Chapter 5

Growth of Bi$_2$Te$_3$ quantum dots/rods in glass and its Magneto-<br> optical Faraday rotation measurements

5.1 Introduction

Magneto optical material has immense importance in photonics, especially in isolators or optical diodes. In such devices optical isolation is achieved by altering the propagation of light by application of an external magnetic field. The magnitude of Faraday rotation Verdet is governed by a constant which is a characteristic property of the material. Most current devices rely on single crystals to provide a large Verdet constant at an acceptable level of optical attenuation. Today’s benchmark materials are terbium yttrium garnet (TYG) and terbium gallium garnet (TGG) [1, 2]. However, a very preliminary study is reported on porous [3], ionic glasses as well as rare earth doped glasses [4–6]. The design, synthesis, and study of magneto-optic (MO) materials with ferromagnetic [7, 8], dilute magnetic [9] and diamagnetic nanoparticles embedded in diamagnetic host matrices such as polymer [10] and ion exchange resins [11] have been reported previously and have attracted significant interest over the last decade. However, the Verdet constant obtained is much lower than the conventional TYG and TGG. A new class of composite i.e. semiconductor doped glasses also show a tendency of enhancement in magneto optical properties. However, it needs further improvement by tuning the fabrication process.

Preliminary studies on MO effects in semiconductor nanocrystals embedded in glass have been investigated by few investigators [12–18]. The primary focus in this case was on the Faraday effect in metals and semiconductors, due to their potential application in laser sources as Faraday rotators (isolators). Information obtained was useful for elucidation of electronic states, effective masses, and to further the understanding of the theory of solids in a magnetic field. Kratzer and Schroeder [12] measured the Faraday rotation (FR) of plane polarized light from quantum dots of cadmium sulfide, cadmium telluride and cadmium selenides embedded in borosilicate
They have showed that the shift in the electronic transition energy is associated with the increase in the Faraday rotation. Nikitin13 demonstrated the FR effect, showing a strong nonlinearity in semi-magnetic Cd$_{1-x}$Mn$_x$Te nanocrystals embedded in a SiO$_2$ matrix. Neto et al. [14] demonstrated synthesis and magneto optical properties of Cd$_{1-x}$Mn$_x$S. They described the influence of the Mn$^{2+}$ ion localization and quantum confinement on polarization degree. Few reports are available on the Faraday rotation properties of ferromagnetic nanoparticles in a glass matrix [15–17]. Fe$_2$O$_3$/Fe$_3$O$_4$ nanoparticles doped glasses were prepared and magneto optical properties have been investigated. However, very marginal enhancement in Verdet constant was observed. The study of such semiconductors is still at a primary stage and needs some attention. Recently, we demonstrated the magneto-optical Faraday effect with different quantum dot sizes of bismuth sulfide in silicate glasses [18a]. However, the work reported on these bismuth chalcogenides grown in glass was at a very primary stage and needs to be examined for its compatibility and structural effects due to nanophases created in the amorphous matrix. Considering the compatibility of such materials, in the present investigation, we have grown Bi$_2$Te$_3$ quantum dots in a glass matrix successfully for the first time. Surprisingly, we obtained enhanced Verdet constant i.e. comparable to single crystals for the first time.

In this context, our current investigation demonstrates the optical and magneto-optical study of Bi$_2$Te$_3$ quantum dots grown in silicate glasses by a conventional melt and quench method. The nanostructures developed in the glass were characterized using techniques such as HRTEM, UV-Vis NIR spectroscopy, PL spectroscopy etc. The magneto-optical Faraday rotation properties of the glass were investigated with respect to quantum dot sizes. The intention of this work is to investigate the possibility of promoting magneto optical applications of Bi$_2$Te$_3$ nanocrystals in different glasses.

