**Physical, Optical and Spectroscopic properties of Quaternary glass systems**

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*The glasses with compositions 64TeO2-15ZnO-(20-x)CdO-xLi2O-1V2O5, 64TeO2-15CdO-(20-x)ZnO-xLi2O-1V2O5 where 0 mol%, were prepared by conventional melt quenching technique. X-ray diffraction was used to confirm the amorphous nature. The optical absorption studies revealed that the cut-off wavelength () decreases while optical energy gap (Eopt) and Urbach energy (∆E) values increase with an increase of Li2O. Refractive index () evaluated from Eopt was found to decrease with increase of Li2O content. The physical parameters such as density (ρ), molar volume (Vm) and oxygen packing density (OPD) have been analyzed and discussed. The electron paramagnetic resonance (EPR) spectra of VO2+ glasses have been recorded on X-band () at room temperature. The spin Hamiltonian parameters of VO2+ ions have been calculated. It has been found that V4+ ions in these glasses exist as VO2+ in octahedral coordination with a tetragonal distortion. FTIR and Raman spectroscopic studies showed that the glass network consists of TeO4, TeO3+1****/****TeO3 and ZnO4 units as basic structural units. The glass transition temperature (Tg), onset crystallization (To) and thermal stability () were determined from Differential Scanning Calorimetry (DSC).*

**Keywords**: XRD, SEM, Optical absorption, DSC, Raman, FTIR and ESR

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**1. Introduction:**

Tellurium dioxide belongs to the intermediate class of glass forming oxides since it does not form glass by itself unless usual preparation conditions were changed or by adding some oxides such as Li2O, BaO, CdO, ZnO, Bi2O3, Nb2O5 or WO3 [1]. Tellurite glasses have superior properties like high dielectric constant, high refractive index, high chemical stability, wide IR transmittance and low phonon energy when compared to silicate, borate and phosphate glasses and exhibit a wide range of transmission wavelengths [2-5]. Tellurite glasses are not only of academic interest but also have potential applications such as pressure sensors, data storage, optical displays, and optical amplifiers as new laser hosts, optical modulators and optical memory storage systems [6]. The effect of addition of alkali and alkaline earth oxide materials on the properties of tellurite glasses have been studied and reported [7,8]. The tellurite glass with different compositions of ZnO-TeO2 glasses were prepared and characterized [9-13]. The glass systems Li2O-TeO2 [14] and TeO2-CdO [15] were prepared and studied. The glass composition of ZnO-CdO-TeO2 [16] was also reported the optical and thermal analysis. The structure of telurite glass is similar to that of paratellurite which is based on a three dimensional network of TeO4 trigonal bipyamids linked by Te-O-Te linkages to structure of infinite chains. Addition of ZnO, CdO and Li2O to TeO2 results in breakage of Te-O-Te linkages thereby resulting in systematic conversion of TeO4 to TeO3 structural units. The addition of ZnO, CdO and Li2O were added to TeO2 to form the quaternary TZCL and TCZL glass systems to enhance the thermal stability. In the present study ZnO, CdO and Li2O have been taken as Intermediates and modifier respectively to modify the glass structure. The authors are interested to study the influence of Li2O, CdO on ZnO-TeO2 and Li2O, ZnO on CdO-TeO2 glasses. The addition of ZnO and CdO increases the non bridging oxygen (NBO) in the glass matrix. The changes in glass structure by the addition of Li2O observed by measuring different physical properties and correlating with various optical parameters. Study of the structural, thermal and optical properties of 64TeO2-15ZnO-(20-x)CdO-xLi2O-1V2O5 and TeO2-15CdO-(20-x)ZnO-xLi2O-1V2O5 glasses in mol% was done using FTIR, Raman spectroscopy, DSC, optical, and physical studies. One mol% of V2O5 is added for EPR spectroscopy studies.

**1.1 64TeO2-15ZnO-(20-x)CdO-xLi2O-1V2O5**

**1.1.1 Experimental**

In the present study stoichometric mixture of TeO2 (sigma Aldrich-99+ purity), ZnO (merck-99% purity), CdO (merck-99% purity) and Li2O (merck-99.9% purity) chemicals have been prepared by melt quenching technique with each composition in powder form with a weight of 10 g. The powder was weighed using a digital balance with an accuracy of ±0.0001.The powders were thoroughly mixed using a mortar and pestle. The contents were taken in the porcelain crucibles and stirred well to ensure homogeneity of the chemicals. The porcelain crucible with homogeneous mixture was covered with a lid and placed in a high temperature furnace for heating to avoid the volatility of the powder compound or contamination from the furnace. The crucibles were heated to a temperature of 400 for 30 min, for removing any water vapors from the powder composition. The temperature of the furnace is then increased up to 850-900 depending on the glass composition. The mixture was agitated by swirling the crucible frequently using tongs for 1 hr to ensure bubble free liquid. The liquids were quickly poured into a stainless steel plate maintained at 200 and was pressed with another stainless steel plate maintained at the same temperature. The glass samples were allowed to cool in it for 12 hrs to remove thermal strains. The prepared samples were clear, bubble free and transparent. The amorphous nature was confirmed by X-ray diffraction. The glass samples with chemical composition 64TeO2-15ZnO-(20-x)CdO-xLi2O-1V2O5,  where x = 0, 5, 10, 15 and 20 mol% TZCL series were prepared five samples by varying CdO and Li2O. The prepared glass samples are having 1mm thickness. Each glass sample was coded as TZCL1, TZCL2, TZCL3, TZCL4 and TZCL5. The composition of the glass samples are given in the Table 1.1.1.



The X-ray diffraction analysis of powdered glass samples were carried out using copper target (Kα=1.54 Å) on Philips PW (1140) diffractometer at room temperature.

The densities of the glass samples at room temperature were determined by standard Archimedes principle. The values were measured using a sensitive balance and xylene (0.865 g/cm3 was used as an immersion fluid. From these density values, the molar volume of glasses was calculated. Oxygen packing density (OPD) of each glass was then calculated from the density and composition of the glass samples.

The IR spectra of glass samples were recorded at room temperature using a perkin-Elmer spectrometer model 1605 using KBr disc technique. The investigation sample were grounded to fine particles and then mixed with KBr in the ratio (0.002:0.2 g) glass to KBr respectively. The weighed mixture was then subjected to pressure of 5tons/cm2. The transmission spectra were measured immediately after preparing the desired disks.

