

## Refractive Index and Density Properties of Bismuth Sulfide ( $\text{Bi}_2\text{S}_3$ ) Glass Nanocomposite

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### Abstract

We report the synthesis of the  $\text{Bi}_2\text{S}_3$  doped silica glass, growth of semiconductor nanocrystallites which is essentially striking temperature dependent. We also present the change in the density property and the refractive indices variations. It has been observed on thermal treatment, crystal size and distribution of semiconductor nanocrystals. This significant enhancement using these novel  $\text{Bi}_2\text{S}_3$  quantum dot glass nanocomposites is reported in this work. Such quantum dot-glass nanocomposites will have potential applications in optical current sensors and isolators. The present paper is the investigation of quantum dot-glass nanosystems by confining nano bismuth sulfide in designated glass. The  $\text{Bi}_2\text{S}_3$  quantum dots were grown in a special glass matrix, which involved a sequence of steps. X-Ray diffraction pattern confirms the amorphous nature of glass samples. It was found that bismuth oxide  $\text{Bi}_2\text{O}_3$  can improve structural and optical properties of silicate glass and also showed a strong quantum confinement effect. The growth of nanocrystals is well known in glass matrix. Semiconductor micro crystallites grown in the glass matrix impart strong optical nonlinearities to the glass.

**Keywords:** Refractive index, density, bismuth sulfide, doping, nanocrystals, glass.

## INTRODUCTION

During the past decade tremendous efforts has been dedicated to synthesize quantum confined semiconductor nanocrystals or QDs with a large surface to-volume ratio, size-dependent optical properties, arising from the spatial confinement of the electron-hole wave functions with great interest of investigations and versatile applications. Bismuth is quite unique material among the heavy metals and it can be considered as harmless, non-toxic and non-carcinogenic material. It is valuable in electronics application, ceramic production and good element for “warm” superconductors because of the high polarizability of  $\text{Bi}^{3+}$  cations. Previous research reported that silicate and borate glasses contained bismuth (III) oxide demonstrate good radiation shielding properties which can be used as radiation shielding material<sup>1-3</sup>. Bismuth borate glass is of great interest in optoelectronic devices due to its low melting temperature (600–800°C), extensive glass formation range, high refractive index ranging from 1.9 to 2.3, high physical and chemical stability, and nonlinear optical property. Sample of glass can be differentiating by density, but the source of origin of two samples should not same. Doing comparison of density with refractive index limited discrimination may be possible. Different glass samples have different densities because they have different sources of origin. In spite of density is considered as one of the most important and characteristic properties which can be used only for confirming the structure of different types of glass. Density of solids is mostly the simplest physical property that can be measured. Some workers considered that density of the glass is additive and can thus be calculated on the basis of the glass composition<sup>4-7</sup> this is not always true and a number of involved formula was derived to relate the glass density to the glass composition<sup>8-12</sup>. Jen and Kalinowski<sup>13</sup> suggested a model for describing the bridging to non-bridging oxygen ratio as a function of the glass composition and the calculated values of glass density based on this model, were excellent agreement with the experimental values.

## EXPERIMENTAL DETAILS

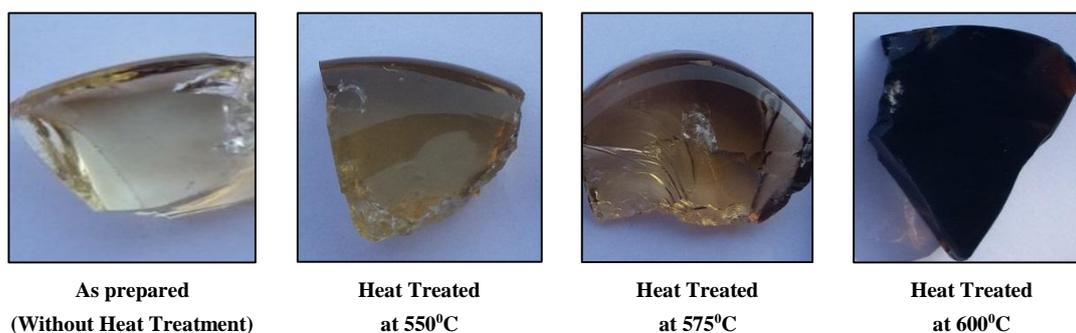
### *Raw Materials*

The  $\text{Bi}_2\text{S}_3$  doped glasses of various compositions were prepared by conventional melt-quench technique using analytical grade compounds  $\text{SiO}_2$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{ZnO}$ ,  $\text{TiO}_2$ ,  $\text{Bi}_2\text{S}_3$  and Starch as starting materials.

