

Full Length Research Paper

A study of structural, optical and dielectric properties of Eu_2O_3 doped borate glass

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Recent technological applications have generated more interest in the studies of different types of glasses. The wide applications of glasses take place due to their interesting properties such as low thermal expansion, high softening temperature, high resistance to chemical attack, high refractive index with low dispersion and mechanical strength. Eu_2O_3 doped borate glasses were successfully synthesized by melt quenching method. The X-ray diffraction (XRD) spectra revealed that these glasses had amorphous nature. Optical properties of prepared samples were characterized by photoluminescence studies. The dielectric properties of glass samples were studied for different frequencies and different temperatures.

Key words: Glass, melt quenching method, europium oxide, X-ray diffraction (XRD), photoluminescence and dielectric studies.

INTRODUCTION

The rare earth (RE) doped borate glasses are among those materials which have a number of optics and photonics applications (Marimuthu et al., 2009). Borate based glasses are the best choice, which more clearly show the relationship between glass structure and optical properties of RE ions (Hai et al., 2005). An interesting characteristic of the borate glass is the appearance of variations in its structural properties when RE cations is introduced. Borate glass is a suitable optical material for RE ions with high transparency, low melting point, high thermal stability, good RE ion solubility (Hai et al., 2005); Deva and Madhukar, 2012) and shows more clear relationship between glass structure and physical

properties. When rare earth elements are added to a glass matrix as dopant, a change in its electronic energy level structure is induced and also its absorption characteristics get modified. Among these the Borate glasses exhibit a more complex action of alkali ions than the silicate glasses and have Boric acid as the major component. The promising characteristic of borate is to produce the materials with small coefficient of thermal expansion and make it superior in glass industry to the silicate glasses. Also Boric acid is used in the manufacture of special type of fiberglass as it prevents devitrification in glass production, increases the durability and can be used as a heterogeneous catalyst (Sakashita

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and Shimoda, 1991). Boric acid improves glass melting besides enhancing the glass properties. Addition of Boric acid can increase the refractive index of glass. Due to the presence of alkali ions, Boric acid can dissolve uniformly in simulated physiological liquids at normal temperature. But with the addition of other cations in small amount, the dissolution becomes non uniform and it is likely that a new compound is obtained. For example, by adding Yttrium oxide as one of the components, it modifies the structure of glass and makes it resistant to heat or chemical attack. In this non-silicate glass composition, Boric acid acts as network former and lithium carbonate plays the role as a modifier. Lithium carbonate here helps to lower the melting point. It has to be emphasized that recent studies have focused on Borate glasses due to their remarkable properties like low melting temperature, thermal stability and radiation, which make it more advantageous in communication field. Even though by nature borates are easily crystallized and fairly stable, by adding some reagents like rare earth elements, they can overcome the demerits and improve their optical characteristics. Europium doped glasses belong to an important class of materials because they can be employed in a variety of applications such as two-dimensional x-ray imaging sensors, high-density memory devices, blue emitting phosphors for plasma display panels, and x-ray storage (Aitasalo et al., 2003; Qiu et al., 1997). Divalent Europium doped materials find applications as luminescent sources in the UV to blue-green region of the electromagnetic spectrum, as well as sensor devices, because the divalent Eu emission intensity is strongly dependent on the temperature (Shelby, 1994). On the other hand, the trivalent Eu doped materials present optical properties of interest in the orange-red region. The advantage of using glasses as hosts for such dopants in relation to crystals lies in their homogeneity and ease of fabrication into various shapes, such as flat boards, fibers, and rods. In this paper, the structural, optical, and dielectric properties of Eu_2O_3 doped borate glass system have been presented.

EXPERIMENTAL PROCEDURE

In order to substantiate the study and compare how the addition of rare elements can change glass structure and its characteristics, the common technique of melt quenching was followed. It is based on the principle of melting the oxide so as to reduce the temperature suddenly below the transition temperature. For the purpose of comparison, two samples were prepared using the melt quenching method. In the first sample (Sample 1), Alkaline earth borate glasses of composition $60.5 \text{ H}_3\text{BO}_3 + x\text{ZnO} + x\text{Li}_2\text{CO}_3 + x\text{Sr}_2\text{O}_3 + x_1\text{Y}_2\text{O}_3$ were bought (x in molecular % ranging from 10 to 50 and x_1 in molecular % of 0.01) from Aldrich 99.995% pure. Next the required quantities were thoroughly mixed together with a constant proportion and finely ground using mortar and pestle for 10 min. After this the ground raw materials were placed in a silica crucible and kept in the electronic furnace to melt the mixture under nearly 1150°C , with the continuous examination over a time of 3 h. After 3 h, the melted sample was transported to another furnace with