The room temperature Raman spectroscopic measurements were performed in the range 100-1000 cm-1, where in an Ar+ laser beam of 488 nm (E=2.53 eV) coupled with Jobin-Yvon Horiba (LABRAM HR-800) micro Raman spectrometer equipped with a 50x objective lens to focus the laser beam. The incident laser power was focused in a diameter of and a notch filter was used to suppress Rayleigh light. Samples used for the measurements were of 1 mm thickness and 1cm in diameter. Raman shifts are measured with a precision of 0.3 cm-1 and the spectral resolution is of the order 2 cm-1.

The glass transition temperature (Tg) was recorded using a temperature Differential Scanning Calorimeter (DSC). All the glass samples were heated at a rate of 10 /min in aluminum pans.

The optical absorption spectra of the present glass sample were recorded using a double beam schimadzu UV-Vis-NIR-3100 spectrophotometer in the wavelength range 250 to 800 nm at room temperature. The uncertainty in the observed wavelength is about ±1 nm.

Theglasses contains 1 mol % of V2O5 were recorded on an electron paramagnetic resonance spectrometer (BRUKER) operating in the X-band frequencies (9.305 GHz) with a modulating frequency of 100 KHz. The magnetic field was scanned from 2200 to 4200 G with a scan speed of 250 G/min. The glass sample was taken in a quartz tube for EPR measurements.

**1.1.2 Results & discussion:**

**1.1.2.1 Physical properties**

The X-ray diffraction analysis is a useful technique because it is possible to detect readily grown crystal matrix. The X-Ray diffraction pattern of an amorphous material is distinctly different from that of crystalline material and consists of few broad diffuse haloes rather than sharp rings. The XRD patterns of 64TeO2-15ZnO-(20-x)CdO-xLi2O-1V2O5 glass samples shown in Fig.1.1.1. The figure showed broad humps typical of amorphous phase of glasses, obtained at around , these range suggests that some short range order in the present glasses are prevented. The absence of short, strongly diffracted beam in the X-ray diffraction pattern of glasses indicated that there were no well defined planes in the structure on or around which the constitute atoms were regularly arranged.

The densities of the present glass samples at room temperature were determined by standard Archimedes principle shown below. With increase of Li2O (decrease of CdO) from 0 to 20 mol% density decreased from 5.672 to 4.911 gm/ccare given in Table 1.1.2. The density () is the physical parameter of a material which is an important tool to detect the structural changes in the glass network. The density is supposed to change abruptly when there is a change in the structure of the glass, geometrical configuration, coordination number, crosslink density and dimension of interstitial spaces in the glass [17]. From the obtained values of density, molar volume of the glass sample was found to increases from 25.008 to 26.661cc/mole with increase of Li2O content as shown in Table 1.1.2. From Fig.1.1.2 shows variation of Molar volume (Vm) and density () with Li2O content, it is expected that with increase of Li2O both density and molar volume should show opposite behavior to each other. From the Table 1.1.2 and Fig.1.1.3, it is clear that oxygen packing density (OPD) values decreases from 67.177 to 63.012mol/l with the Li2O content. The oxygen packing density in each sample is decreased as the number of oxygen atoms available in the glass composition is decreased. Molar volume (Vm) and oxygen packing density (OPD) are calculated and values are mentioned in Table 1.1.2. From the above values it is clear that the density ( has deceased and molar volume () has increased with increase of Li2O in place of CdO. This could be due to the lower molecular weight of Li2O than that of CdO. The increase in molar volume with decrease of CdO and increase of Li2O indicates an increase in free volume. The larger values of radial bond length of Li-O to Cd-O gives rise to an increase of molar volume. Change in OPD values with the composition of different glass samples are tabulated in Table 1.1.2. From this it is found that OPD values decrease with decrease in CdO and increase in Li2O content. This indicates the formation of TeO4 and ZnO4 units which prevents the increase in number of non bridging oxygen (NBO).

**1.1.2.2 FTIR spectra**

FTIR spectra of 64TeO2-15ZnO-(20-x)CdO-xLi2O-1V2O5 glass system is shown in Fig.1.1.4.The band at around 438-458 cm-1 is due to Te-O-Cd/Te-O-Zn stretching vibrations and bending vibrations of Te-O-Te or O-Te-O linkages. The band at 458 cm-1 has been assigned Cd-O group vibrational motion. As Li2O content increases from 0 to 20 mol% the absorption band is shifting from 438-458 cm-1. This indicates that due to substitution of Li2O bridging Cd-O/Zn-O bands are increasing.The structure of TeO2 rich glasses consists of TeO4 trigonal bipyramidal building units, where one equatorial site is occupied by a pair of electrons and the equatorial oxygen in one unit is the axial site of the next, in analogy with α-TeO2. In the present glass system also, broad absorption band is observed at 677 cm-1 for TZCL1 which is due to the presence of TeO4 tetragonal pyramids. As concentration of Li2O increases this absorption band shifts to 701 cm-1, which is a characteristic band of TeO3 trigonal pyramids. This introduction of Li2O destroys the three-dimensional network, creating non-bridging oxygen (NBO) species and gradually transforming the TeO4 units into TeO3+1 and TeO3. The band at 759-787 cm-1 which indicates the formation of Te-O-Zn bonds in the glass network, suggests that the formation of TeO4 units have changed to TeO3 units all the above band positions and assignments are shown in Table 1.1.3. At low percentage of ZnO from 10-20 mol%, Zn+2 enters the glass network by breaking up of Te-O-Te bonds. When increasing the Li2O content, the band is observed around 911 to 914 cm-1 is assigned to the vibrations of metal and its neighboring non bridging oxygen.