### *Glass Preparation*

The new glass composition 54 $\text{SiO}_2$ , 08 $\text{Na}_2\text{O}$ , 04 $\text{MgO}$ , 08 $\text{B}_2\text{O}_3$ , 08 $\text{K}_2\text{O}$ , 12 $\text{ZnO}$ , 06 $\text{TiO}_2$ , 01Starch,  $\text{Bi}_2\text{S}_3$  dopant 0.5-0.8% was used for the study. The different raw materials were weighed as per the above composition and mixed in pestle mortar to obtain homogeneous charge, The amount of semiconductor dopants like  $\text{Bi}_2\text{S}_3$  were selected depending on the type of filter and added into the composition followed by

further mixing. The composition prepared was taken in recrystallized alumina crucible and melted in an electrically heated muffle furnace at 1200-1300 $^{\circ}\text{C}$ . The melt was soaked for the period of 3-4 hrs. After refining, the glass melt was quenched in air on hot brass plate and processed immediately for annealing. The glass was annealed in programmable furnace at its transition temperature ( $T_g$ ) i.e. 470-480 $^{\circ}\text{C}$  and slowly cooled to room temperature to remove the residual stresses. The glass samples were heat treated at 550, 575 and 600 $^{\circ}\text{C}$  for time 6hrs for crystal growth. The glass obtained was polished with emery papers of different grades. The melting of optical quality glasses for optical system is quite difficult because of its high requirement of homogeneity. To achieve good homogeneity, good melting facility is essential. The melting of the semiconductor doped glasses is quite critical than the normal optical glasses. Many compositions have been melted and few of them were optimized. Among the compositions optimized, the composition containing silica content 54% has shown good homogeneity. The same composition has been selected for making glasses. The glass were prepared by following the above method and characterized by various techniques.



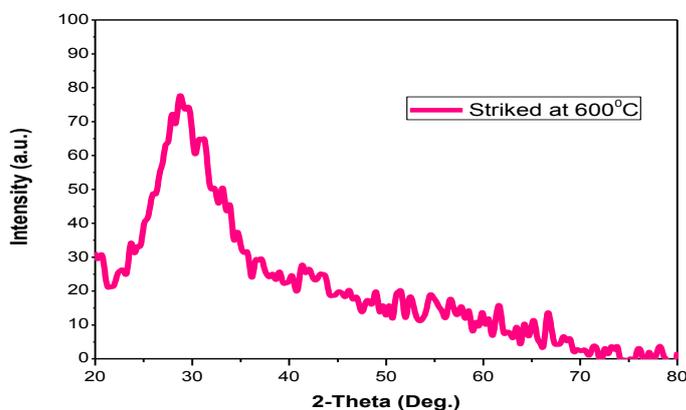
**Figure 1.** Photographs of  $\text{Bi}_2\text{S}_3$  Doped Glass Nanocomposite

### ***Characterization***

Prepared glasses were characterized by X-ray diffraction technique to check for possible crystallinity of glasses. Using X-ray diffractometer (model, Rigaku Miniflex II Desktop) with  $\text{CuK}$  radiation, the XRD patterns were recorded in the  $2\theta$  range 20-80 degree with scanning rate 10/mint. Refractive index is measured by using travelling microscope for all glass samples. Density was measured for all glass samples at room temperature using xylene as the immersion liquid. Density is generally measured by the fluid displacement method depending on Archimedes principle.

## RESULTS AND DISCUSSION

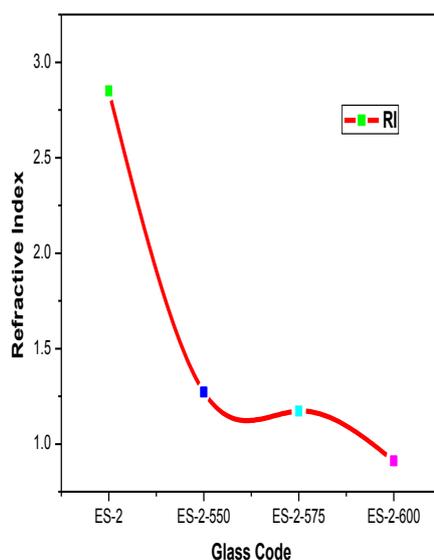
### *X-ray Diffraction Study*



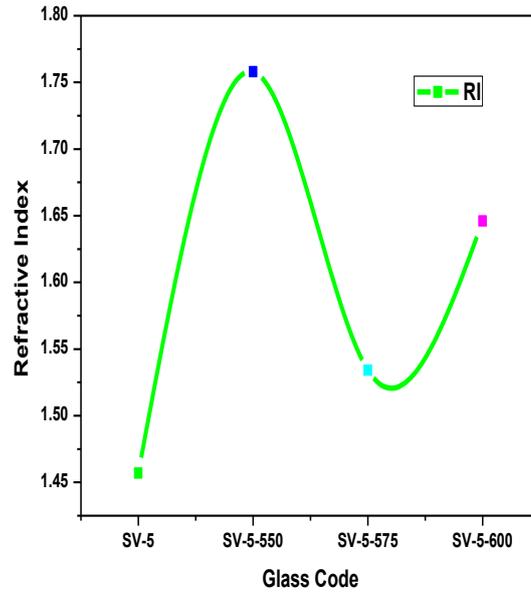
**Figure 1.** XRD pattern of 0.6%  $\text{Bi}_2\text{S}_3$  glass heat treated at  $600^\circ\text{C}$  for 6 hrs