temperature below 400°C in order to prevent breakage during the processing and placed for 3 h. This process is called annealing. After this annealing process, the sample was gradually cooled at the room temperature. The second sample (Sample 2) was also prepared following the same procedure but with the addition of 0.5% of Europium oxide in the composition as a dopant. Finally, the samples were polished for further characterization.

RESULTS AND DISCUSSION

XRD characterization

The XRD pattern of the samples was recorded by using a powder X-ray diffractometer (Schimadzu model: XRD 6000 using $\text{CuK}\alpha$ radiation, $\lambda=0.154 \text{ nm}$), with a diffraction angle between 20° and 0° . Figure 1 show the characteristic X-ray diffraction spectra of the glass samples. The spectra of each glass sample contain a broad bump located at 2θ value 21.005° and 'd' spacing 4.22595 \AA for both the samples and no sharp lines are observed in the spectra which suggest that all the prepared glass samples confirm the amorphous (glassy) nature.

Optical characterization

The optical properties of the samples were studied by means of photoluminescence characterization. The fluorescent emission and absorption were performed with time correlated single photon counting instrument (purchased from Horiba Jobin Yvon, New Jersey). The xenon arc lamp was used as an excitation source at 450 Watt Power. The entire system consisted of two separate excitation and emission monochromators and detectors with red sensitive photomultiplier tube (R928p). The Luminescence spectra for samples under excitation at 260 nm were recorded. The photoluminescence studies revealed that by increasing the concentration of Eu^{3+} , the spectrum gradually shifted from red to near UV region. The position of the excitation purely depended on Eu^{3+} concentration in glass. The emission and excitation spectra of the divalent Eu ions mainly contained two types of electronic transitions, $4f-5d$ transition for high energy region and weak $4f-4f$ transition at low energies.

The excitation spectra for the samples recorded from 240 to 420 nm at an emission wavelength of 260 nm are shown in Figure 2. The excitation spectra for sample 2 consisted of several bands of wavelength 250, 320, 352, and 415 nm. The excitation spectra of Eu^{3+} were monitored at ${}^5\text{D}_0-{}^7\text{F}_2$ transitions with a sharp peak at 262 nm. At the same time in sample 1 excitation bands appeared at 261, 343, and 350 nm. From the study it could be concluded that on the addition of dopants to sample1, the excitation wavelength slightly changed. Depending on the type of host material, the optical properties vary. Several emission bands were observed