**1.1.2.3 Raman studies**

The Raman spectra were performed at room temperature in the range of 100-1400 cm-1. An Ar+ ion with a wavelength of 488 nm (E=2.53 eV) was used for pumping excitation. Raman spectra of all the glasses are shown in Fig.1.1.5. The positions of the Raman bands of these glasses and their assigned vibrational modes are listed in Table 1.1.5 and Table 1.1.6 respectively. From Fig.1.1.5, a Raman band observed at 220-235 cm-1 in the glass samples were attributed to the Cd-O vibrational modes [18-20]. The band observed at ~ 408 cm-1 is assigned to the symmetrical stretching or bending vibrations of Te-O-Te linkages that are formed by corner sharing of TeO4, TeO3+1 polyhedra and TeO3 units [21,22]. The peak at 665 cm-1 is ascribed to the axial symmetrical stretching vibrational modes of Te-O of TeO4 tetrahedra [23-26]. A peak at 748 cm-1 isassigned to the equatorial symmetrical and asymmetrical Te-O vibrational modes of TeO3+1 polyhedra or TeO3 trigonal bipyramid units [27-29]. Significant changes in the Raman spectra of glasses are observed with the addition of Li2O content. The broadness of peak 408cm-1 gradually diminishes as well as shifts from lower wavenumber to higher wavenumber (451 cm-1)with the addition of Li2O content, which indicates that the Te-O-Te/Te-O-Zn/Te-O-Cd bonds are broken. It can be observed from Fig.1.1.5, that when CdO is replaced by Li2O content, the intensity of peak has decreased and shifted from 665 to 674 cm-1, while the intensity of peak has increased and shifted from 748 to 770 cm-1. These observations indicate that the structural changes are taking place in the glass network. It suggests that the addition of Li2O content could break the axial Te-O bonds of TeO4 units and then transforms into TeO3 tp via TeO3+1. This suggests an increase in lower coordination units (TeO3) as compared to higher coordination units (TeO4). The band is observed from 904 to 911 cm-1 indicating that metal non bridging oxygen vibrations [30] are shifted to lower wavenumber with increasing of Li2O.

**1.1.2.4 Glass transition temperature (Tg)**

DSC thermogram shown in Fig.1.1.6 shows three steps in the graph corresponding to the glass transition temperature (Tg), the onset crystalline temperature (To) and crystallization temperature (Tp) respectively. These values are presented in Table 1.1.7. It is observed from the Fig.1.1.7 that Tg has decreased from 326 to 255 with the addition of Li2O content from 0 to 20 mol%. The decrease in Tg is ascribed to a decrease in density and OPD of the glass network.

In accordance with literature it is well known that (To-Tg ) is a measure of thermal stability (∆T) of glasses. These values are determined and presented in Table 1.1.7. The thermal stability of glasses has increased with increase of Li2O content and it indicates that the process of crystallization is delayed in comparison to CdO content and hence there is increase in the thermal stability of the present glasses.

**1.1.2.5 Optical studies**

Theoretical optical basicity (Λth) for the glass sample is the ability of oxygen to donate negative charge and has been calculated by Duffy and Ingram [31,32] assigned to the individual oxides that is,

Λth= x(TeO2)Λ(TeO2) + x(ZnO)Λ(ZnO) + x(CdO)Λ(CdO) + x(Li2O)Λ(Li2O) +

x(V2O5)Λ(V2O5) (1.1.1)

Where x(TeO2), x(ZnO), x(CdO), x(Li2O),and x(V2O5) are the equivalent fractions of different oxides and Λ(TeO2 = 0.93), Λ(ZnO = 1.08), Λ(CdO = 1.115), Λ(Li2O = 0.87) and Λ(V2O5 = 1.04) are optical basicity values assigned to the constitute oxides taken from ref [33]. The calculated values of optical basicity changed from 0.990 to 0.941 are listed in Table 1.1.2. It can be observed that basicity has decreased with decrease in CdO and increase in Li2O content. This could be due to the larger basicity of CdO than lower basicity of Li2O.

Optical absorption spectra of present TZCL glass system has been recorded and shown in Fig.1.1.8. The wavelength values corresponding to absorption edge, where the intensity reaches the maximum value in absorption spectra are taken as cut-off wavelengths as shown in Fig.1.1.8. These values are given in the Table 1.1.8. From the Fig. 1.1.9 it is clear that fundamental absorption edge was shifted to lower wavelength side as Li2O content is increased from 0 to 20 mol%. Shifting of absorption edge to lower wavelength is due to the decrease of oxygen packing density and lower optical basicity of Li2O. This could also be due to the difference between the energy gap of L2O and CdO.

In the near absorption edge, absorption coefficient of the glass sample of thickness ‛t’ can be calculated by using the following equation [34].

The above equation (4) can be written as

(1.1.2)

Where A corresponds to absorbance and t is the thickness of the sample. In many crystalline and non- crystalline semiconductors, the depends exponentially on the h. This exponential dependence of on h is known as the Urbach rule near the absorption edge can be written as. (1.1.3)

Where B is the constant, is the width of the band tails of the localized states.

In general, for both direct and indirect transitions can occur in a semiconducting material for many glasses and amorphous materials, is given by the relation [35].

(1.1.4)

Where Eopt is the optical energy gap, h is the photon energy and B is a constant called band tailing parameter. Here n is found to represent the experimental results. The value of n is taken as 2 which apply to indirect allowed transitions also. From the obtained data a plot is drawn as shown in Fig.1.1.10. Hence the above equation becomes

The indirect band gap is determined from linear region of the Tauc’s plot as shown in Fig.1.1.10 and the corresponding values are shown in Table 1.1.8. The results show that the indirect band gap values increase with increase in Li2O content. The value of optical band (table 1.1.8) varies from 2.244 to 2.428 eV. Band tailing parameter is determined from slope of the graph and h.Its value lies between 45.298 to 21.103; refractive index () is determined from optical energy gap using the relation proposed by Dimitrov and Sakka [36] and is shown as

(1.1.5)

From the above relation it is clear that refractive index decreases with increase of Eopt, with the increase in Li2Oand decrease in CdO content is shown in Fig.1.1.12. The values of refractive index decreased from 2.637 to 2.570, which may be due to increase in ionicity of Li+ ions and the decrease in optical basicity. Urbach plots are the plots where natural logarithm of absorption coefficients (ln) is plotted against photon energy (h). Urbach plot for present glass system is shown in Fig.1.1.11. The values of Urbach energy (∆E) were calculated by determining slopes of the linear region of the curves at lower phonon energies and taking their reciprocals. It is found that Urbach energy increases with increase of Li2­O. This is attributed to increase in fragility nature of the glass network [37]. In the present glass system the values of Urbach energy lies between 0.452 to 0.872 eV. The values of Urbach energy for a range of amorphous glasses Bi2O3-P2O5-TeO2 lies in the range 0.17 to 0.67 eV depending on glass composition [38-40] and for amorphous semiconductors [41] it lies between 0.45 to 0.567 eV. Higher Urbach energies observed for the present glasses suggest that the present glass system is having high defective nature [42]. The density of a glass plays an important role in controlling the refractive index [43]. In most cases, the decrease in the refractive index is accompanied by the decrease in density [44]. In the present study, the refractive index decreases with the decreasing density of the glass.