5.2 Experimental Section

As discussed in the Chapter I, for magneto-optical Faraday rotation measurement study, we were used He-Ne laser of wavelength 632.8 nm. Hence, Bi$_2$Te$_3$- glass nanocomposite samples should be transparent at the 632.8 nm (at list 30 %T) and uniform throughout glass sample to avoid the variation of result within same sample.
Considering these requirements, we are tried to synthesize the Bi$_2$Te$_3$ - glass nanocomposite.

In present investigation, the designed composition of the host glass is 52SiO$_2$–6B$_2$O$_3$–10ZnO–12K$_2$O–10Na$_2$O–6MgO–4TiO$_2$ (weight %) with an additional 0.3 – 1 % of Bi$_2$Te$_3$ (weight %). Detailed description of glass composition is given in table I. The composition (100 gm) was mixed thoroughly and melted in an alumina crucible at 1000°C for 30 min. The melt was air quenched by pouring into a brass mould and annealed at 450°C. The glass was then heat-treated at 550–600°C for time periods varying from 1 to 5 hours for the growth of Bi$_2$Te$_3$ QDs of different sizes. This quantum dot –glasses were optically polished and used for further analysis.

Table I: Glass composition and its synthesis parameters.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Glass component material</th>
<th>Source material of component</th>
<th>Weight %</th>
<th>Glass Fabrication parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SiO$_2$</td>
<td>SiO$_2$</td>
<td>52.00</td>
<td>Melting Temperature: 1150°C</td>
</tr>
<tr>
<td>2</td>
<td>Na$_2$O</td>
<td>Na$_2$CO$_3$</td>
<td>10.00</td>
<td>Annealing Temperature: 300°C</td>
</tr>
<tr>
<td>3</td>
<td>MgO</td>
<td>MgO</td>
<td>06.00</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>B$_2$O$_3$</td>
<td>H$_3$BO$_3$</td>
<td>06.00</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>K$_2$O</td>
<td>K$_2$CO$_3$</td>
<td>12.00</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>ZnO</td>
<td>ZnO</td>
<td>10.00</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>TiO$_2$</td>
<td>TiO$_2$</td>
<td>04.00</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Bi$_2$Te$_3$</td>
<td>Bi$_2$Te$_3$</td>
<td>0.3-1 gm</td>
<td></td>
</tr>
</tbody>
</table>

As discussed in chapter III for Bi$_2$S$_3$, in this chapter, we studied three sets of glass depending on the Bi$_2$Te$_3$ concentration in glass. In the first set, the glass
nanosystem (Glass I) was fabricated with 0.3 wt % of bulk Bi$_2$Te$_3$ in above composition (given in table I). The glass composition melted at 1000°C after mixing uniformly and quenched at 450°C with quenching rate 10°C/sec as discussed in Experimental section. After quenching at 450°C, glass was annealed from room temperature with annealing rate 42°C/hr. Glass nanosystem was heat treated at 600°C for 6 hr. For glass nanosystem, it was observed that after heat treatment, there was nominal change in the colour and in the band gap (see figure 5.1 P & Q, Table I). In second set (Glass II), glass nanosystem was prepared using same method used for first set except the concentration of Bi$_2$Te$_3$ i.e. 0.9 wt % instead of 0.3 wt % of Bi$_2$Te$_3$. For Glass II, there was non-uniform grayish colour observed in glass (inset of Figure 5.1C) and transmission edge was slightly shifted toward longer wavelength before heat treatment (Figure 5.1D) due to growth of Bi$_2$S$_3$ quantum dots in glass matrix. The % transmittance of this glass nanosystem was 7.8. The detailed band gap vitiation is shown in table II. The % transmittance at the wavelength 632.8 nm for Glass I was excellent (60 to 75 %) for these glasses but the growth of quantum dots in the matrix is non-uniform and it was clearly shown from inset of figure 5.1 C. It may be due to evaporation of Bi$_2$Te$_3$ or small amount of the Bi$_2$Te$_3$ act as glass former component. For the Glass II, % transmittance is around 7.8 % only and it is below the limit of Faraday rotation measurement. In the third set, glass nanosystem was fabricated using the concentration from 0.5 and 0.7 wt % of Bi$_2$Te$_3$ with same fabrication parameters and methodology. In this case the quantum dots were uniformly distributed in the glass matrix and the % transmittance is good for measurement of magneto optical Faraday rotation. The detailed description of the optical, structural, morphological and magneto optical Faraday rotation study is explained in the upcoming sections.