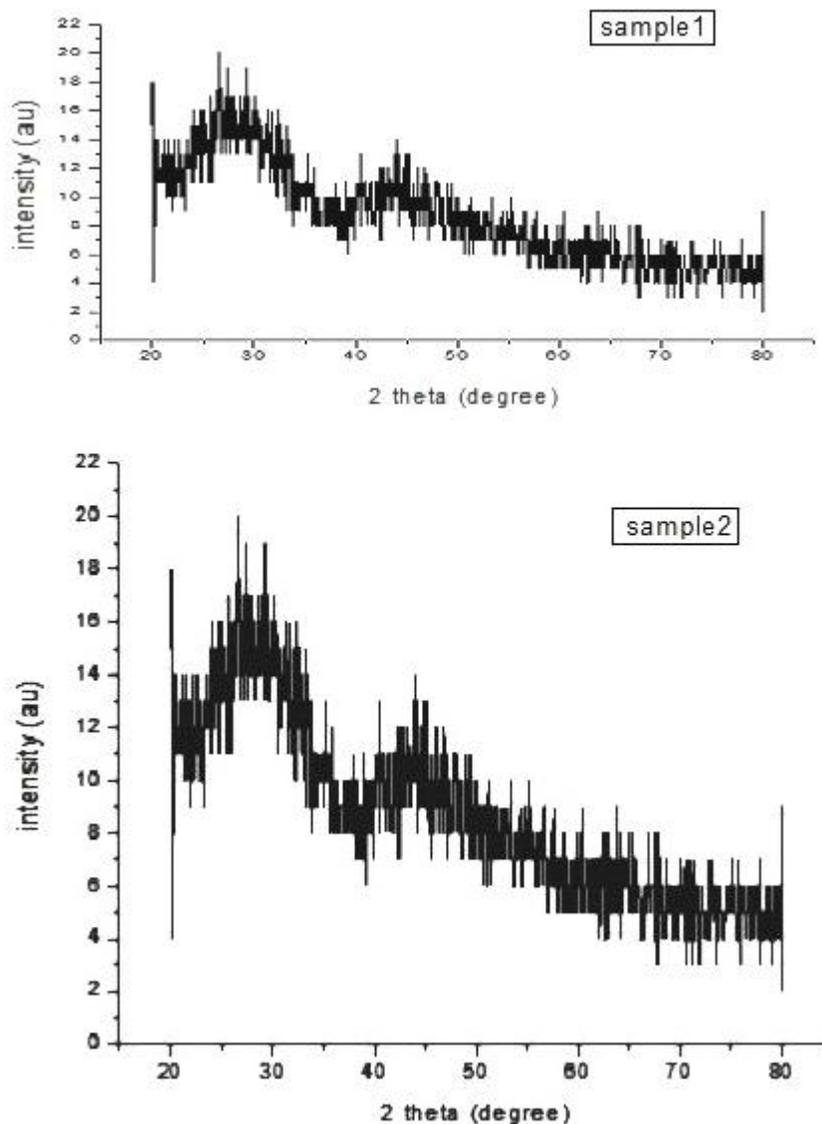


Figure 1. XRD pattern of sample 1(pure) and sample 2 (doped).

as shown in Figure 4. The excitation spectra show the characteristic features of Eu^{3+} excitation without any spectral shift in all samples under 613 nm emission. Swapna et al. (2015) reported that among all excitations in Eu^{3+} high intense emission peaks were observed at 364, 383, 395, 413, 467, 528, and 532 nm with the corresponding transitions being ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4, {}^2\text{G}_5, {}^5\text{L}_6, {}^5\text{D}_3, {}^5\text{D}_2, {}^7\text{F}_1 \rightarrow {}^5\text{D}_1$ transitions of Eu^{3+} (Swapna et al., 2015). In the present study, the observed emission spectra of Eu^{3+} showed excitation peaks at 391, 412, 436, and 452 nm (Figure 2 and 3). In general Eu^{3+} characteristics emission lay between 540 and 780 nm. But in the emission spectra of Eu^{3+} , among all bands, band near 436 nm showed a sharper peak than the other bands in the glass. The sharper the emission wavelength, the more intense the emission will be. It suggests that the

glass provides more intensity at 436 nm. The emission spectra of sample 1 consisted of peaks at 388, 413, 437, and 453 nm wavelengths as shown in Figure 3. On the addition of dopant like Europium oxide, the peak positions slightly changed.

In this case, the intrinsic excitation bands of Eu^{3+} were placed near UV spectral range (~ 360 nm to 420 nm). From the graph, it is clear the highest peak value of Eu_2O_3 is 436 nm. The Parity-forbidden nature of Eu^{3+} absorption results only in low absorption cross-section. Yang et al. (2004) reported that the emission spectra of the different morphologies of Eu^{3+} sample exhibited orange and red emission, where the luminescence intensity of orange was approximately equal to red emission (Yang et al., 2004). The orange and red light emissions were associated with transitions of ${}^5\text{D}_0 \rightarrow {}^5\text{F}_1$