The molar Refractivity is directly proportional to the polaraizabilities of the constituent ions of the glass. The molar refractivity Rm is given by the expression

Rm= Vm (1.1.6)

Where Vm is the molar volume of the glass and is the refractive index at the wave length of measurement. The molar volume is the ratio of molecular weight of the glass to its density. In many cases, apparently anomalous trends in refractive index are resolved when the data is converted to molar refractivities which increase from 16.630 to 17.371 with the increase of Li2O in mol% (1.1.13). The use of the molar refractivity indicates the role of ionic packing in controlling the refractive index of a glass [45].

The condition for predicting metallic or insulating behavior in the condensed state matter in metallization criterion [46] and given by the expression



(1.1.7)

If then the material show metallic behavior and if they exhibits insulating behavior. The so called metallization parameter values of present glasses are found to be less than one and are given in Table 1.1.8. Hence the present glass system with their metallization parameter values shows increased tendency for metallization.



**1.1.2.6 Electrons spin resonance spectra**

Vanadyl ion (VO2+) has been used as a spectroscopic probe for characterization of glasses because their EPR spectra are rich in hyperfine structure due to 51V nucleus and is easily observable at room temperature. The present study has been carried out to observe the effect of substitution of lithium oxide (Li2O) and decreasing of heavy metal oxide (CdO) with zinc oxide on the microstructure around VO2+ in tellurite glasses. EPR spectra of the samples were recorded at room temperature (300 K) in the X-band (9.305 GHz) on an EPR spectrometer (JEOL-JM Fe 3). Magnetic field was modulated by 100 KHz. Polycrystalline DPPH was used as a standard marker. EPR spectra of the VO2+ in the present glasses are shown in Fig.1.1.14. These spectra shows similar features to those found in various glasses doped with vanadyl ion. The EPR spectra are characteristic of a hyperfine interaction arising from an unpaired electron with a 51Vnuclear having nuclear spin 7/2.

The axial spin Hamiltonian [47] used is of the from

+ (1.1.8)



Where, in the Bohr magnetron,



, are the parallel and perpendicular components of the g tensor,



,  are the parallel and perpendicular principal components of hyperfine coupling



tensor,

Bx ,By ,Bz are the components of the magnetic field,

Sx ,Sy ,Sz and Ix ,Iy ,Iz are the components of spin operator of the election and nucleus

respectively.

The solutions of the spin – Hamiltonian for the parallel and perpendicular hyperfine orientations are

(1.1.9)



(1.1.10)



Where mI is the magnetic quantum number of the vanadium nucleus, which takes the values and .



Spin Hamiltonian parameters of theVO2+ ion in all samples were determined by using the following equation and and tabulated in Table 1.1.9. The and values were determined using the following equations were tabulated in Table 1.1.9.



(1.1.11)



(1.1.12)

From the values of the parameters, the dipolar hyperfine coupling parameter p is evaluated using , is gyro magnetic , is Bohr magnetron , is the nucleus magnetron and r-3 is average size of the vanadium. Fermi contact interaction term K is evaluated using the expressions developed by Kivelson and Lee [48] as shown below



(1.1.13)



(1.1.14)



Where ; and ge (2.0023) is the g factor of free electron. A detailed analysis of the g tensor in the presence of trigonal symmetry was given by Gladney and Swalen [49]. The term –PK in above equations is due to the s-character of the magnetic spin of the vanadium. Basically this s-character results from the partial unpairing or polarization of the inner s-electrons as a result of an interaction with the unpaired d-electrons [50] and the contribution to the hyperfine coupling due to the term –PK is included. From the molecular orbital theory [51] it can also be shown that the components and consists of the contributions and of the 3dxy electron to the hyperfine structure and the PK term arises due to the anomalous contribution of the s-electron. The above equations can be written in the following manner



(1.1.15)



(1.1.16)



The values of and were calculated and tabulated in Table 1.1.9. The values of which measures the tetragonality of VO2+ site are calculated and presented in Table 1.1.9. An octahedral site with a tetragonal compression would give and [52,53]. The g and A values obtained in the present work when Li2O is increased and CdO is decreased and agree with this relationship and are close to those vanadyl complex were already reported by others [54,55]. It is therefore confirmed that the vanadyl ions in lithium cadmium zinc tellurite glasses exist as VO2+ ions in octahedral coordination with a tetragonal compression.



**1.2 64TeO2-15CdO-(20-x)ZnO-xLi2O-1V2O5**

**1.2.1 Experimental:** In the present study stoichometric mixture of TeO2 (sigma Aldrich-99+ purity), ZnO (merck-99% purity), CdO (merck-99% purity) and Li2O (merck-99.9% purity) chemicals have been prepared by melt quenching technique with each composition in powder form with a weight of 10 g. The preparation technique and experimental procedure were discussed in above glass system 1.1 glass system. The glass samples with chemical composition

64TeO2-15CdO-(20-x)ZnO-xLi2O-1V2O5, where x = 0, 5, 10, 15 and 20 mol% TCZL series were prepared five samples by varying ZnO and Li2O. Each glass sample was coded as TCZL1, TCZL2, TCZL3, TCZL4 and TCZL5. The composition of the glass samples are given in the Table 1.2.1.

