 ESR Analysis

Electron spin resonance (ESR) experiments have been conducted to learn more about the electronic state of the Au in Ba-B-Au and Li-B-Au samples. Figure 9 and Figure 10 display the ESR spectra of every sample that is being studied. The ESR activity and paramagnetic nature of Au^{2+} are well known [18]. Several intriguing complexes can be formed by them. However, for ESR, Au^0 and Au^+ are dormant. It is evident that the entire spectrum lacks both a strong signal and a hyperfine split, indicating that the samples do not contain unpaired electrons or paramagnetic ions. Hence the presence of AuNPs must be either in Au^0 or Au^+ electronic state. As per the traditional way of preparing similar ruby glasses, prior to achieving the ruby hue, gold dissolves in the Au^+ or Au^{+3} form which strong oxidant ion [6,19]. Further, Au^{+3} could be reduced to Au^o with the help of any other metal ions as reducing agents such as Cu or Sn added to the composition. For instance, the reactions taking place are known as redox processes, i.e., $Au^{+3} + 3e^- \rightarrow Au^0$ and $Sn^{+2} \rightarrow Sn^{+4} + 2e^-$, where the overall reaction is $2Au^{+3} + 3Sn^{+2} \rightarrow 2Au^0 + 3Sn^{+4}$[21]. Additionally, the size of the AuNPs could be manipulated to achieve the brilliant ruby red hue under visible light by further heat treatment mechanism [6,18–20]. However the mechanism of Au^+ or Au^0 to agglomerate the AuNPs in the prepared samples appears to be complex in the current investigation, as evidenced by the reddish ruby (crimson) color without the aid of any reducing chemical agent and heat treatment. The long-range order in the binary borate-based glass network may provide sufficient room for the neutral Au atoms to seize in the nanoscale without the requirement of reducing agents, which would then be the cause of the reddish ruby hue [21].

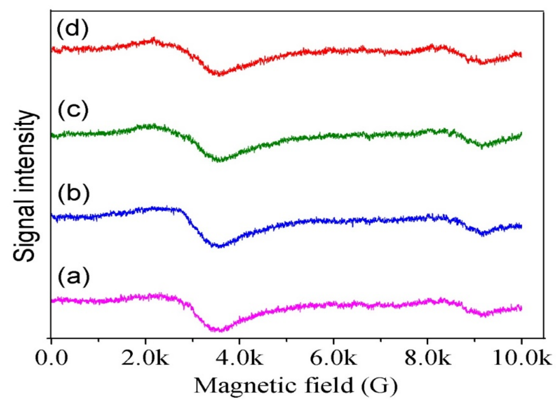

Fig 9. ESR spectra of (a) Ba-B, (b) Ba-B-Au1, (c) Ba-B-Au2, (d) Ba-B-Au3 samples

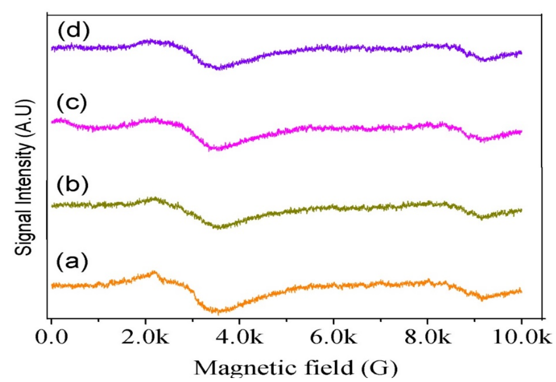

Fig 10. ESR spectra of (a) Li-B, (b) Li-B-Au1, (c) Li-B-Au2 (d) Li-B-Au3 samples

4 Conclusions

Both barium-borate and lithium-borate glass networks have been used to synthesize the AuNPs in the host glass matrix by a simple melt-quenching technique. As anticipated, the base glasses were quite transparent, whereas doped glass samples exhibited a pronounced reddish ruby coloration due to the presence of AuNPs in the amorphous glasses without the need for heat treatment or the use of any reducing agent. This is the simple and novel synthesis route of preparing the ruby glasses in a wide network of borate-based glasses compared to the earlier reports. The presence of AuNPs has been confirmed through the experimental analysis of the optical absorption spectra, in which the distinctive standard peak formed at around 560 nm due to the surface plasmon resonance (SPR) mechanism. Further, XRD and SEM techniques have been used to characterize a morphological change brought about by the addition of gold dopant. The reflection caused by the presence of gold is visible in XRD examinations of Li-B-Au glass samples containing AuNPs. According to SEM studies, adding gold improves growth kinetics. According to ESR characterization studies, the presence of gold atoms is either in the Au^0 or Au^+ electronic states. As per the earlier reports, in the other combination of glasses, the gold dissolves in the form of the Au^+ or Au^{+3} state and hence they need the addition of reducing agents to form the neutral gold atoms (Au^o) to form AuNPs. This redox mechanism is not necessary for the presented binary borate-based glasses as they can provide the required wide network to agglomerate the neutral Au atoms to form AuNPs as such without the need for any reducing agents. These two distinct binary borate-based ruby glasses synthesized in such a simple technique are open for researchers to reproduce and make use of them for further studies on the optical and electronic properties as they find potential applications in the respective fields.

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