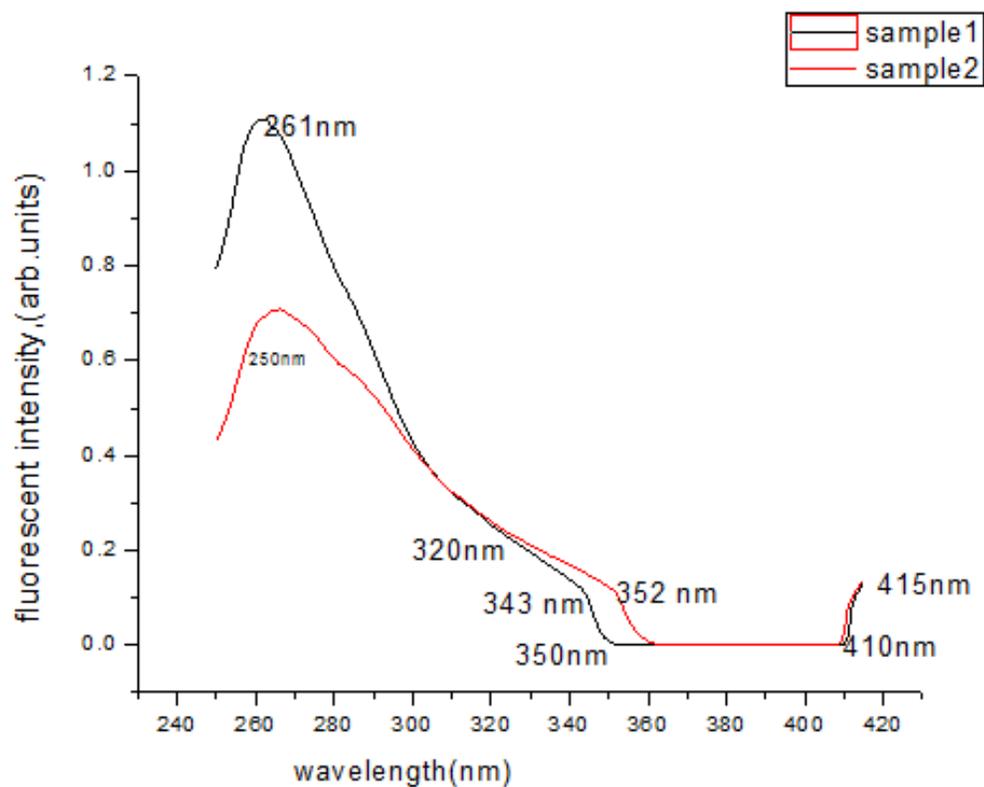


Figure 2. Excitation spectra for sample 1 and sample 2.

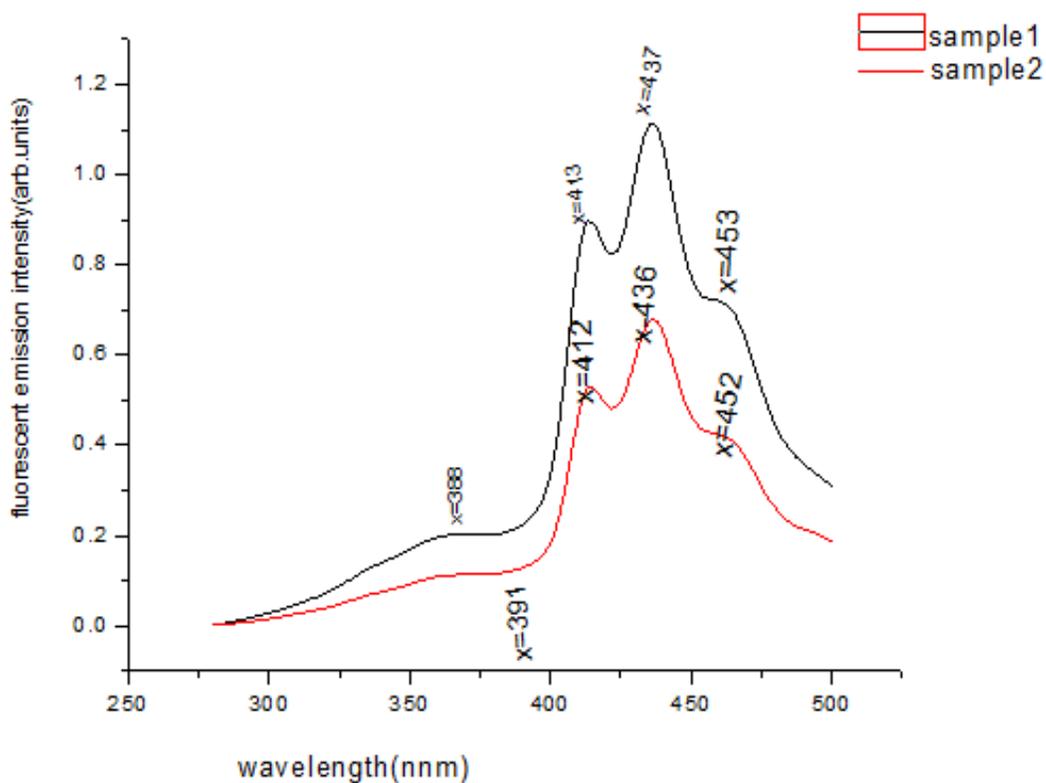


Figure 3. Emission spectra for sample 1 and sample 2.

