
CHAPTER 7
DISSUSSION

The materials $x\text{CuI}-(1-x)\text{AgI}$, ($0.1 \leq x \leq 0.4$) have been prepared by the sintering method. The sintering temperature chosen was $250\text{ }^\circ\text{C}$ which is about half the melting point of AgI. At this temperature, CuI exists as γ (zincblende) –CuI and AgI should have undergone transformation from γ -AgI to β -AgI and finally to α -AgI. It is expected that the varying composition of AgI and CuI and the sintering process which lasted for 5 hours will produce materials of different electrical properties.

Since these materials were prepared by pelletizing the mixtures, it is expected that there will be grain boundaries at the surface and also in the bulk of the sample. Thus, it is expected that the Cole-Cole plot of these samples exhibit two semicircles or part of two semicircles. The first semicircle will show the bulk resistance and the second semicircle will show the grain boundary resistance. This has been shown in Figure 4.1 to Figure 4.5. Grain boundary resistance will impede the transport of charge carriers and reduce the conductivity of the sample. The value of R_b has increased to $(1.66 \pm 0.50) \times 10^5 \Omega$ for the pellet $0.1\text{CuI}-0.9\text{AgI}$ compared to $(2.51 \pm 0.74) \times 10^4 \Omega$ for pure AgI. However, the decrement in R_b started when more than 10 wt % CuI is added to the binary system. The addition of CuI was stopped at 40 wt % because additional amount of CuI decreases the mechanical strength of the pellet. The conductivity increased as the amount of CuI increased to 40 wt %.

On addition of 10 wt % CuI to the pellet content, the conductivity decreased. This can be attributed to the increase in grain boundary resistance in the material by more than one order of magnitude from $(5.87 \pm 0.19) \times 10^4 \Omega$ to $(1.58 \pm 0.49) \times 10^6 \Omega$. As a result, the bulk resistance also increases. On addition of 20 wt %, 30 wt % and 40 wt % of CuI, the conductivity increases. This is due to the decrease in grain boundary resistance and bulk resistance to $(1.31 \pm 0.03) \times 10^3 \Omega$ and $(2.84 \pm 0.64) \times 10^3 \Omega$ respectively at 40 wt % CuI or $x = 0.4$. The reduction in grain boundary resistance is accompanied by the reduction in bulk resistance. Reduction in grain boundary resistance implies that the number of grain boundaries have decreased. The decrease in grain boundary is attributed to the sintering process which has merged the grain boundary and probably forms a more conducting phase to which the charge carriers can easily be transported. Values of R_b and R_{gb} are listed in Table 4.1. Hence, it can be inferred that the increase in conductivity with CuI content from 20 wt % onwards as depicted in Figure 4.6 is due to the decrease in R_{gb} which leads to decrease in R_b as the bulk material contains less grain boundaries.

The variation of total conductivity (see equation (4.1)) with frequency at different temperatures for $x\text{CuI}-(1-x)\text{AgI}$, ($0.1 \leq x \leq 0.4$) are given in Figure 4.7 to Figure 4.11. It can be seen from these figures three distinct regions viz., a region of decreasing conductivity with decreasing frequency, a region of frequency independent conductivity and a region where conductivity increase with frequency. In the low frequency region, the decreasing in conductivity with decreasing frequency is due to electrode polarization effects at the electrode and pellet interface. As the frequency decreases, more and more charge accumulate at the electrode and pellet interface, which lead to a decrease in charge carriers in the bulk that results to the drop in conductivity. In the intermediate frequency region between 4 to 5 kHz, the conductivity is almost constant and found to be frequency

independent. The plateau value is equal to the true d.c conductivity. In the high frequency region, closer to the relaxation times, the mobility of the charge carriers is high and hence, the conductivity increases with frequency. It is to be noted that in some samples containing 30 wt % and 40 wt % CuI, the three distinct regions may not be quite observable. For example, the d.c plateau may not be easily observed. For sample containing 20 wt % the d.c plateau is not so visible at 423 K. However, the d.c conductivity at different temperatures can be determined experimentally and verified by calculating the conductivity at $Z_r = R_b$ (Figure 4.12 to 4.16).