**Table II: Band gap variation with doping and heat treatment temperature.**

<table>
<thead>
<tr>
<th>Glass</th>
<th>Wt % of Bi$_2$S$_3$</th>
<th>Band gap variation at (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>As prepared glass</td>
</tr>
<tr>
<td>I</td>
<td>0.1</td>
<td>3.01</td>
</tr>
<tr>
<td>II</td>
<td>0.3</td>
<td>2.06</td>
</tr>
</tbody>
</table>
High-resolution scanning transmission electron micrographs (HR-TEM, Technai, 300 kV) were taken to investigate the size and shape of the QDs. Transmission and absorption spectra were recorded between 300–1500nm using a UV/Vis/NIR spectrophotometer (Lambda 950, Perkin Elmer) at room temperature. Photoluminescence of glasses was measured using a photoluminescence spectrometer (LS55, Perkin Elmer). Magneto-optical Faraday rotation of 2 mm thick glass nanosystem was recorded using a phase sensitive detection technique.

Figure 5.1: Photograph (A, C) and transmission spectra (B, D) of the glass as prepared glass and heat treated glass at 600°C doped with 0.1 and 0.3 Wt. % of Bi$_2$S$_3$. 
5.3 Result and Discussions

The quantum dot glass nanosystem was processed at 580°C and 600°C for different heat treatment times and a highly stable Bi$_2$Te$_3$ quantum dot glass nanosystem was obtained. Initially (as prepared), the glass nanosystem was light yellow colored and highly transparent. It was observed that there is a formation of very tiny quantum dots in glass at quenching itself. After heat treatment at 580°C and 600°C for 1-5 hours, the color gradually changed into dark brown due to the growth of the QDs in the glass (see Figure 5.2 and Figure 5.3).

Figure 5.2 Photographs of (A) synthesized host glass (B) as prepared glass, (C, E, F, G) glass heat treated at 580°C in a different time
Figure 5.3: Photographs of (A) synthesized host glass (B) as prepared glass, (C, D, E, G) glass heat treated at 600°C in a different time

5.3.1 XRD studies

Figure 5.4 shows the XRD pattern of the host glass and Bi$_2$Te$_3$ in glass matrix heat treated at 580°C for 3, 4 and 5 hr and heat treated at 600°C for 3 hr. XRD clearly shows peak of (221) plane which is a 100% intensity peak along with characteristic hump of amorphous glass while host glass shows only hump at same position observed in glass containing Bi$_2$Te$_3$ quantum dots and rods (see figure 5.4). From XRD pattern of Bi$_2$Te$_3$ in glass, it was concluded that the Bi$_2$Te$_3$ has hexagonal structure (JCPDS No – 85-0439). Figure 5.4 also shows slight hump from 2θ = 50-70° may be due to the merging of some peaks of Bi$_2$Te$_3$. Generally, it is very difficult to obtain the XRD of Quantum dots embedded in glass matrix because quantum dots are surrounded by dielectric amorphous glass. Another important reason is that the concentration of dopent is very low in present glass nanosystem (0.7 wt % ).
Figure 5.4: XRD pattern of Host glass and the Bi$_2$Te$_3$ in glass matrix heat treated at 580°C (R) for 3 hr (A), 4 hr (B) and 5 hr (C) and 600°C (S) for 3 hr.

5.3.2 TEM analysis

It is also very difficult to obtain TEM image of such glass systems because of above reasons. Transmission of electrons through the dielectric medium (glass) is also quite difficult. However, very thin glass sample (100 nm) can show some images of quantum dots. Considering this problem we have made thin samples and subjected to TEM analysis.