and ${}^5D_0 \rightarrow {}^5F_2$ respectively. The present work suggests that the excitation spectra arises from the transition of ${}^5D_2 \rightarrow {}^5F_0$ and also agrees with the studies done by Lourenc-o et al. (2011). It confirms the feasibility of using this glass for UV green LED excitation.

Dielectric properties

The dielectric constant and the dielectric loss of the glass samples were studied at different temperatures using a HIOKI 3532-50 LCR HITESTER in the frequency range of 50 Hz to 5 MHz. The dielectric constant of a material may be defined as the ratio of the field strength in vacuum to that in the material for the same distribution of charge. The dielectric constant of a substance is a property of the constituent ions. The dielectric constant or relative permittivity can be defined as:

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} \quad (1)$$

We know that

$$\epsilon = \frac{Cd}{A} \quad (2)$$

Thus, we have

$$C = \epsilon_r \epsilon_0 A / d \quad (3)$$

Where A is the area of the sample and d is the thickness of the sample. The relative permittivity (ϵ_r) is usually known as dielectric constant. It is always greater than unity. Suppose a parallel plate condenser has a capacitance of C_0 in air; then its capacitance, when the space between the plates is filled by a medium of dielectric constant (ϵ_r), is given by:

$$C = C_0 \epsilon_r$$

$$\epsilon_r = \frac{C}{C_0} \quad (4)$$

When a dielectric is subjected to an alternating electric field, the electric field strength changes as:

$$E = E_0 \cos \omega t \quad (5)$$

The induced current in the dielectric does not change exactly with the applied voltage. The current is found to lead the potential in phase. In a similar way, the electrical

displacement (D) is also not in phase with respect to E. Now the expression for D becomes

$$D = D_0 \cos(\omega t - \delta)$$

$$D = D_0 \cos \omega t \cos \delta + D_0 \sin \omega t \sin \delta \quad (6)$$

The factor $\sin \delta$ is a measure of the energy absorbed by the dielectric. It is known that in a capacitor the dielectrics usually have a resistance R and impedance Z that are related to the phase angle. Assuming R to be very large,

$$\sin \delta \approx \tan \delta = 1 / \omega RC \quad (7)$$

The factor $\tan \delta$ is referred to as the dielectric loss. Dielectric constant can be found from the measurement of capacitance. The dielectric constant in any direction of the medium can be considered as a measure of electrostatic binding strength between the ions in the direction. The higher the dielectric constant, the lower the electrostatic binding and hence higher is the lattice energy. Dielectric properties of pure and doped glasses are due to the contribution of electronic, ionic, dipole orientations and space charge polarizations. The charge carriers in a glass cannot move freely through but they could be displaced and thus become polarized depending upon the applied alternating field. The variation of dielectric constant and the dielectric loss with frequency and temperature for pure and doped glasses is shown in Figures 4 and 5. It can be seen that the dielectric constant and the dielectric loss gradually decrease with increase in frequency and decrease in temperature. Increase in dielectric constant and dielectric loss is more pronounced at lower frequencies. This behavior can be attributed to the applied electric field, which assists electrons hopping between two different sites in glasses. At high temperatures, the jump frequency of the charge carrier becomes large and comparable with the frequency of the applied field. Accordingly at low frequency the charge carriers hop easily out of the sites with low free energy and tend to accumulate at sites with high free energy barriers. This leads to a net polarization and gives an increase in the dielectric constant and the dielectric loss. However, at high frequency, the charge carriers will no longer be able to rotate sufficiently rapidly, so their oscillation will begin to lie behind this field resulting in a decrease of dielectric constant and dielectric loss. At low temperatures, jump frequency of the charge carries becomes smaller than the frequency of the applied field. The periodic reversal of the applied field takes place so rapidly that there are no excess charge carriers jumping in the field direction and the polarization is due to the disappearance of the charges piling up at high free energy barrier sites, which leads to a decrease in the values of the dielectric constant and the dielectric loss (Sindhu, et al., 2005; Szu and Lin, 2003). Similar variation of the dielectric constant and the dielectric loss

