CHAPTER 3

EXPERIMENTAL METHODS

3.1 Sample Preparation

The desired weight ratios of AgI and CuI were weighed and put in an agate mortar and ground until the two compounds have been well mixed. The mixtures were then pelletized at pressure of 400 atm using an ENERPAC hydraulic press. The diameter of the pellets is 2 cm. The pellets were heated in a furnace at 250°C for five hours and then cooled down to room temperature. The weight ratios of AgI and CuI chosen in this work is shown in Table 3.1.

Table 3.1: Weight ratios of AgI and CuI used to prepare AgI-CuI pellets in this work.

AgI/gram	CuI/gram	Weight % CuI	Weight % AgI
2.0	0.0	0	100
1.8	0.2	10	90
1.6	0.4	20	80
1.4	0.6	30	70
1.2	0.8	40	60

3.2 Sample Characterization

3.2.1 Impedance Spectroscopy

Impedance Spectroscopy is a tool for determining the bulk, grain boundary and charge transfer resistances. Impedance spectroscopy refers to the measurement of real and imaginary parts of impedance at different frequencies. Thus, it is possible to differentiate the true bulk conductivity with conduction due to the grain boundary, electrode-electrolyte junction and other relaxation phenomena. Accurate measurements of electrical conductivity is useful for the characterization of ionic and electronic conductors but the interpretation of ionic conductivity can be complicated due to the interfacial problems (Chandra, 1981)

In impedance spectroscopy, an alternating voltage $V(t) = V_m \sin(\omega t)$, is applied across the sample, where V_m is the voltage amplitude, $\omega = 2\pi f$, with f being the frequency, which changes throughout the experiment until the range is completed. The resulting current that flows through the sample is $i(t) = I_m \sin(\omega t + \theta)$. Here θ is the phase difference between the voltage and the current. θ is zero for a purely resistive behavior, $I_m = V_m / Z$ where Z is the amplitude of impedance.

Impedance is a more general concept than resistance because it takes phase difference into account and can be expressed as a complex quantity $Z(\omega) = Z_r + jZ_i$ where Z_r is the real impedance and Z_i is the magnitude of imaginary impedance. Thus, the magnitude of the real and imaginary impedance can be written as:

$$Z_r = Z(\omega)\cos\theta$$

$$Z_i = Z(\omega)\sin\theta$$

The relationship between complex impedance and complex admittance is given by:

$$A(\omega) = \frac{1}{Z(\omega)}$$

$$= \frac{Z_r}{Z_r^2 + jZ_i^2} - \frac{jZ_i}{Z_r^2 + jZ_i^2}$$

The relationship between complex permittivity and complex impedance is given by:

$$\varepsilon(\omega) = \frac{1}{\mu Z(\omega)}$$

$$= -\frac{Z_i}{\omega C_0(Z_r^2 + Z_i^2)} - \frac{jZ_r}{\omega C_0(Z_r^2 + Z_i^2)}$$

The relationship between complex electrical modulus and complex permittivity can be evaluated from the following equation:

$$M(\omega) = \frac{1}{\varepsilon(\omega)}$$

$$= \frac{\varepsilon_r}{\varepsilon_r^2 + \varepsilon_i^2} - \frac{j\varepsilon_i}{\varepsilon_r^2 + j\varepsilon_i^2}$$

The symbols in the above equations are defined by:

$$\omega = 2\pi f \quad \text{(angular frequency)}$$

$$C_0 = \text{vacuum capacitance}$$

$$Z_r = Z \cos \theta$$

$$Z_i = Z \sin \theta$$

$$j = \sqrt{-1}$$

$$\mu = j\omega C_0$$

The four basic response quantities stated above can be denoted by a general term called immittance, I (ω) = I$_r$ + j I$_i$. The relations between the four basic immittance functions are listed in Table 3.2.

Table 3.2: Relations between four basic immitance functions.

	M	Z	Y	E
M		MZ	μY^{-1}	ε^{-1}
Z	$\mu^{-1} M$		Y^{-1}	$\mu^{-\varepsilon}$
Y	μM^{-1}	Z^{-1}		$M\varepsilon$
E	M^{-1}	$\mu^{-1} Z^{-1}$	$\mu^{-1} Y$	

Earlier studies revealed that the impedance spectra representing polarization events in a solid sample are similar to the semicircles obtained from a series equivalent circuit comprising a resistor and a capacitor connected in parallel. In fact, the response of a single parallel RC circuit in the complex impedance plane for a frequency range wide enough is a perfect semicircle (Badwal 1988), intersecting the real axes (Z_r) at 0 and R, the centre

which is $(\frac{R}{2},0)$. This distribution of impedance, known as Debye type is ideal and is

seldom observed with experimental data due to dispersion of local conductivity and

dielectric loss. The phenomenon is physically explained by the variation of the capacitive

effect with frequency. The semicircles representing the actual processes have their centre

below the Z_r axis and the corresponding distribution of the impedance is known as Cole-

Cole type. In this case, the response of a single parallel RC circuit is an arc the radius of

which is bigger than R and its centre A is $(\frac{R}{2},\frac{R}{2}\times\tan\beta)$ where β is the angle of

depression.