**1.2.2 Results & discussion:**

**1.2.2.1 Physical properties**

XRD patterns of 64TeO2-15CdO-(20-x)ZnO-xLi2O-1V2O5 glass samples are shown in Fig.1.2.1, there are no noticeable sharp peaks so we confirm the samples are of amorphous nature. The measured density (, molar volume (Vm) of the glass samples are given in Table 1.2.2. The densities of the present glass samples at room temperature decreases from 5.629 to 5.053, from which we get molar volume of the glass sample which increases from 24.780 to 27.309. Oxygen packing density (OPD) in each of the sample decreases with the decrease in number of oxygen atoms available in the glass composition. Molar volume (Vm) and oxygen packing density (OPD) values are tabulated and calculated in Table 1.2.2. From the above values it is clear that the density ( has deceased and molar volume () has increased on addition of Li2O replacing ZnO content which could be due to the lower molecular weight of Li2O resulting in increase of molar volume. The larger values of radial bond length of Li-O to Zn-O also become a reason of increase in molar volume. Change in OPD values with the composition of different glass samples are tabulated in Table 1.2.2. From this it is found that OPD values decrease with decrease in ZnO content and increases with Li2O at constant [64TeO2-15CdO] indicating the formation of TeO4 and ZnO4 units indicating the increase in number of non bridging oxygen (NBO).

**3.2.2.2 FTIR spectra**

The FTIR spectra of all the glass are shown in Fig.1.2.2. The position of the FTIR bands of these glasses and their assigned vibrational modes are listed in Table 1.2.3 and Table 1.2.4. The peaks at 438-458 cm-1 are due to tetrahedral ZnO4, are reported in the range of 550-400 cm-1[56,57] Finally, the narrow bands at 438, 440, 445 and 458 cm-1 are related to stretching vibrations of Cd-O bonds. The pure tellurite glasses have an absorption band at 640 cm-1 attributing to tetragonal pyramids. The IR absorption band range from 677-771 cm-1 region, explores the stretching vibratios of equatorial and axial Te-O bonds in the TeO4 tbp and TeO3 tp respectively. These broad peaks are probably due to the distribution of bond-angles, bond radius, and fluctuation of the local electronic atomic environment in the amorphous state [58]. The two higher frequency peaks correspond to stretching vibrational modes of Te-O bonds, at 677 cm-1 for bridging oxygen (bonded to one Te ion on either side) and at 787 cm-1 for non-bridging oxygen ions (bonded to only one Te ion and charge compensated by either Zn+2). The TeO2 glass network mainly comprise of TeO4 trigonal biptramid structural units, where each oxygen atom is shared between two trigonal bipyramid units. Addition of modifier leads to the transformation of TeO4 units into TeO3 polyhedral units (The coordination of the Te atom changes progressively from 4 to 3 through 3+1). Compared with TeO4, TeO3 units contain a non-bridging ion (NBO) with a double bond to tellurium, two bridging oxygen ions and a lone electron pair. These TeO3 and TeO4 bonds form a continuous network by sharing a bridging bond. The type and concentration of the modifier oxide in the glass matrix determines the number distribution/density of various TeO3 units. The band observed from 911 to 914 cm-1 is due to the metal- non bridging oxygen vibrations with increasing Li2O content.

**1.2.2.3 Raman studies**

Raman spectra of all the glasses are shown in Fig.1.2.3. The positions of the Raman bands of these glasses and their assigned vibrational modes are listed in Table 1.2.5. From Fig.1.2.3, Cd-O vibrational modes were found at 222-231 cm-1 in Raman band of the glass samples and the band found at ~ 465 cm-1 signifies the symmetrical stretching or bending vibrations of Te-O-Te linkages formed by corner sharing of (TeO4), (TeO3+1) polyhedra and (TeO3) units. The peak at 678 cm-1 is attributed to the axial symmetrical stretching vibrational modes of (Teax-O)s of TeO4 tetrahedra and a peak at 762 cm-1 issubjected to the (Teeq-O)s and (Teeq-O)as vibrational modes of TeO3+1 polyhedra or TeO3 trigonal bipyramid units. Addition of Li2O content in the Raman spectra of glasses provides noticeable changes. The broadness of peak 451 cm-1 gradually vanishes as well as moves from lower wavenumber to higher wavenumber (465 cm-1)on adding Li2O content, which indicates that the Te-O-Te/Te-O-Zn/Te-O-Cd bonds are broken. It can be observed from Fig.1.2.3, that when ZnO is replaced by Li2O content, the intensity of peak has increased and shifted from 674 to 678 cm-1and also the intensity of peak has increased and shifted from 758 to 762 cm-1 respectively. The observations in the glass network show structural changes. Which advice that the addition of Li2O content could break the axial Te-O bonds of TeO4 units and then transforms into TeO3 tp via TeO3+1. Which prove an increase in lower coordination units (TeO3) compared with higher coordination units (TeO4). The band observed from 912 to 901 cm-1 indicates the metal non bridging oxygen vibrations shifted to lower wavenumber with increasing Li2O content.

**1.2.2.4 Glass transition temperature (Tg)**

Differential scanning calorimetry (DSC) is used to exemplify the glass and determine the glass transition temperature (Tg), which alters the compositional changes thereby affecting structure modifications that are due to Tg is very sensitive to any change of the coordination number of the network-forming atoms and also to the formation of non bridging oxygens. The transformation to a glass does not take place at a defined temperature, but with in a temperature range, representing the transformation region. The width of the later depends on the properties of the material studied (low temperature edge) and on the thermal history of the sample (high temperature edge). The homogeneity of the glass forms basis for single endothermic glass transition. Tg indicates the strength and rigidity of the glass structure. DSC plot of present glass system shown in Fig.1.2.4 put forward an endothermic peak corresponding glass transition temperature. The Tg values are tabulated in Table 1.2.7. The Fig.1.2.4 shows increasing of Tg with Li2O content addition. Density of 64TeO2-15CdO-(20-x)ZnO-xLi2O-1V2O5 glasses decreases and molar volume increases on increasing Li2O content showing the glass network becoming more compact.