The sizes of the quantum dots were investigated using a Transmission Electron Microscope (TEM). Figure 5.5 represents the TEM images of Bi$_2$Te$_3$ quantum dots / rods for the as prepared (without heat treated) glass nanosystem (Figure 5.6 A) and glass nanosystem heat treated at 580°C for different heat treatment time (Figure 5.6 A-D), respectively. From these images, it is seen that the size of the quantum dots varied from 4 to 14 nm with increase in further heat treatment time.

From the figure 5.6 A, it is quite clear that 4 nm size quantum dots are formed during glass quenching itself. Figure 5.5 and 5.6 B shows the HRTEM image of Bi$_2$Te$_3$ QD -
glass nanosystem obtained at 580°C for 1 hr. It shows that the glass nanosystem consist of 7 nm Bi₂Te₃ quantum dots embedded in the matrix (Figure 5.6 B). There is an augmentation of QD size to ~10 nm when QD – glass nanosystem heat treated at 580°C for 3 hr (Figure 5.6 C). Typical EDS spectra of sample heat treated at 580°C for 3 hr shows the presence of Bismuth and tellurium along with glass composition (See Figure 5.7). Figure 5.6 D shows ~14 nm quantum dots grown in glass matrix after heat treated at 580°C for 4 hr. Inset of Figure 5.6 D reveals the single Bi₂Te₃ quantum dot under high magnification and the inset also shows the FFT pattern. The diffraction pattern obtained is identical with bulk Bi₂Te₃ and exhibit hexagonal structure with a lattice constant of 0.215 nm thereby confirming the formation of Bi₂Te₃ QDs in the glass matrix. On the basis of inter-planar distance, it was confirmed that quantum dots are grown along the direction of <1 1 3> crystal plane. Surprisingly, we obtained quantum rods of Bi₂Te₃ of size 6 X10 nm in glass nanosystem heat treated at 580°C for 5 hr for the first time (displayed with arrows in figure 5.6 E). SAED pattern of these Bi₂Te₃ quantum rods (Figure 5.6 F) in glass nanosystem shows the rings with few bright spots which show the polycrystalline nature of Bi₂Te₃. The d spacing values calculated from the SAED pattern are in good agreement with the JCPDS data of hexagonal Bi₂Te₃ (JCPDS No – 85-0439) and this result consistent with XRD pattern (Figure 5.4). The TEM and ED pattern of the glass nanocomposite heat treated at 600°C for 1hr is shown in figure 4a and b. From figure, we conclude that glass nanocomposite consist of 8 to 10 nm particles which is higher than nanocrystalline size of the Bi₂Te₃ – glass nanocomposite heat treated at 580°C for same heat treatment period i. e. 1 hr. It is due to the increase in heat treatment temperature. The ED pattern of the nanocomposite shows the presence of Bi₂Te₃ nanocrystals in glass matrix.
5.3.3 Growth mechanism

Formation of such quantum rods in glass matrix invites discussion. Generally, the dopants are present in ionic form within the glass. It is proclaimed that the Bi$^{3+}$ and Te$^{2-}$ ions are randomly oriented in the glass melt. During the quenching, some of these Bi$^{3+}$ and Te$^{2-}$ ions come closer and forms Bi$_2$Te$_3$ nuclei. Subsequently, the glass is annealed at near to transition temperature which stabilise Bi$_2$Te$_3$ quantum dots. The further growth of these quantum dots is accelerated by prolonged thermal treatment at further high temperature due to Ostwald ripening [18b]. Further, the tiny quantum dots at prolonged heat treatment (580°C for 5 hr) are self organized in the glass matrix and forms quantum rods of size 6 X 10 nm.
Figure 5.6: TEM image of a single Bi$_2$Te$_3$ quantum dot glass nanosystem A) as prepared, B) treated at 580$^\circ$C for 1 hr, C) treated at 580$^\circ$C for 3 hr, D) treated at 580$^\circ$C for 4 hr and E) treated at 580$^\circ$C for 5 hr. Inset of D shows Fast Fourier Transformation (FFT) pattern (d) of the single QD and magnified image of single QD. F) ED pattern of the QD-glass nanosystem heat treated at 580$^\circ$C for 1 hr. (Scale bar for A, B and E is 20 nm and for C and D is 50 nm. Scale bar for ED pattern is 2.00 nm$^{-1}$)
5.3.4 Optical studies