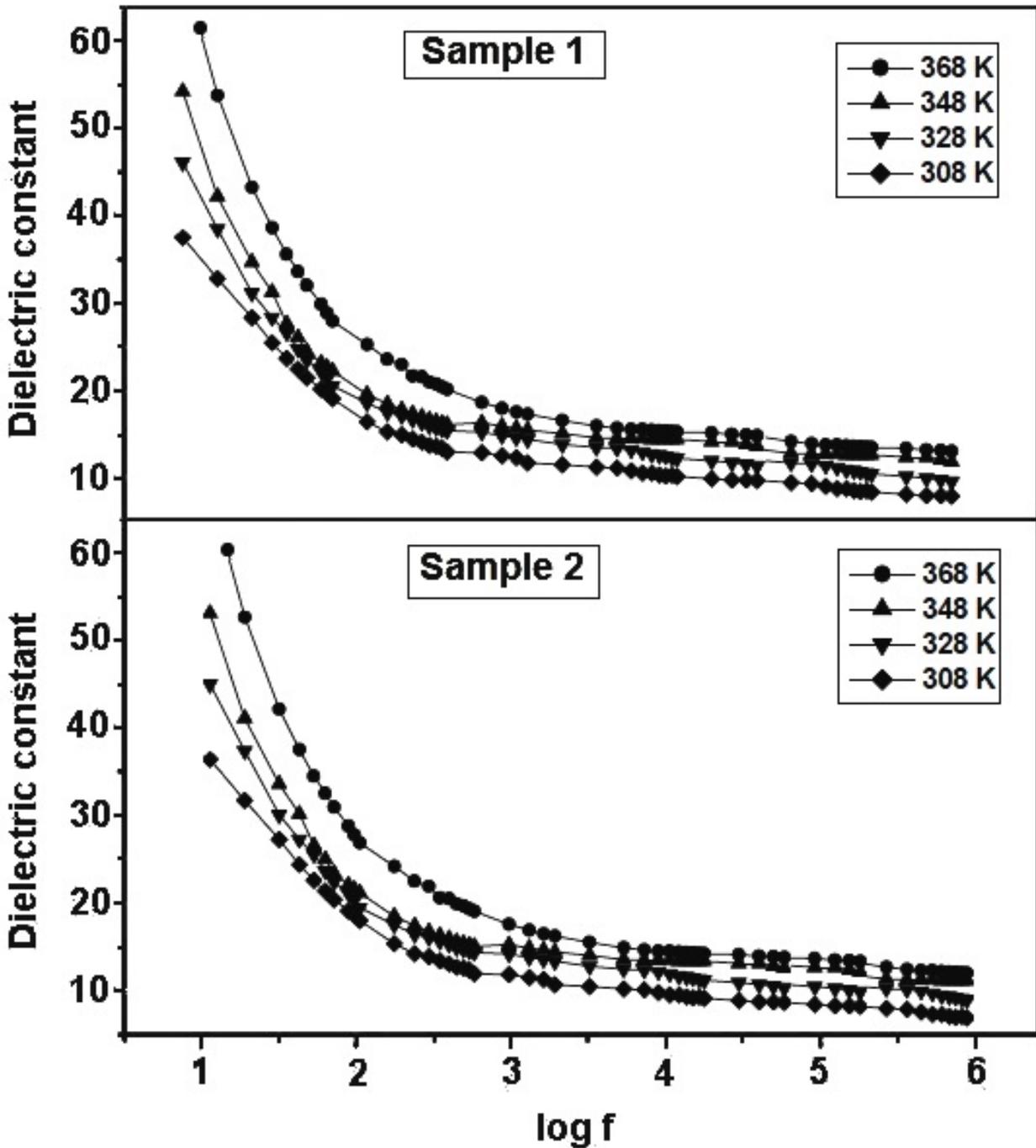


Figure 4. Variation of dielectric constant with log frequency.

was observed for other glass samples.