X-ray diffractometry of glass sample of 0.6%  $\text{Bi}_2\text{S}_3$  glasses heat treated at  $600^\circ\text{C}$  for 6 hrs QDs in the matrix as shown in figure 1. X-ray diffraction patterns were obtained using Rigaku Model and Diffraction scans over a range of  $2\theta$  from  $20\text{--}80^\circ$  for the  $\text{Bi}_2\text{S}_3$  dopant glasses. In these glasses, one relatively diffuse peak was observed on a sloping background that is the portion of the broad ‘halo’ characteristic of diffraction of nanocrystals in glass, which implies the nanocrystalline nature of  $\text{Bi}_2\text{S}_3$ . Since silica is a major constituent in the glass, the growth of quartz is quite obvious. This is the clear indication of amorphous nature within the resolution limit of XRD instrument.

### *Refractive Index and Density Measurements*



**Figure 2.** Refractive Index of 0.6%  $\text{Bi}_2\text{S}_3$  Doped Glass Nanocomposite



**Figure 3.** Refractive Index of 0.7%  $\text{Bi}_2\text{S}_3$  Doped Glass Nanocomposite

**Table 1:** Density and Refractive index of 0.6%  $\text{Bi}_2\text{S}_3$  Glass Nanocomposite

Sr. No	Sample Code	Composition X mole %	Thickness of Sample (cm)	Density (g/cc)	Refractive Index (cm)
1	ES-2	0.6	1.091	1.788	2.850
2	ES-2-550 <sup>0</sup> C	0.6	1.350	1.928	1.272
3	ES-2-575 <sup>0</sup> C	0.6	1.172	2.089	1.173
4	ES-2-600 <sup>0</sup> C	0.6	1.024	2.554	0.912

**Table 2:** Density and Refractive index of 0.7%  $\text{Bi}_2\text{S}_3$  Glass Nanocomposite

Sr. No	Sample Code	Composition X mole %	Thickness of Sample (cm)	Density (g/cc)	Refractive Index (cm)
1	SV-5	0.7	1.253	1.544	1.457
2	SV-5-550 <sup>0</sup> C	0.7	1.492	2.331	1.758
3	SV-5-575 <sup>0</sup> C	0.7	1.147	1.985	1.534
4	SV-5-600 <sup>0</sup> C	0.7	1.318	2.293	1.646

Refractive index of the all glass samples heat treated at 550, 575 and 600<sup>0</sup>C at for time 6hrs respectively is obtained by the using travelling microscope method. Here in the table (1 and 2) and graph (2 and 3) shows that the increase in striking temperature the refractive index of the 0.6%  $\text{Bi}_2\text{S}_3$  decreases from 2.850 to 0.912 cm and 0.7%

$\text{Bi}_2\text{S}_3$  doped glasses indices increases from 1.457 to 1.646cm from all the observation shows that increase in  $\text{Bi}_2\text{S}_3$  dopant the refractive index also increases. Refractive index is an important property for optical uses of glass. In the other hand density of glass is one of the simplest physical properties that can be measured. It can be defined as the degree of compactness of a substance/glass structure. Density of 0.6%  $\text{Bi}_2\text{S}_3$  varies from 1.788 to 2.554g/cc and 0.7%  $\text{Bi}_2\text{S}_3$  doped glasses also increases from 1.544 to 2.293g/cc. The increase in density observed is attributed to increase in the rigidity of glass. This is may be due to compactness of glass network formation. Density measurements showed that the density of the composite systems increases by doping and also increases with increasing the size of  $\text{Bi}_2\text{S}_3$  nanoparticles. Fluegelet.al.,<sup>14</sup> reported that the density values increases from 2.354 g/cc and 2.415 g/cc are obtained at 1200°C and 1000°C this value is good agreement with our values. The data obtained for density and refractive index for 0.6%  $\text{Bi}_2\text{S}_3$  and 0.7%  $\text{Bi}_2\text{S}_3$  doped glasses are shown in table 1 and 2. The density was measured by Archimedes method. Density for both glass systems are increased as  $\text{Bi}_2\text{O}_3$  contents increase.

## CONCLUSIONS

In conclusion,  $\text{Bi}_2\text{S}_3$  quantum dots were grown in a special type of 54%  $\text{SiO}_2$  containing multi component glass systems. A uniform distribution of quantum dots and wires in the glass matrix was observed. Structural and optical properties of two different glass systems have been studied. The highest density in bismuth glass nanocomposite is 2.554g/cc for 0.6%  $\text{Bi}_2\text{S}_3$  dopant glass at heat treated 600°C. The density of glass system is dependent on the composition which is the higher the compactness of the structure, the higher the density. Higher refractive index of the preferred glass sample is obtained 0.6%  $\text{Bi}_2\text{S}_3$  2.850cm at unstriked glass sample which is due to present of non-bridging oxygen in glass matrix. Hence, it was found that bismuth oxide  $\text{Bi}_2\text{O}_3$  can improve structural and optical properties of silicate glass and also showed a strong quantum confinement effect.

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