Figures 5.8 show the % transmittance spectra and corresponding Tauc plots recorded in as prepared and the glass heat-treated at 580 and 600°C. The transmittance spectra was recorded in the wavelength range of 200-1500 nm. The transmission spectrum of host glass is shown in figure 5.8 and it indicates that the band gap of the host glass is about 4.00 eV. There are clear absorption bands in the visible region and their peak positions (2.65 to 1.25 eV for glasses heat treated at 580°C and 2.45 to 1.22eV for glasses heat treated at 600°C) indicate a blue shift in the photon energies compared to the band gap of the bulk material, 0.14 eV (Figure 5.8). Additionally, with increasing heat-treatment time, the peak positions moved to the longer wavelength side (red-shift), indicating the strong quantum confinement effect of Bi$_2$Te$_3$ QDs.

![Figure 5.7: EDS of the Bi$_2$Te$_3$ quantum dots](image)
Figure 5.8: Transmission spectra for host, as prepared glass and glasses heat treated at 580°C for 1, 3, 4, 5 hr (a) and at 600°C for 1, 2, 3, 5 hr (c). Tauc plot are shown in b, c of corresponding optical transmission spectra.

5.3.5 Photoluminescence studies

Photoluminescence spectra of the treated glasses containing Bi$_2$Te$_3$ QDs are shown in figure 5.9 (B). Inset of figure 5.9 (B) shows the photoluminescence spectrum of host glass. Visible luminescence spectra were obtained with the peak centre wavelengths increasing from 584, 600, 603, 610 and 612 nm as the heat-treatment time increased from 1 to 5 hr, respectively. The photoluminescence plots showed a Stokes shift [19, 20] of approximately 175 meV compared to the absorption edge. In addition, the intensities
of the photoluminescence decreased as the duration of the thermal treatment increased owing to the growth of Bi$_2$Te$_3$ quantum dots / rods. Growth of the quantum dots decreases the surface to volume ratio and thereby, increases the quenching of the photoluminescence on the surface of the QDs [21].

Figure 5.9: Photoluminescence spectra for as prepared glass (a) and glass nanosystem i.e. glasses heat treated at 580$^\circ$C for 1 hr (b), 3hr (c), 4hr (d) and 5hr (e). Inset of B is PL spectrum of Host glass.

The average size of Bi$_2$Te$_3$ nanocrystals of the samples was estimated based on their optical absorption spectra from the energy position of the first confinement related maxima, which is clearly revealed in the spectra of treated samples. The first confinement-related peak position in the absorption spectrum $E_1$ is given by

$$E_1 = E_g + \frac{\hbar^2 r^2}{2 \tau} \left( \frac{1}{n_e^2} + \frac{1}{n_h^2} \right), \quad \text{(5.1)}$$
where, $E_g$ is the band gap energy of bulk Bi$_2$Te$_3$ and ‘r’ is average dot size in nm. $m^*e = 0.0821 \, m_0$ and $m^*h = 0.105 \, m_0$ are effective masses of electron and hole, respectively for Bi$_2$Te$_3$. Due to the small value of electron and hole effective mass and large values of dielectric constant, bismuth telluride has a large Bohr radius (57 nm) [22].

Scheme 1. Schematic illustration of growth process of Bi$_2$Te$_3$ quantum dot / rods in glass matrix with heat treatment time

From equation (5.1), we obtained the average quantum dot size about 5 to 10 nm for glasses treated at 580$^\circ$C for 1-5 hr. The results of nanocrystals with average size assessment based on the absorption data are in good agreement with TEM data of glass treated at 580$^\circ$C for 4 hr.

