In this Chapter, Eu$^{3+}$-doped Li-K-Zn fluorotellurite glasses of the composition $(70-x)$ TeO$_2$ + 10 Li$_2$O + 10 K$_2$O + 10 ZnF$_2$ + x Eu$_2$O$_3$ with $x$ (mol%) = 0.0, 0.1, 0.5, 1.0, 1.5 and 2.0, were characterized for their structural and dielectric properties. For the present glass system, the amorphous nature and thermal stability were established using X-ray diffraction technique and differential scanning calorimetry, respectively. Vibrational properties of the structural groups present in the glasses were also analyzed using Fourier transform infrared spectroscopy. Dielectric properties of the glass samples were also investigated. Power-law and the Cole-Cole parameters were calculated and their dependence on the concentration of Eu$^{3+}$ ions was discussed.
3.1 Introduction

Trivalent rare earth (RE$^{3+}$) doped oxide glasses have been investigated widely because of their potential applications in various fields such as solid state lasers, optical data storage, planar waveguides, flat panel displays, fiber amplifiers etc. [1-3]. Tellurite based glasses are of special interest because of their peculiar physical properties such as low melting point, high dielectric constant, high refractive index, infrared (IR) transmittivity over a wide range and high chemical durability [4, 5]. Even though TeO$_2$ rarely form glass under normal conditions, in the presence of modifiers they readily form glass phase. It has already been reported that the addition of alkali gives rise to different structural units depending upon the alkali content in the glass [4, 6]. These alkali tellurite glasses also exhibit high ionic conductivity. Addition of network modifiers like Li$_2$O and K$_2$O produce appreciable changes in the properties such as melting point and stability of the glass network. Fluoride contents in the glass can move the IR cut-off edge towards longer wavelengths, creating them extremely suitable for fiber amplifiers [7]. Also fluorine can react with OH group to produce hydrogen fluoride, which diminishes the OH absorption in the glass matrix [8]. Anions like oxygen become non-bridging when the divalent cations like zinc are incorporated in the glass network [9] thereby affecting the dielectric properties of the matrix.

Eu$^{3+}$-doped glasses find a number of applications in a variety of optoelectronic devices such as red emitting phosphors and optical storage devices [10]. At the same time, many researchers have reported dielectric and ac conductivity studies of glasses by introducing different RE$^{3+}$ ions and transition metal ions [11, 12]. By suitable selection of the glass constituents, one can develop an entire range of electrical conductors, from
purely ionic to purely electronic. Glasses with such properties have found applications in the development of integrated microbatteries [13]. In the present study, the structural and dielectric studies of Eu$^{3+}$ -doped Li-K-Zn fluorotellurite glasses were carried out and the effect of Eu$^{3+}$ on the dielectric properties have been discussed. X-ray diffraction (XRD), Differential Scanning Calorimetry (DSC) and Fourier transform infrared (FTIR) studies have been done and analyzed. The power-law and Cole-Cole parameters were also calculated along with dielectric analysis.

### 3.2 Experimental

Eu$^{3+}$ doped (70–x) TeO$_2$ + 10 Li$_2$O + 10 K$_2$O + 10 ZnF$_2$ + x Eu$_2$O$_3$ with x = 0.0, 0.1, 0.5, 1.0, 1.5 and 2.0 mol% (Glass codes from TLKZnF to TLKZnFEu20) were prepared by conventional melt quenching technique. The systematic procedures for glass synthesis and polishing along with the optical properties of the present glasses were discussed in Chapter 2 [14].

The samples were characterized by XRD, DSC and FTIR studies. The X-ray diffraction pattern of the glass was measured using an Xpert Pro PANalytical X-ray diffractometer with Cu Kα line. Spectral data were recorded for 20 values over the range of 10-90°. DSC measurements for the glass were studied using a TA-Q20-2047 Differential Scanning Calorimeter in nitrogen purge in the temperature range 30-600°C with an increasing rate of 10°C/min. FTIR spectrum of the glass was taken using Perkin Elmer spectra 400 FTIR imaging system. Dielectric studies of the glasses were performed at room temperature using Agilent impedance analyzer E4980A.
3.3 Results and Discussion

3.3.1 X-ray Diffraction

The XRD spectrum of 1.0 mol% Eu$^{3+}$-doped glass sample (TLKZnFEu10) is shown in Figure 3.1. The amorphous nature of the sample is clearly evident from the diffraction pattern, in which no diffraction peaks appear.