**1.2.2.5 Optical studies**

The ability of oxygen to donate negative chargeis the optical basicity (Λth) of the glass sample and can be calculated by Duffy and Ingram suggested to the individual oxides that is,

Λth= x(TeO2)Λ(TeO2) + x(CdO)Λ(CdO) + x(ZnO)Λ(ZnO) + x(Li2O)Λ(Li2O) +

x(V2O5)Λ(V2O5) (1.2.1)

Where x(TeO2), x(ZnO), x(CdO), x(Li2O),and x(V2O5) are the equivalent fractions of different oxides and Λ(TeO2 = 0.93), Λ(CdO = 1.115), Λ(ZnO = 1.08), Λ(Li2O = 0.87) and Λ(V2O5 = 1.04) are optical basicity values assigned to the constitute oxides taken from ref [33]. The calculated values of optical basicity changed from 0.988 to 0.946. It can be observed that basicity has decreased with decrease in ZnO and increase in Li2O content and decrease of ZnO decreases basicity which is due to the larger basicity of ZnO.

Optical absorption spectra of present TCZL glass system has been recorded and shown in Fig.1.2.5. This corresponds to the amorphous nature due to absence of sharp peaks. The wavelength values corresponding to absorption edge are taken as cut-off wavelengths where the intensity reaches the maximum value in absorption spectra as shown in Fig.1.2.5 and the values are given in the Table 1.2.8. From the table we confirm that the fundamental absorption edge was shifted to lower wavelength side as Li2O content is increased from 0 to 20 mol%. The lowest cutoff wave length or highest band gap observed in 0 mol% of Li2O glass system is due to the formation of TeO4 units that are changed with CdO4 units. In the near absorption edge, absorption coefficient of the glass sample of thickness ‛t’ can be calculated by using the relation (1.1.2) of Chapter 1.1.1. The related equation between absorption coefficient and phonon energy of incident radiation given by the relation (1.1.4) of Chapter 1.1 is used to calculate Eopt the optical energy gap constant B called band tailing parameter. For indirect transition the relation (1.1.4) can be written as

(1.2.2)

Using above relation Eopt values are determined by extrapolation of linear region of the plots of against to = 0 as shown in Fig.1.2.6 and the values of Eopt thus obtained for all glass samples are given in Table 1.2.8. In the present glasses optical energy gap increases with increase of Li2O (decreases of ZnO mol %) content. This produces a breakdown of continuous glass network reflected in the absorption spectra by a significant shifting of absorption edge to lower wavelength side. The shift of absorption edge is due to structural rearrangements of relative concentrations of various fundamental units. Stevels suggested that the movement of absorption band to lower energy correspond to the transition from the non-bridging oxygen that binds an electron more loosely than bridging oxygen. Band tailing parameter is determined from the slope of against (Fig.1.2.6) whose value lies between 69.909 to 93.368 (cm eV)-1.

Refractive index is calculated from the optical energy gap using the relation (1.1.5) proposed by Dimitrov and Sakka mentioned in Chapter 1.1. From the relation it is clear that refractive index decreases with increase of Eopt, with varying Li2Oand ZnO contents. The values of refractive index decreases from 2.638 to 2.528, which may be due to increase in ionicity of Li+ ions and the decrease in optical basicity. Natural logarithm of absorption coefficients (ln) is plotted against photon energy (h) is plotted by Urbach plots for present glass system shown in Fig.1.2.7. The value of Urbach energy (∆E) are calculated by determining slopes of the linear region of the curves at lower phonon energies and taking their reciprocals and is found that Urbach energy increases with increase of Li2­O which is attributed to increase in fragile nature of the glass network. In the present glass system the values of Urbach energy lie between 1.128 to 0.632 eV and the higher Urbach energies indicates glass system of high defective nature.

The density of a glass plays a vital role in controlling the refractive index. In most cases, the decrease in the refractive index is accompanied by the decrease in density and is also observed in present glass system study. The molar Refractivity can be calculated by the relation (1.1.6) of Chapter 1.1. In many cases, apparently anomalous trends in refractive index are resolved when the data is converted to molar refractivities which increase from 16.485 to 17.550 with the increase of Li2O in mol%. The molar refractivity enhances ionic packing in controlling the refractive index of a glass. The condition for predicting metallic or insulating behavior in the condensed state matter in metallization criterion is given by the expression (1.1.7) in Chapter 1.1. In the equation, if indicates insulating behavior and the values are noted in Table 1.2.8.

**1.2.2.6 Electrons spin resonance spectra**

The ESR spectra of vanadium doped with 64TeO2-15CdO-(20-x)ZnO-xLi2O-1V2O5 glass system at room temperature is shown in Fig.1.2.8. From the figure, the spin- Hamiltonian parameters are calculated using the axial spin Hamiltonian equations (1.1.8) of Chapter (1.1) presented in Table 1.2.9. The present study proceeds to observe the effect of addition of Li2O and decrease of ZnO on the microstructure around VO2+ in tellurite glasses. The spectra shows alike features to those found in different glasses doped with vanadyl ion. The EPR spectra are characterizes by hyperfine interaction raised due to unpaired electron with a 51Vnuclear having nuclear spin 7/2.

The solutions of the spin – Hamiltonian for the parallel and perpendicular hyperfine orientations are given by the equations 1.1.9 and 1.1.10 in Chapter 1.1.

Spin Hamiltonian parameters of the VO2+ ion in all samples are found by the following equation and and tabulated in Table 1.2.9. Thevalues were determined using the equations 1.1.11 & 1.1.12 were tabulated in Table 1.2.9.



From the values of the parameters, the dipolar hyperfine coupling parameter p is evaluated using , is gyro magnetic , is Bohr magnetron , is the nucleus magnetron and r-3 is average size of the vanadium. Fermi contact interaction term K is calculated by using the expressions 1.1.13 & 1.1.14. The term –PK in above equations is due to the s-character of the magnetic spin of the vanadium. Basically this s-character results from the partial unpairing or polarization of the inner s-electrons due to interaction with the unpaired d-electrons and the contribution to the hyperfine coupling due to the term –PK is included. From the molecular orbital theory it can also be shown that the components and consists of the contributions and of the 3dxy electron to the hyperfine structure and the PK term which is due to the anomalous contribution of the s-electron. Following equations 1.1.13 & 1.1.14 can be written in the following manner



(1.2.3)



(1.2.4)



The values of and are calculated and tabulated in Table 1.2.9 and the values of measures the tetragonality of VO2+ site are calculated and presented in Table 1.2.9. An octahedral site with a tetragonal compression would give and . The g and A values can be obtained in the present work by altering Li2O and ZnO contents. Hence we confirm that the present glass system is satisfying the above condition where the vanadyl ions in 64TeO2-15CdO-(20-x)ZnO-xLi2O-1V2O5 glasses exist in octahedral coordination with a tetragonal compression.



