Abstract

The main motivation of this thesis is to study the long standing problem of mixed alkali effect (MAE) in oxyfluro vanadate glass systems from the point of view of structural arrangement and to investigate the effect of two rare earth ions, namely, erbium and europium on the structure of tellurium dioxide based glass. In glass science, it is well known that when one alkali in a glass matrix is gradually replaced by another alkali, leads to a non-linear variation in some of the physical properties. There are many a theories trying to explain this effect. Recently the renewed interest lies in explaining MAE in-terms of structural consideration. Rare earth (RE) ion doped glasses are of interest in a variety of applications in photonics because of the special optical properties exhibited by these materials. Atomic like *f-f* transitions of RE ions depend on the local environment of the these ions. A particular glass matrix may be able to bring out the optical properties of a RE ion better than the other matrix. In this regard structural characterization of a glass matrix with different RE ions for optical properties is of importance. Spectroscopic techniques are best suited to investigate structural arrangement in glasses and in this thesis we have used techniques like Raman, electron paramagnetic resonance (EPR), impedance, photoluminescence and UV- visible absorption spectroscopies.

The thesis comprises of five chapters and an appendix. Chapter 1 consists of brief introduction of general properties of glasses and their behavior under different spectroscopic techniques. Chapter 2 deals with the sample preparation and the experimental techniques

used in this work. Chapter 3 elaborates on the Raman and EPR spectroscopic studies on the structural arrangement of the mixed alkali oxyfluro vanadate glass systems. Chapter 4 focuses on the ac and electrical modulus analysis to study the MAE in the above samples. Chapter 5 deals with the optical spectroscopic techniques used to study the compatibility of RE ions (erbium and europium) with the tellurium dioxide based glass matrix.

Chapter 1: Disordered materials pose a challenge to understand their structure mainly because of their random arrangement of the constituent units. In this chapter the glassy systems and the different experimental techniques used to study them are discussed in general. The behavior of glassy systems to the external stimuli in various frequency ranges is highlighted. A short review of mixed alkali effect in glasses mainly covering the advances in the last two decades is given. Brief outline of the theory of Raman, EPR and ac impedance spectroscopy are given.

Chapter 2: This chapter discusses the major experimental techniques used in the thesis to study the glass systems at block diagram level. The Raman and EPR spectrometers are discussed. Experimental technique used in ac impedance measurement is outlined. Different methods of preparing glass are listed and melt quenching technique is discussed in detail.

Chapter 3: This chapter discusses the results and analysis of Raman and EPR study in oxyfluoro vanadate glasses emphasizing MAE. The glass having batch formula $40V_2O_5$ - $30BaF_2$ - (30 - x) LiF - xRbF (x = 0 – 30) is prepared by melt quenching technique. Raman spectroscopic study in back scattering geometry is performed to see the effect of alkali ions on the V – O bond length of VO_6 polyhedra in the glass. The de-convoluted Raman peaks corresponding to V = O and VO_2 are considered and the effect of alkali mixture on these bonds are studied.

- The peak shift of V = O and VO_2 bonds shows that V = O is affected only a little by the replacement of lithium (Li) by rubidium (Rb), while VO_2 bond gets affected

to a larger extent.

- From the peak shift the most probable value of the bond length and the spread in it are estimated. The bond length corresponding to V = O is found to increase and that of VO_2 decrease as a consequence of alkali replacement.
- From the FWHM of the corresponding Raman peaks, it is concluded that O - Rb coordination sphere around VO_6 polyhedra is more homogeneous than either O – Li or O - Li /Rb coordination.

These results are published in J. Non-Cryst. Solids **370** (2013) 6.

EPR studies on the samples are carried out in X band frequency and spin – Hamiltonian parameters were extracted by simulating and fitting the EPR spectra to experimental data using EasySpin which is a Matlab toolbox.

- It is observed that the ratio $\triangle g_{||}/\triangle g_{\perp}$, which is a measure of tetragonality of octahedral crystal symmetry of V_2O_5, varies non-monotonically with Rb content.
- A model based on this observation is proposed. The essential idea of this model is that Rb atoms that are substituted for Li atoms initially prefer terminal positions over planar positions. Continued substitution then replaces planar Li atoms. It is seen that this model of "preferential substitution" explains the observation very well.
- Another observation is that the EPR signal intensity, which is due to concentration of V^{4+} ions, also shows non-monotonous behavior with Rb content. This is also explained using preferential substitution, taking into consideration the oxidation states of the vanadium ions.
- The value of $\triangle g_{||}/\triangle g_{\perp}$, is a minimum for all rubidium environments around V_2O_5, which infers that Rb coordination is more symmetric than all Li or Li–Rb.
- A good correlation is found between Raman and EPR study of the above system.

These results are published in J. Phys. Chem. A **118** (2014) 573.

Chapter 4: The chapter brings out the results of ac conductivity and electrical modulus study of MAE in the glass system mentioned above. The Agilent 4294A precision impedance analyzer operating in frequency range 40 Hz to 110 MHz, is used for performing impedance and capacitance experiments carried out in this thesis. Impedance measurements in our studies are performed in sandwich geometry.

- Room temperature dc conductivity shows a decrease as Li is replaced by Rb and reaches its minimum - five orders less than its all Li value at 0.33 molar fraction of Rb, which is attributed to MAE. This observation is explained using the structural aspect.
- Using the linear response theory the number of mobile ions participating in the conduction is estimated.
- Imaginary part of the electrical modulus is fitted to Kohlrausch – Williams – Watts (KWW) relation by using a complex nonlinear least squares fitting procedure given by Bergmann.
- The stretching parameter β estimated from the above procedure is found to exhibit MAE. The observed variation in β with Rb mole fraction is explained by taking into considerations the contributions from fast and slow processes, and coupling between different relaxing sites.

The manuscript is under preparation.

Chapter 5: This chapter illustrates the optical study of RE doped TeO_2 based glasses to determine the suitability of a particular RE ion with a given glass matrix. TeO_2 based glasses having a general formula (in mol %) $65TeO_2$ – $5BaF_2$ – $30ZnF_2$ (TBZ) were prepared by usual melt quenching technique. RE doping was done at the expense of TeO_2. 3 mol % of Eu or Er are added to prepare RE doped glass. Raman, PL, UV-visible absorption studies are carried out on the glass samples.

- From the peak shift, intensity variation and FWHM of the Raman spectra of the

glass samples it is observed that Eu doped TBZ glass has a greater tendency towards depolymerizing the glass matrix by influencing the conversion of TeO_4 units into the formation of TeO_3 units.

- PL spectra of the glass samples shows emission due to different possible transitions. Position of the peak of the de-convoluted spectra shows the position of the particular Stark component and the FWHM is a measure of the inhomogeneous broadening.
- The UV-visible absorption spectra are used to calculate the optical density and fitted to the Mott equation to determine the band edge of the glass samples. It is seen that Eu doped TBZ glass has a lesser band gap than that of Er doped glass.

The manuscript is submitted to Bul. Mat. Sci.

Appendix : This consists of a collection of details of EDS study carried on the VBL series glasses and some MATLAB codes used to simulate the EPR spectrum for VBL series glasses.