The graph of d.c conductivity versus $1000/T$ for $x\text{CuI}-(1-x)\text{AgI}$, ($0.1 \leq x \leq 0.4$) are depicted in Figure 4.12 to Figure 4.16. The hump in the graph which is more visible at high AgI content has been attributed by Kumar et. al (2003) to the interfacial phase transition due to strong surface interaction aided by the small difference in free energy between the competing β -AgI and γ -AgI. For the pure AgI sample, the abrupt change in the slope of the graph occurs at 420 K. For the sample containing 90 wt % AgI at 412 K. For sample containing 80 wt % AgI at 387 K. For sample containing 70 wt % AgI at 386 K and for sample containing 60 wt % AgI at 385 K. The change in slope could be related to the phase transition temperature of AgI. The sudden increase in the conductivity observed around 400 K in the case of all the samples reveals the presence of α -AgI as one of the phases in these compositions, since β to α phase transition of AgI is known to give sudden increase in conductivity at this temperature (Murugesan, Wijayasinghe, Bergman, 2008). A corresponding plot of pure AgI sample is shown in Figure 4.12 as well. It is clear from the Figure 4.12 that the magnitude of the sudden change in conductivity for pure AgI at 420 K decreases to 40 wt % AgI at 385 K which suggests that the increasing amount of CuI into

the binary system fasten the phase transition to α -AgI. This is quite opposite to that observed by Kumar et. al (2003) who prepared their samples by the gradual addition of the required molar aqueous solution of the silver and copper salts. The trend however quite similar to that observed in the case of bromine substituted AgI.

The dielectric constant and dielectric loss at room temperature for $x\text{CuI}-(1-x)\text{AgI}$, ($0.1 \leq x \leq 0.4$) follows the trend of conductivity with increase in CuI content at room temperature. The dielectric constant for pure AgI shows the decrease in $\epsilon_r(\omega)$ after 363 K. It is known that γ -AgI changes to β -AgI at 137°C (410 K). It may be possible that the drop in $\epsilon_r(\omega)$ is indicating to this conversion. The sintering effect at 250°C for 5 hours may have accelerated the conversion from γ - to β -AgI after 90°C . This could also be the reason why β -AgI peaks are observed in the XRD pattern for pure AgI (Figure 6.1). This may also be true for 0.1CuI-0.9AgI but the incorporation of CuI increases $\epsilon_r(\omega)$ at 393 K instead of 403 K as in pure AgI. This is an indication that the incorporating of CuI is stabilizing samples containing γ -AgI. With the incorporation of 20 wt% CuI, this transition in $\epsilon_r(\omega)$ after 363 K is no longer observed. This is also true for the sample with 40 wt% CuI further strengthen the inference that CuI is stabilizing γ -AgI. In fact in the XRD pattern of samples containing 20 wt % to 40 wt % CuI, no β -AgI peaks are observed. It is not understood why the sample with 30 wt% CuI shows a drop in $\epsilon_r(\omega)$ at 403 K to 423 K. However this drop occurs at temperatures higher than that for sample with 10 wt % CuI implying the stabilizing effect of CuI on γ -AgI. From the graph of $\ln \epsilon_i$ versus $\ln \omega$, the value of exponent s was evaluated for each temperature. A plot of s versus T indicates that the

transport mechanism can be understood to follow the QMT model since s seems to be quite independent of temperature.

Modulus representation in particular M_i versus frequency indicates that pure AgI and those containing 10 wt % and 20 wt % CuI are ionic conductors (Mellander and Albinson, 1996). The long tail in the low frequency region for M_r versus log frequency and M_i versus log frequency indicates that the samples are capacitive in nature. Samples with 10 wt% CuI and 20 wt% CuI show relaxation peaks at the high frequency end. However, for samples with 30 wt% and 40 wt% CuI, the samples could be mixed conductors since CuI is a mixed electron-hole conductor at room temperature as the amount of CuI has increased in these samples. Even temperature studies confirmed the absence of peaks for samples containing 30 wt % and 40 wt % AgI. Should these samples remain ionic in nature, peaks should appear with increase in temperature.

Since the sample with 10 wt% CuI has the lowest conductivity, it also has the largest relaxation time compared to other samples containing CuI as depicted in Figure 5.41. In general, the relaxation time tends to increase with temperature and saturate at high temperatures. This shows that conductivity of the sample is thermally assisted

From XRD, it can be seen that all samples produce a diffraction broadening which can be assumed arises from small crystallites and internal stresses (Mohan and Sunandana, 2004).

The crystallite size, t of the samples prepared can be calculated from full width at half maximum (FWHM) of prominent peaks using Debye-Scherrer formula:

$$t = [(0.90\lambda) / (B \cos \theta)]$$

Here λ is the wavelength of the X-ray emission, B is the FWHM, and θ is the Bragg's angle. Figure 6.11 shows the crystallite size versus wt % of CuI for $x\text{CuI}-(1-x)\text{AgI}$ system, ($0.1 \leq x \leq 0.4$). Bigger crystallite size was observed in 0.1CuI-0.9AgI, because it has the highest intensity and γ -AgI phases. With addition of more than 20 wt % CuI, crystallite size decreases.

From the results as our preceding discussion, it can be deduced that samples containing from 10 wt % to 20 wt % CuI have Ag^+ ions as the main charge carrier and samples with more than 20 wt % CuI are mainly electron and hole conductors.