5.3.6 Magneto-Optical Studies

In the present study, Faraday rotation was measured for the Bi$_2$Te$_3$ nanosystems at room temperature. These glass nanosystems were studied under magnetic fields ranging from 2 to 5.6 mT, with a helium-neon laser (632.8nm). The Faraday rotation angles
were calculated from the following equation,

$$\theta_f = \frac{\Delta I}{2I_0}$$

(5.2)

where $\Delta I$ is the relative change in light intensity due to the external applied magnetic field and $I_0$ is the incident intensity with the blank sample.

The quantum dot-glass nanosystems demonstrated FR with quantum confinement effects for applied external magnetic fields. Due to the slight crystallization during quenching of the bismuth telluride in glass, the Faraday rotation and Verdet constants for the as prepared quantum dot–glass samples were observed to be much greater than those for host glass. Figure 5.10 A and 5.11 A shows the linear variation of Faraday rotation with respect to quantum dot size and with magnetic field ranging from 2-5.6mT. The detailed explanation of dot size (optical band gap) and Verdet constant for the samples and host is given in Table I. There is a significant enhancement of Faraday rotation in Bi$_2$Te$_3$ quantum dot glass nanosystem with respect to host glass (Table I). An untreated glass nanosystem with Bi$_2$Te$_3$ quantum dot having 3.1 eV band gap (i.e. glass nanosystem) showed high Verdet constant (77.35 deg/T-cm) which is 70 times higher than the host glass (1.10 deg/T-cm). The Verdet constant of glass nanosystems heat treated at 580°C as well as at 600°C decreases drastically with heat treatment time (Figure 5.10 B and 5.11 B) leading to an inference that the Verdet constant of the glass nanosystem decreases with increase in size of Bi$_2$Te$_3$ quantum dots. Table 1 and 2 shows the detailed description of variation of Verdet constant with dot size. Host glass (Eg= 3.95 eV) shows the lowest Verdet constant. As prepared glass nanosystem having quantum dot size of 3-5nm showed the Verdet constant about the 77.35 deg/T-cm. It is noteworthy that Verdet constant obtained for these glasses is nearly equivalent to that the reported by TGG (Terbium Gallium Garnet) single crystals [23]. The enhancement is due to the presence of tiny nuclei in Bi$_2$Te$_3$ doped glass matrix. Verdet constant of the glass heat treated at 580 and 600°C for 1 hr was 23.35 degree /T-cm and 18.25 degree /T-cm, respectively. At the same temperatures, when the glass was heat treated for 3 hours, the Verdet constant dropped to 6.80 degree/T-cm and 5.1 degree /T-cm, respectively. Similarly, for the glass treating time of 5 hrs, the Faraday rotation angle (Verdet constant) decreased to 3.10 and 29.2 mdeg (6.25 degree /T-cm and 51.8 degree
\( \theta_F = \frac{\text{const}}{n_0} \left\{ \frac{1}{(\omega_g + \omega)} - \frac{1}{(\omega_g - \omega)} \right\} + \frac{\Delta}{\nu} \left[ \sqrt{\omega_g} - \sqrt{\omega} \right] \left[ \sqrt{(\omega_g - \omega)} - \sqrt{(\omega_g + \omega)} \right] \right\} \tag{5.3} 