![XRD spectrum of 1.0 mol% Eu$^{3+}$-doped TLKZnF glass](image)

**Figure 3.1** XRD spectrum of 1.0 mol% Eu$^{3+}$-doped TLKZnF glass

3.3.2 Differential Scanning Calorimetry analysis

The DSC curve of 1.0 mol% Eu$^{3+}$-doped glass is given in Figure 3.2. Inset of the figure shows the magnified DSC curve to clearly identify the onset points of glass transition and crystallization temperatures. A single endothermic peak corresponding to the glass transition temperature $T_g$ is obtained around 244°C with a glass transition width ($\Delta T_g$) of 58°C. The onset point of glass transition is taken as the glass transition temperature. The onset of crystallization is also clearly visible from the figure given in the inset of
Figure 3.2. The value of $\Delta T$ is obtained as 120°C, which is the difference between the glass transition temperature ($T_g$) and the onset of crystallization ($T_x$). $\Delta T$ is usually considered as a rough estimate of the glass stability against crystallization. If $\Delta T > 100$, the glass can be considered as having relatively good thermal stability. The obtained value of $\Delta T$ for the present glass system is large compared to many reported works [12, 15]. The endothermic peak at the glass transition is due to the quick variation in enthalpy ($dH$) and the exothermic variation is due to the change in viscosity due to crystallization.

![DSC spectrum of 1.0 mol% Eu$^{3+}$-doped TLKZnF glass. Inset shows the onset points of $T_g$ and $T_x$.]

At the glass transition region, the change in enthalpy $dH$ was obtained as 3.797 J/g. The specific heat capacity can be evaluated using the expression

$$C_p = \frac{dH}{dT}$$  \hspace{1cm} (3.1)
and is obtained as 0.292 J/g °C. The thermodynamic fragility ($F$) of the glass was obtained using the equation

$$F = \frac{0.151 - \chi}{0.151 + \chi} \quad \ldots \ldots (3.2)$$

where $\chi = \Delta T_g / T_g$ [16]. The value obtained for $F$ is -0.22. The negative value of $F$ is an indication of the strength of the glass matrix formed.

**Figure 3.3** FTIR spectrum of 1.0 mol% Eu$^{3+}$-doped TLKZnF glass

### 3.3.3 FTIR spectrum

In the FTIR spectrum of the glass (Figure 3.3), the prominent absorption band is centered at 596 cm$^{-1}$. This band has been attributed to the stretching vibrations of TeO$_4$ trigonal bipyramid structure. The band around 665 cm$^{-1}$ is due to the TeO$_3$ trigonal pyramids and deformed TeO$_4$ groups [17, 18]. The absorption around 1640 cm$^{-1}$ is due to the O-H bending and the broad absorption around 3200 cm$^{-1}$ is due to the stretching vibrations of Te-O-H bonds present in the sample [19]. It is seen that the
intensity of absorption due to the O-H group is much less compared to the tellurite group. This is due to the effect of fluorine which in turn reduces the O-H content in the glass [8].

3.3.4 Dielectric studies

When a sinusoidal voltage of frequency $\omega$ is applied across a sample, the real part of dielectric constant is given by the relation

$$\varepsilon' = \frac{C_p t}{\varepsilon_0 A} \quad \ldots(3.3)$$

The imaginary part of dielectric constant is given by

$$\varepsilon'' = \varepsilon' \tan \delta \quad \ldots(3.4)$$

where $\varepsilon_0$ is the permittivity of free space, $C_p$ is the parallel plate capacitance across the glass sample and $\tan \delta (=1/\tan \theta)$ is the loss tangent or dissipation factor. Figures 3.4 (a) and (b) show the real and imaginary part of the dielectric constant versus log $f$, respectively.

From the plot for real part of dielectric constant with frequency (Figure 3.4 (a)), it can be observed that the dielectric constant initially decreases upto a frequency of 5 kHz and thereafter maintains a more or less constant value over a range of frequencies. Also it is seen that the dielectric constant increases for the dopant concentration of 0.1 mol% Eu$^{3+}$. For 0.5 mol% Eu$^{3+}$-doped glass, at lower frequencies the dielectric constant shows an increase, but as the frequency increases, it falls to lower values. For all other glasses, the dielectric constant decreases with concentration. From the observed values of dielectric constants, it can be concluded that the glasses under examination is a charge transfer type insulator. Also, it is clear that a fine tuning of the dielectric constant can be achieved by carefully adjusting the concentration of Eu$_2$O$_3$. At low frequencies, the dipolar and space charge polarizations are the predominant factors which decide the value of the dielectric constant.
Figure 3.4 (a) Variation of real part of dielectric constant with log f for Eu$^{3+}$-doped TLKZnF glasses