Conclusion

Eu_2O_3 doped Borate glasses were successfully synthesized by melt quenching method. The X-ray diffraction characterization strongly indicated the

amorphous nature of the prepared glasses. The photoluminescence graph made it clear that the small variation in the peak value occurred when the sample was doped with a rare earth element. This indicated that the wavelength of excitation purely depended upon the material composition. The dielectric properties of glass samples were studied for different frequencies and different temperatures.

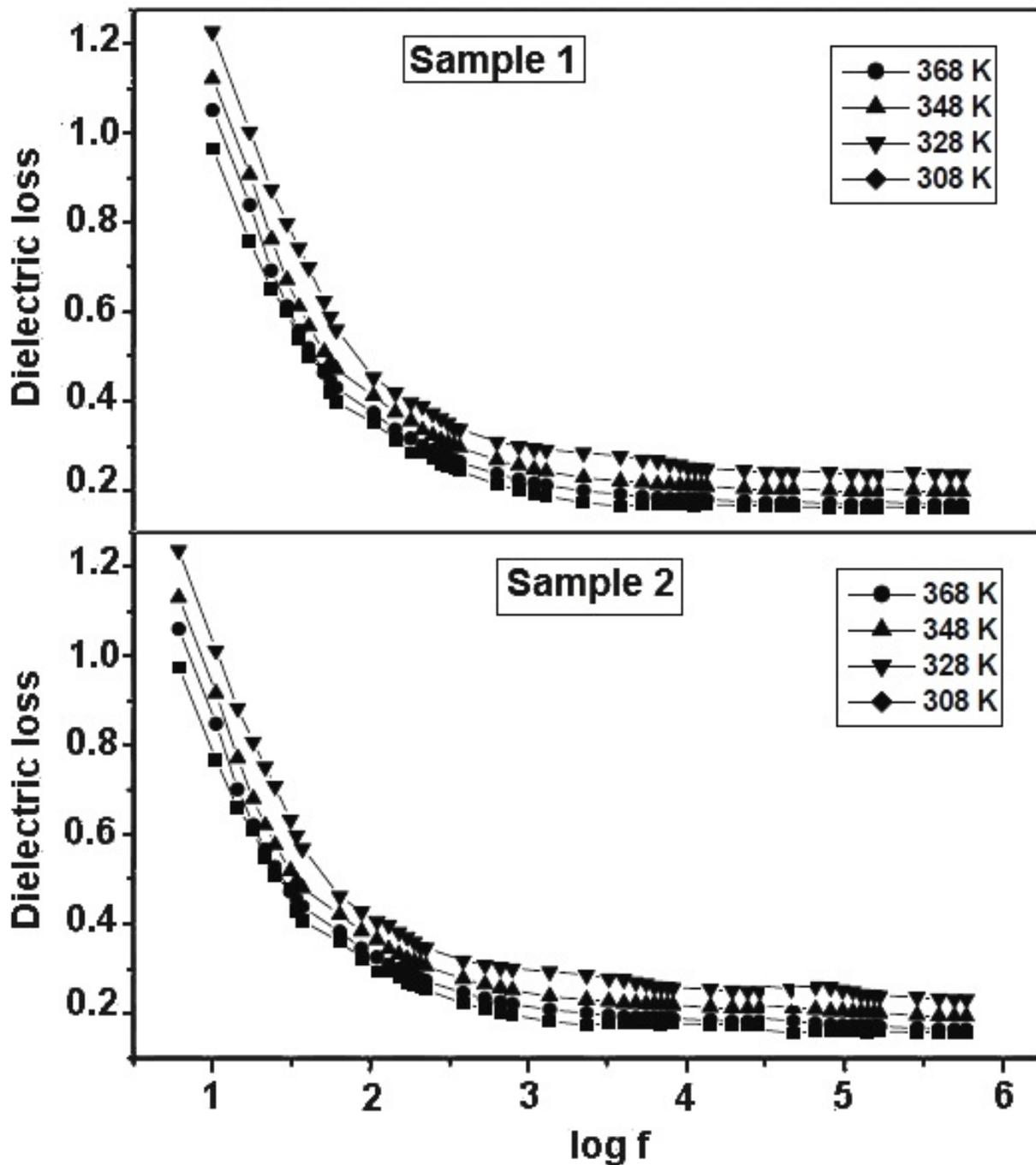


Figure 5. Variation of dielectric loss with log frequency.

Conflict of Interest

The authors have not declared any conflict of interest.

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