In both Debye and Cole-Cole distributions, there is a characteristic frequency f at

which the imaginary part of the impedance is maximum. The peak frequency determines

the relaxation time, τ_0=RC of the process. In ionic transport occurs inside the bulk of the

material, the time constant, τ_0 must be interpreted as the inverse of the rate constant of the

exchange process between the complexion sites. Therefore, τ_0 may be correlated with the

level of the conductivity. The real part of the conductivity varies with frequency as a result

of the distribution of relaxation time (Julien and Massot, 1990).

To account for the depressed semicircle and spike inclination, a type of circuit

element called the constant phase element (CPE) is required. The equivalent circuit for such

a semicircle consists of a CPE in parallel with a resistor. The impedance of the CPE, Z_{CPE}

is given by:

$$Z_{CPE} = \mathrm{k}\,(j\omega)^{-\alpha}$$

Here $0 \leq \alpha \leq 1$. When $\alpha = 0$, $Z_{CPE} = k$, the bulk impedance, R_b. When $\alpha = 1$, $Z_{CPE} =$

$-\dfrac{j}{(\omega k^{-1})}$. Here, (ωk^{-1}) is the capacitive resistance with k^{-1} corresponding to a

capacitance C.

In the present work, impedance was measured using a HIOKI 3531 LCR HI Tester that was interfaced to a computer. A micrometer screw gauge was used to measure the thickness of the sample (pellet). The sample was placed in a conductivity mount between two circular blocking stainless steel plates. The mount was then placed in a container filled with silica gel and connected to the HIOKI Tester.

To study ionic conductivity and its temperature dependence, the conductivity mount and the sample was kept in a temperature controlled oven. From the Cole-cole plot or complex impedance plot, the bulk resistance, R_b was determined and the conductivity calculated following the equation:

$$\sigma = \frac{t}{R_b A}$$

Here A is the surface area of the pellet in contact with stainless steel electrode and t is the thickness of the pellet.

3.2.2 X-ray Diffractograms

X-ray diffraction technique is a useful technique to detect the degree of crystallinity of materials. The wavelength of the X-rays is of the same order of magnitude as the distance between atoms or ions in either molecule or crystal. A crystal diffracts an X-ray beam passing through it to produce beams at a specific angle depending on the X-ray wavelength, the crystal orientation and the structure of the crystal.

X-ray diffractometers consist of an X-ray generator, a goniometer, sample holder and X-ray detector such as photographic film or a movable proportional counter. X-ray tubes generate X-rays by bombarding a metal target with high energy (10 – 100KeV) electrons that knock out core electrons. An electron in an outer shell fills the hole in the inner shell and emits an X-ray photon. Two common targets are magnesium and copper .X-ray emission has wavelength of $0.71073 \overset{0}{A}$ and $1.5418 \overset{0}{A}$, respectively. In this present work, a Cu target is used. X-ray can also be generated by decelerating electrons in a target or a synchrotron ring. These sources produce a continuous spectrum of X-rays and require a crystal monochromator to select a single wavelength. The X-ray pattern of salt compositions sometimes shows partially crystalline and amorphous phases. To check for the complexation and crystallinity in salt compositions, the X-ray pattern of the pure salt, and the dispersions must also taken be into account.

Many researchers have used XRD to study the structural behavior of materials whether the material is amorphous or crystalline and to determine the crystallite size of the sample (Sammes, 1997 and Jak, 1997). The structural characterization of AgI-CuI samples

was carried out using monochromatic CuK_α radiation on a Philips X-ray diffractometer Model PW1729. High temperature X-ray powder data was collected on Philips Expert PRO with an Anton Parr high temperature attachment. A platinum heater was used as the stage for the sample. The temperature was controlled with an accuracy of 1K using a Eurotherm temperature programmer. Data was collected with a sealed tube X-ray generator (40kV, 300mA), CuK_α ($\lambda = 1.5418 \overset{0}{A}$) radiation in the Bragg-Brentano mode using a proportional counter. A small amount (~100mg) of sample was ground and mounted on the platinum heater. The XRD patterns were recorded in a flowing helium atmosphere in the Bragg angle range $20^0 < 2\theta < 80^0$ with a scan range of 2^0 per minute at selected temperatures (holding time at end temperature 10 minutes). Silicon was used as the reference material to calibrate the observed sample impurities.

3.3 Summary

To the author's knowledge, sintering process is one of the important techniques in the present work. It has been clearly specified that the phase transition of AgI happened around 420 K. AgI exhibits Ag^+ ion conductivity at temperatures above 147ºC, while CuI is a mixed ionic-electronic conductor up to 473 K. Therefore, the sintering process will be carried out at 250°C to maintain the sample as a mixed conductor. To characterize the sample as ionic and electronic conductors, an accurate measurement of electrical conductivity is needed. Therefore, Electrical Impedance Spectroscopy (EIS) technique will be used to achieve the objective. X-ray diffraction (XRD) technique will be carried out to characterize the structure of AgI-CuI binary system.