Abstract

The superionic glass system $(50-x)P_2O_5$-$xAgI$-$40Ag_2O$-$10Fe_2O_3$, [x= 0,5,10,15,20,30] were prepared by casting the melt mixtures of appropriate amounts of $NH_4H_2PO_4$, AgI, Ag_2O and Fe_2O_3 in the powder form . The mixture was heated at 950 °C for 6 hrs and the melt was poured on stainless steel plate kept at 0.0 °C.

The obtained glass systems have been characterized using X-ray diffraction , Infrared absorption (IR) , differential thermal analysis (DTA) and Mossbauer effect (ME) spectroscopy.The X-ray diffraction pattern showed that no sharp peaks appeared which confirm the amorphous nature of the prepared glass system. The Infrared spectroscopic analysis (IR) showed the structural groups and different chemical bonds such as PO_4 , FeO_4 , P=O , $P\text{-}O^-$, P-O-P and P-O-Ag which characterizing phosphate glasses.The DTA study illustrates an endothermic peak arouned (356 – 375 K) indicating the glass transition temperature (T_g) and an exothermic peak arouned (528 – 761 K) refers to the crystallization temperature (T_c) of the glasses.

Mossbauer spectra showed that iron ions occupy only the ferric state [Fe^{3+}] and consequently it occupies the tetrahedral coordination state which revealed also that iron ions are most probably occupy the network forming positions in these glasses . Mossbauer parameters showed that all samples are considered paramagnetic host glass around the iron ions.

The ac conductivity $\sigma_{tot}(\omega)$ of the glasses are studied as a function of frequency (50 Hz- 5 MHz) in temperature range (303-513 K).The obtained data obey the following relation , $\sigma_{tot}(\omega) = \sigma_{dc} + A\omega^S$. The obtained values of the

power S are less than one correspond to the successful hopping motion where S>1 correspond to the unsuccessful hopping motion.

The zero frequency conductivity , σ_{dc} , of the glasses are studied as a function of temperature which obeys Arrhenius plot . The values of σ_{dc} lie in the range ($7.97x10^{-5} - 9.85x10^{-1}$ $\Omega^{-1}.cm^{-1}$) and activation energy (0.209–0.423 eV) confirm the superionic conduction in the present glasses.

The very hight frequency conductivity , σ_{bl} , of the glasses are studied as a function of temperature which obeys Arrhenius plot and revealed that one type of conduction mechanism dominates at high frequencies .

The dielectric properties of the prapered glasses have been studied between room temperature and 513 K in the frequency range (50 Hz-5 MHz).The result showed that , the dielectric constant ε' decreases with increasing frequency and shifted to higher values as the temperature increases . In addition , the dielectric loss ε`` attenuates as the frequency increases and shifts to higher values as the temperature increases. Also the peak in ε``-T relation appears and it shifts to higher temperature range with increasing frequency .The tan δ –F curves shows a maximum at a certain frequency which is shifted towardes higher frequency with increasing temperatures. This behaviour is characterizing the ionic glasses and consistent with Debye model for dielectric relaxition.

The obtained values of relaxation time τ attenuate with increasing temperature obeying Arrhenius relation .The charge carrier concentration are estimated which increases when the xAgI content was increased and also increases when the temperature was increased and subsequently the diffusion

coefficient D is calculated which show an increase with increasing temperature

The effect of asymmetric electrodes (Ag/SE/Ag_2S) on conduction and dielectric properties of superionic solid electrolyte powder show that the Ag_2S forms a good blocking with solid electrolyte glass which is suitable for solid battery applications.

The I-V characterestic relationships , for the superionic solid electrolyte powder using asymmetric electrodes in the forward and backward direction , showed a similar metal-semiconductor Schottky diode rectification. Accordingly,the superionic solid electrolyte glass for the rechargeable battery application was performed.The study was extended to the effect of solid electrolyte thickness , solid electrolyte prepared using different pressures , different circuit load resistances , different ambient temperatures , different annealing times and different storage times on the charging-discharging of the obtained solid electrolyte batteries.

The results of superionic solid electrolyte glass for solid electrolyte battery application at different conditions showed that , the smaller the electrolyte thickness and /or the higher pressures results in an increase of both charging and discharging current as well as the discharging voltage . In addition , as the load resistance increases both cell voltage and discharge current increase which controls the battery current drain . Also the cell voltage and discharge current showed lower values with increasing ambient temperature because of the solid electrolyte structure relaxation assistes charge leakage .The values of the cell voltage and discharge current for the virgin sample are higher than these of heat treated sample because of expected barrier height reduction as well as solid electrolyte amorphous-amorphous transition which releases the structure stresses. Also , the cell voltage decreases as the storage time increased which can be attributed to the charge leakage (recovery process).