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**Fig 1.1.1 XRD patterns of lithium cadmium zinc tellurite glass system**



**Fig 1.1.2 Variation of density and molar volume with Li2O mol%**



**Fig 1.1.3 Variation of Molar volume and oxygen packing density with Li2O mol%**



**Fig 1.1.4 FTIR spectra of lithium cadmium zinc tellurite glass system**



**Fig 1.1.5 Raman spectra of lithium cadmium zinc tellurite glass system**



**Fig 1.1.6 DSC of lithium cadmium zinc tellurite glass system**



**Fig 1.1.7 Variation of glass transition temperature with Li2O mol%**



**Fig 1.1.8 Optical absorption spectra of lithium cadmium zinc tellurite glass system**

****

**Fig 1.1.9 Variation of optical absorption maxima with Li2O mol%**



**Fig 1.1.10 Tauc,s plots of lithium cadmium zinc tellurite glass system.**



**Fig 1.1.11 Urbach plot of lithium cadmium zinc tellurite glass system**



**Fig 1.1.12 Variation of optical energy gap and refractive index with Li2O mol%**



**Fig 1.1.13 Variation of refractive index and molar refractivity with Li2O mol%**



**Fig 1.1.14 EPR spectra of VO2+ ion for lithium cadmium zinc tellurite glass system**

**containing 1mol% V2O5.**



**Fig 1.2.1 XRD patterns of lithium zinc cadmium tellurite glass system**



**Fig 1.2.2 FTIR spectra of lithium zinc cadmium tellurite glass system**



**Fig 1.2.3 Raman spectra of lithium zinc cadmium tellurite glass system**



**Fig 1.2.4 DSC of lithium zinc cadmium tellurite glass system**





**Fig 1.1.5 Optical absorption spectra of lithium zinc cadmium tellurite glass system**



**Fig 1.2.6 Tauc,s plots of lithium zinc cadmium tellurite glass system.**



**Fig 1.2.7 Urbach plot of lithium cadmium zinc tellurite glass system**



**Fig 1.2.8 EPR spectra of VO2+ ion for lithium zinc cadmium tellurite glass system**

**containing 1mol% V2O5.**



|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sample code** | **TeO2** | **ZnO** | **CdO** | **Li2O** | **V**2**O5** |
| TZCL1  TZCL2  TZCL3  TZCL4  TZCL5 | 64  64  64  64  64 | 15  15  15  15  15 | 20  15  10  5  0 | 0  5  10  15  20 | 1  1  1  1  1 |

**Table 1.1.1 Compositions of TZCL glass system (mol %)**

**Table 1.1.2 Physical parameters of TZCL glass system.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample**  **Code** | **Density**  **ρ (g/cc)** | **Molar Volume**  **Vm (cc/mol)** | **Oxygen Packing**  **Density(O.P.D)(mol/l)** | **Optical basicity**  **(Λ)** |
| TZCL1  TZCL2  TZCL3  TZCL4  TZCL5 | 5.672  5.475  5.259  5.032  4.911 | 25.008  25.407  25.933  26.562  26.662 | 67.177  66.121  64.782  63.247  63.012 | 0.990  0.978  0.966  0.953  0.941 |

**Table 1.1.3 FTIR band position of TZCL glass system**

|  |  |
| --- | --- |
| **Sample Code** | **Band position (cm-1)** |
| TZCL1  TZCL2  TZCL3  TZCL4  TZCL5 | 440 674 760 912  438 680 752 904  438 682 758 901  442 682 761 895  446 688 780 888 |

**Table 1.1.4 FTIR band assignments of TZCL glass system**

|  |  |
| --- | --- |
| **Wavenumber (cm-1)** | **Assignments** |
| 440-446  674-688  760-780  888-912 | Vibrations of CdO and ZnO tetrahedral  Streching vibrations of Te-O bonds in TeO3 and TeO4 groups  Vibrations of Te-O-Te / Te-O-Zn bonds which suggests the formation of TeO4 units and at the expence of TeO3 units  Streching vibrations of Te-NBO and metal-NBO vibrations |

**Table 1.1.5 Raman band position of TZCL glass system**

|  |  |
| --- | --- |
| **Sample Code** | **Band position (cm-1)** |
| TZCL1  TZCL2  TZCL3  TZCL4  TZCL5 | 235 408 665 748 911  226 415 670 761 909  226 431 672 764 909  221 442 672 766 909  221 451 674 770 904 |

**Table 1.1.6 Raman band assignments of TZCL glass system**

|  |  |
| --- | --- |
| **Wavenumber (cm-1)** | **Assignments** |
| 220-235  408-451  665-674  748-770  904-911 | Cd-O vibrations  Symmetric stretching vibrations of Te-O-Te linkages and vibrations of  Zn-O bonds from ZnO4 groups  Antisymmetric stretching vibrations of Te-O-Te linkages constructed by  two unequivalent Te-O bonds  Te-O streching vibrations of TeO3+1 and TeO3groups  Streching vibrations of Te-Non bridging oxygens, vanadium-Non  brdging oxygens bond present in TeO3 tp units or in TeO3+1 polyhedra |

**Table 1.1.7 DSC Parameters of TZCL glass system**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample code** | **Tg (** | **Tx (** | **Tp (** | **Tx – Tg (** |
| TZCL1  TZCL2  TZCL3  TZCL4  TZCL5 | 326  295  277  265  255 | 364  351  343  368  379 | 386  384  355  379  448 | 38  56  66  103  124 |

**Table 1.1.8 Optical parameters of TZCL glass system.**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Sample code** | **CutOffWave Length(nm)** | **Optical Energygap Eopt(eV)** | **Urbach Energy ∆E (eV)** | **BandTailing Parameter(B) (cm eV)** | **Refractive Index (n)** | **Molar Refractivity (Rm)** | **Metallizatin Parameter (M)** |
| TZCL1  TZCL2  TZCL3  TZCL4  TZCL5 | 546  514  501  479  450 | 2.224  2.286  2.320  2.401  2.428 | 0.452  0.672  0.717  0.771  0.872 | 45.298  39.998  28.625  25.519  21.103 | 2.637  2.621  2.060  2.580  2.570 | 16.630  16.816  17.100  17.358  17.371 | 0.334  0.338  0.340  0.346  0.348 |