Figure 3.4 (b) Variation of imaginary part of dielectric constant with log f for Eu$^{3+}$-doped TLKZnF glasses
At very low frequencies the dipoles have sufficient time to align with the field before it changes direction and the dielectric constant is high. But as the frequency increases, the dipoles do not have sufficient time to align before the field changes direction and hence the dielectric constant is lower. At higher frequencies, ionic and electronic polarizations become the deciding factors of dielectric constant [20]. At low concentrations, Eu$^{3+}$ acts as a modifier depolymerizing the glass matrix and facilitating the migration of free ions. These free ions develop space charge [21], which in turn increases the dielectric constant. As the concentration increases to 0.5 mol\% and above, the dielectric constant is found to decrease. This may be due to the decrease in the degree of disorder of the matrix, reducing the freedom of movement of the dipoles [21]. This suggests that the rigidity of the glass network has been increased by the presence of Eu$_2$O$_3$. This reduces the freedom of dipoles to orient in the direction of the external field, causing a decrease in the dielectric parameters.

Figure 3.4 (b) shows the variation of imaginary part of dielectric constant with frequency. Significant variation is observed at low frequencies, but the values become constant above 10 kHz. At low frequencies, the variation in $\varepsilon''$ is due to the ion migration in the material. At intermediate frequencies, the main contributions to the dielectric loss are due to the ion jump, conduction loss of ions and ion polarization loss [22]. The high frequency variation is mainly due to the ion vibrations because of the rapidly varying electric field. It has been reported that the decrease in dielectric values are observed only when the metal ions in the glass network are in divalent state [23]. Hence the dielectric relaxation mechanisms are due to the dipoles resulting from the pairing of divalent ions of zinc together with other cationic vacancies present [9].
The ac conductivity of the sample can be calculated using the equations

\[ \sigma_{ac} = \omega \varepsilon_0 \varepsilon'' \]  
\[ \sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon' \tan \delta \]

For all the samples, conductivity shows a weak dependence on frequency at lower values up to 10 kHz, thereafter shows a sharp increase with frequency, as shown in Figure 3.5. This can be attributed to the change in the type of polarization from space charge to ionic as the frequency increases. To understand the dependence of conductivity on frequency, correlated barrier hopping (CBH) model may be used, according to which, the electrons are able to hop among the charge defects across the coulomb barrier.

![Figure 3.5](image)

**Figure 3.5** Variation of ac conductivity with log f for Eu\(^{3+}\)-doped TLKZnF glasses

A convenient formalism used to investigate the frequency dependence of conductivity in a material is based on the power-law relation proposed by Jonscher [24],

\[ \sigma_T = \sigma_0 + A\omega^\delta \]
where $\sigma_f$ is the total conductivity, $\sigma_0$ is the frequency independent (dc) conductivity, and the coefficient $A$ and the exponent $s$ are material and temperature dependent parameters. The term $A \omega^s$ comprises the ac dependence and characterizes all dispersion phenomena. This term gives the frequency dependence of ac conductivity and explains the variation in the dielectric coefficients. In general, the values of exponent $s$ lie between 0 and 1 and is a measure of the correlation between the ac conductivity and frequency. As the correlation increases, $s$ value tends to unity and for uncorrelated hopping its value reduces to zero. The power-law parameters for the prepared samples are given in Table 3.1. It can be seen that the value of $s$ is in the range 0.47 to 0.66. So we may conclude that the hopping mechanism is augmented by the extrinsic processes initiated by the impurities or the injected carriers due to the presence of Eu$^{3+}$ ion in an oscillating field.

### Table 3.1 Power-law parameters for Eu$^{3+}$-doped TLKZnF glasses

<table>
<thead>
<tr>
<th>Glass code</th>
<th>$\sigma_0$ ($\times 10^{-11}$)</th>
<th>$s$</th>
<th>$A$ ($\times 10^{-12}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TLKZnF</td>
<td>2.022</td>
<td>0.657</td>
<td>0.211</td>
</tr>
<tr>
<td>TLKZnFEu01</td>
<td>1.257</td>
<td>0.530</td>
<td>1.445</td>
</tr>
<tr>
<td>TLKZnFEu05</td>
<td>2.732</td>
<td>0.472</td>
<td>3.665</td>
</tr>
<tr>
<td>TLKZnFEu10</td>
<td>4.317</td>
<td>0.549</td>
<td>1.089</td>
</tr>
<tr>
<td>TLKZnFEu15</td>
<td>0.792</td>
<td>0.613</td>
<td>0.388</td>
</tr>
<tr>
<td>TLKZnFEu20</td>
<td>0.437</td>
<td>0.629</td>
<td>0.263</td>
</tr>
</tbody>
</table>