Table I: Verdet constant and band gap energy.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Glass sample</th>
<th>(E_g) (eV)</th>
<th>QD size (nm)</th>
<th>F.R. at 5.6 mT (mdeg.)</th>
<th>V (degree/T-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Host</td>
<td>3.62</td>
<td>--</td>
<td>1.67</td>
<td>1.10</td>
</tr>
<tr>
<td>2</td>
<td>As prepared</td>
<td>3.12</td>
<td>4</td>
<td>33.58</td>
<td>77.35</td>
</tr>
<tr>
<td>3</td>
<td>Heat treated at 580°C for 1 hr</td>
<td>2.93</td>
<td>7</td>
<td>8.40</td>
<td>23.35</td>
</tr>
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<td>4</td>
<td>Heat treated at 580°C for 3 hr</td>
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<td>10</td>
<td>3.65</td>
<td>6.8</td>
</tr>
<tr>
<td>5</td>
<td>Heat treated at 580°C for 4 hr</td>
<td>2.69</td>
<td>14</td>
<td>2.06</td>
<td>4.35</td>
</tr>
<tr>
<td>6</td>
<td>Heat treated at 580°C for 5 hr</td>
<td>2.49</td>
<td>Nano rod Dia 6 nm Length 10 nm</td>
<td>3.10</td>
<td>6.25</td>
</tr>
<tr>
<td>7</td>
<td>Heat treated at 600°C for 1 hr</td>
<td>2.65</td>
<td></td>
<td>0.010</td>
<td>18.25</td>
</tr>
<tr>
<td>8</td>
<td>Heat treated at 600°C for 3 hr</td>
<td>1.96</td>
<td></td>
<td>0.038</td>
<td>5.10</td>
</tr>
<tr>
<td>9</td>
<td>Heat treated at 600°C for 5 hr</td>
<td>1.87</td>
<td></td>
<td>0.010</td>
<td>23.60</td>
</tr>
<tr>
<td>10</td>
<td>Heat treated at 600°C for 5 hr</td>
<td>1.27</td>
<td></td>
<td>0.025</td>
<td>51.80</td>
</tr>
</tbody>
</table>

\(E_g\): Band gap, F.R. Faraday Rotation, V: Verdet constant

Regarding the magneto-optical sensitivity with respect to the size of Bi\(_2\)Te\(_3\) nanoparticles in a silicate matrix invite discussions.

The Faraday effect arises due to different indices of refraction for the right and the left circularly polarized light (\(n_+\) and \(n_\)). The Classical equation of motion of a valence
electron in the magnetic field is given as [25],

\[ n_{\pm} = \sqrt{1 - \frac{n_e \varepsilon_0}{(\omega^2 - \omega_0^2) n_e \varepsilon_0 \omega_0}} \quad (5.4) \]

where \( N \) is total valence electrons, \( e \) is an electronic charge, \( m_e \) is the mass of the electron, \( \varepsilon_0 \) is the dielectric constant, \( \omega \) is an operating frequency, with \( \kappa \) being the spring constant to a fixed atomic site, and \( \omega_c \) is a cyclotron frequency. Equation 5.4 shows that left and right circular refractive indices are influenced by the cyclotron frequency and therefore, by the magnetic field. In terms of quantum mechanics, \( n_{\pm} \) are dependent upon transitions between polarization states and their differing energy levels (Scheme 2). Interaction of a photon with the right circular polarization can cause electrons in spin-down (-1/2) states to make the transition to spin up (+1/2) states. Similarly, the left-circular polarization can cause electronic states transitions from (-1/2) states to (+1/2) states. Superposition of these effects of electronic transitions gives the Faraday effect. In quantum dots, infinite potential wells cause excitons and electrons to experience confinement energies as the quantum dot size reduces. A strong confinement influences the exchange interaction of electrons and holes, which mixes different electron and hole spin states causing modifications in the Verdet constant. Hence, the higher Verdet constant obtained for nanosystem having very small quantum dot size is quite explicable.