**Table 1.1.9 Spin Hamiltonian parameters of TZCL glass system.**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Sample code** | **(Kg Gauss)** | **(Kg Gauss)** |  |  | **X 104**  **(cm-1)** | **X 104**  **(cm-1)** | **||x10-4**  **(cm-1)** | **||x10-4 (cm-1)** |  |
| TZCL1  TZCL2  TZCL3  TZCL4  TZCL5 | 3.417  3.390  3.396  3.370  3.365 | 3.283  3.299  3.330  3.274  3.269 | 1.912  1.928  1.924  1.938  1.941 | 1.991  1.981  1.962  1.996  1.999 | 191.08  181.81  181.67  174.19  177.88 | 47.77  45.45  56.60  58.06  57.69 | 61.07  62.49  60.98  64.63  65.21 | 35.42  34.24  32.57  35.92  36.28 | 7.828  3.462  1.961  10.022  18.281 |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sample code** | **TeO2** | **CdO** | **ZnO** | **Li2O** | **V**2**O5** |
| TCZL1  TCZL2  TCZL3  TCZL4  TCZL5 | 64  64  64  64  64 | 15  15  15  15  15 | 20  15  10  5  0 | 0  5  10  15  20 | 1  1  1  1  1 |

**Table 1.2.1 Compositions of TCZL glass system (mol %)**

**Table 1.2.2 Physical parameters of TCZL glass system.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample**  **Code** | **Density**  **ρ (g/cc)** | **Molar Volume**  **Vm (cc/mol)** | **Oxygen Packing**  **Density(O.P.D)(mol/l)** | **Optical basicity**  **(Λ)** |
| TCZL1  TCZL2  TCZL3  TCZL4  TCZL5 | 5.629  5.449  5.329  5.208  5.053 | 24.780  25.528  26.036  26.564  27.309 | 67.794  65.809  64.526  63.241  61.516 | 0.988  0.978  0.967  0.957  0.946 |

**Table 1.2.3 FTIR band position of TCZL glass system (VERIFY\*\*\*\*\*)**

|  |  |
| --- | --- |
| **Sample Code** | **Band position (cm-1)** |
| TCZL1  TCZL2  TCZL3  TCZL4  TCZL5 | 440 674 760 912  438 680 752 904  438 682 758 901  442 682 761 895  446 688 780 888 |

**Table 1.2.4 FTIR band assignments of TCZL glass system**

|  |  |
| --- | --- |
| **Wavenumber (cm-1)** | **Assignments** |
| 440-446  674-688  760-780  888-912 | Vibrations of CdO and ZnO tetrahedral  Streching vibrations of Te-O bonds in TeO3 and TeO4 groups  Vibrations of Te-O-Te / Te-O-Zn bonds which suggests the formation of TeO4 units and at the expence of TeO3 units  Streching vibrations of Te-NBO and metal-NBO vibrations |

**Table 1.2.5 Raman band position of TCZL glass system**

|  |  |
| --- | --- |
| **Sample Code** | **Band position (cm-1)** |
| TCZL1  TCZL2  TCZL3  TCZL4  TCZL5 | 216 410 656 750 895  221 424 663 748 881  223 440 660 750 880  228 444 663 753 884  232 451 665 745 873 |

**Table 1.2.6 Raman band assignments of TCZL glass system**

|  |  |
| --- | --- |
| **Wavenumber (cm-1)** | **Assignments** |
| 215-232  410-451  665  745-750  870-895 | Cd-O vibrations  Symmetric stretching vibrations of Te-O-Te linkages and vibrations of  Zn-O bonds from ZnO4 groups  Antisymmetric stretching vibrations of Te-O-Te linkages constructed by  two unequivalent Te-O bonds  Te-O streching vibrations of TeO3+1 and TeO3groups  Streching vibrations of Te-Non bridging oxygens, vanadium-Non  brdging oxygens bond present in TeO3 tp units or in TeO3+1 polyhedra |

**Table 1.2.7 DSC Parameters of TCZL glass system**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample code** | **Tg (** | **Tx (** | **Tp (** | **Tx – Tg (** |
| TCZL1  TCZL2  TCZL3  TCZL4  TCZL5 | 325  273  261  247  227 | 420  336  310  288 | 438  353  336  297 | 95  75  62  61 |

**Table 1.2.8 Optical parameters of TCZL glass system.**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Sample code** | **CutOffWave Length(nm)** | **Optical Energygap Eopt(eV)** | **Urbach Energy ∆E (eV)** | **BandTailing Parameter(B) (cm eV)** | **Refractive Index (n)** | **Molar Refractivity (Rm)** | **Metallizatin Parameter (M)** |
| TCZL1  TCZL2  TCZL3  TCZL4  TCZL5 | 557  540  528  506  494 | 2.241  2.372  2.431  2.482  2.554 | 0.886  0.651  0.245  0.620  0.632 | 69.909  85.902  86.686  93.368  76.900 | 2.638  2.590  2.569  2.552  2.528 | 16.485  16.736  16.958  17.206  17.550 | 0.334  0.344  0.348  0.352  0.357 |

**Table 1.2.9 Spin Hamiltonian parameters of TCZL glass system.**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Sample code** | **(Kg Gauss)** | **(Kg Gauss)** |  |  | **X 104**  **(cm-1)** | **X 104**  **(cm-1)** | **||x10-4**  **(cm-1)** | **||x10-4 (cm-1)** |  |
| TCZL1  TCZL2  TCZL3  TCZL4  TCZL5 | 3.602  3.618  3.608  3.579  3.612 | 3.486  3.501  3.491  3.511  3.496 | 1.934  1.925  1.931  1.946  1.929 | 1.998  1.990  1.995  1.984  1.993 | 193.798  195.312  195.312  185.546  193.798 | 58.139  68.359  58.593  48.828  58.139 | 82.009  83.572  82.593  81.199  82.976 | 36.235  35.370  35.930  34.790  35.681 | 20.372  6.395  11.161  3.125  8.251 |