A plot between the real and imaginary part of impedance is called Cole-Cole plot. The real ($Z'$) and imaginary ($Z''$) part of impedance can be expressed as

\[
Z' = |Z| \cos \theta \quad \ldots \ldots (3.8)
\]

\[
Z'' = |Z| \sin \theta \quad \ldots \ldots (3.9)
\]

where $\theta$ is the phase angle given by $\tan \theta = Z''/Z'$. 

---

75
Figure 3.6 (a) Cole-Cole plot for TLKZnF glass

Figure 3.6 (b) Cole-Cole plot for TLKZnFEu01 glass
Figure 3.6 (c) Cole-Cole plot for TLKZnFEu05 glass

Figure 3.6 (d) Cole-Cole plot for TLKZnFEu10 glass
Figure 3.6 (e) Cole-Cole plot for TLKZnFeu15 glass

Figure 3.6 (f) Cole-Cole plot for TLKZnFEu20 glass
Figures 3.6 (a), (b), (c), (d), (e) and (f) show the complex impedance plots of the Eu$^{3+}$-doped glasses. The dielectric response of the glasses can be modeled by a parallel RC circuit from which the bulk resistance $R_b$, bulk capacitance $C_b$ and the relaxation time $\tau$ can be calculated using the relations

$$C_b = \frac{1}{2\pi f_p R_b} \quad \ldots\ldots(3.10)$$

$$\tau = R_b C_b = \frac{1}{2\pi f_p} \quad \ldots\ldots(3.11)$$

Single semicircles are obtained for all the samples modeled by the parallel RC circuit. The low frequency intercept made on the real axis by the semicircles gives the bulk resistance. The Cole-Cole parameters for the Eu$^{3+}$-doped TLKZnF glass samples are listed in Table 3.2. It can be seen that the bulk resistance increases up to a concentration of 1.0 mol% of Eu$^{3+}$ ion, and then start to decrease. It is also observed that the relaxation time and bulk resistance are inversely proportional to each other. The relaxation time decreases up to a concentration of 0.5 mol% of Eu$^{3+}$ and then shows an increase.

**Table 3.2** Cole-Cole parameters for Eu$^{3+}$-doped TLKZnF glasses

<table>
<thead>
<tr>
<th>Glass code</th>
<th>$R_b$ (M$\Omega$)</th>
<th>$C_b$ (pF)</th>
<th>$\tau$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TLKZnF</td>
<td>2.457</td>
<td>194.651</td>
<td>0.478</td>
</tr>
<tr>
<td>TLKZnFEu01</td>
<td>7.656</td>
<td>59.252</td>
<td>0.454</td>
</tr>
<tr>
<td>TLKZnFEu05</td>
<td>8.189</td>
<td>55.087</td>
<td>0.451</td>
</tr>
<tr>
<td>TLKZnFEu10</td>
<td>10.201</td>
<td>52.913</td>
<td>0.540</td>
</tr>
<tr>
<td>TLKZnFEu15</td>
<td>6.454</td>
<td>84.208</td>
<td>0.543</td>
</tr>
<tr>
<td>TLKZnFEu20</td>
<td>5.167</td>
<td>109.472</td>
<td>0.566</td>
</tr>
</tbody>
</table>
3.4 Conclusions

The amorphous nature of the Li-K-Zn fluorotellurite glasses doped with Eu$^{3+}$ ions was established by the XRD analysis. The DSC analysis showed that the prepared samples have high thermal stability with a $\Delta T$ value of 120°C. FTIR analysis evidences the presence of TeO$_4$ and TeO$_3$ trigonal pyramid structures. Dielectric studies of the glass systems suggest that a fine tuning of the dielectric parameters can be accomplished by varying the concentration of Eu$^{3+}$ ions. The bulk resistance of the glass increases up to a concentration of 1.0 mol% of Eu$^{3+}$ and the values suggest that it has good insulating capability. Because of low vibrational energies and good dielectric properties, these glasses are promising materials for applications in fiber optic communications, photonic devices and optical energy transport devices.
References