The large Faraday Effect might be attributed to their characteristic spin structure of quantum dots in any matrix. Y. Hasegawa et al showed that effective magneto-optical properties of Eu1-xSe nanoparticles are due to the ferromagnetic phase of Eu (II) ions on the surface [26]. In our case, the Bi\(_2\)Te\(_3\) doped glass nanosystem is ferromagnetic at room temperature as discussed in supporting information (S3). The ferromagnetism in the Bi\(_2\)Te\(_3\) is introduced due to the spin polarization of p electrons of Bi and Te [27]. We expect that effective magneto-optical properties of Bi\(_2\)Te\(_3\) nanoparticles are largely dominated by the special ferromagnetic phase of Bi (III) ions on the surface.
The enhancement in the Faraday rotation angle is possibly realized when the nanocrystals of semiconductor are embedded in a transparent thin film or embedded in transparent material such as glass. In the strong confinement region ($r < \text{Bohr radius}_{\text{B}}$), the oscillation strength is expected to increase with $1/r^3$ because of the strong overlapping of the wave function of the confined electron and hole. For spherical nanoparticles this can be expressed as $\frac{f}{f_{\text{ex}}} = \frac{3}{4} \left( \frac{\hbar}{r} \right)^3$ where, $f_{\text{ex}}$ is the oscillator strength of the 1st exciton in bulk material per unit volume and $f$ is the oscillation strength of $j^{\text{th}}$ level per unit volume. Because the quantum confinement effect in a nanocrystalline semiconductor leads to an increase of oscillator strength and it is well reported that the enhancement of Faraday effect is due to the increment of oscillator strength of nanocrystals in composite material itself [7, 26, 29]. In addition, the dielectric constant of matrix in the composite inevitably influences the...
Faraday rotation angle obtained for the composite material [30].

Recently, some reports showed that the surface anisotropy dominates the magneto-dynamics in the magnetic nanoparticles [31]. The surface area of the particle increases with decreasing the size of quantum dots. It is well known that the surface-to-volume ratio is strongly modified by the particle size variation. It is likely that smaller nanoparticles with higher surface-to-volume ratio exhibit much larger proportion of non-compensated surface spins on the antiferromagnetic core and thus reveal higher magnetization values than those of larger nanoparticles [32].

TEM analysis of the silicate - Bi$_2$Te$_3$ system showed the increment of the QD size i.e. the lowering of surface atoms. This surface-modification effect of the Bi$_2$Te$_3$ nanoparticles is considered to be an additional factor resulting in a large Faraday effect in the silicate - Bi$_2$Te$_3$ system. In our case, the Verdet constant is higher for as prepared glass nanosystem due to the very tiny nanocrystals (quantum dot of size $\sim$ 4 nm). With an increase in the heat treatment time, the size of the quantum dots varies drastically with decreasing the surface-to-volume ratio and hence the magnetization and Verdet constant also decreases. Measurements of size-dependent Verdet constant and magnetism, however, have not been reported yet for Bi$_2$Te$_3$ quantum dots as well as in quantum dot embedded glasses.
Figure 5.10: (A) the variation of Faraday rotation with magnetic field and heat treatment time and (B) Verdet constant with band gap energy.
Figure 5.11: (A) the variation of Faraday rotation with magnetic field and heat treatment time and (B) Verdet constant with band gap energy.
5.4 Conclusions

$\text{Bi}_2\text{Te}_3$ quantum dots were grown in specially customized multi component glasses containing 52-53% $\text{SiO}_2$ for the first time. A uniform distribution of quantum dots and rods was observed in the glass matrix. Increase in $\text{Bi}_2\text{Te}_3$ quantum dot sizes with increase in heat treatment temperature was demonstrated using structural, morphological and optical studies, which also showed strong quantum confinement. A nonlinear magneto-optical response was observed with the quantum dot /rod size in glasses. The highest Verdet constant (77.35 degree/T-cm) was measured for the glass nanosystem containing ~4 nm $\text{Bi}_2\text{Te}_3$ quantum dots, which showed 70 fold enhancements with respect to host glass. It is noteworthy that the Verdet constant obtained is comparable to the reported conventional TGG single crystal. The Verdet constant for 14 nm quantum dots containing glass nanosystem was observed to be 6.25 deg/T-cm, which is 6 times higher than the host glass. This enhancement in Verdet constant with a decrease in quantum dot size can be attributed to the increased confinement of interatomic particles of the quantum dots grown in a glass matrix. Such quantum dot-glass nanosystems will have potential applications in optical current sensors, Isolators and thermo-electric devices. Interestingly, present quantum dot glass nanosystem can be transformed into fibres very easily, which will have an exceptionally high impact on the fabrication of high performance magneto optics devices.
References


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