CHAPTER 3 Experimental Technique

3.1 Preparation of Sample

3.1.1 Copper(II) 4–Aminobenzoate

40.0 g of copper(II) acetate monohydrate [$Cu(CH_3COO)_2 \cdot H_2O$; MW=199.65)] and 55.0g of 4-aminobenzoic acid ($C_6H_4(NH_2)COOH$; MW=137.14) were mixed in 150 cm^3 acetonitrile in a round-bottomed flask connected to a reflux condenser. The mixture was stirred using a magnetic stirring bar and heated under reflux in an oil-bath for 24 hours. The reaction mixture was left to cool to room temperature. The solid obtained was filtered, rinsed with ethanol and dried in an oven at 60^0C for 30 minutes. The yield is 58.1 g.

3.1.2 Copper(II) 4–Aminobenzoate Doped with Iodine

2.0 g copper(II) 4-aminobenzoate was mixed with a known weight of iodine (Table 3.1) in acetonitrile. The mixture was then stirred using a magnetic stirring bar for 24 hours at room temperature. The solid obtained on filtration was dried at 60^0C for about 30 minutes.

Table 3.1 Percentage of I_2 doped in copper(II) 4-aminobenzoate

Mass of I_2/g	% I_2 *
0.083	4.0
0.174	8.0
0.273	12.0
0.381	16.0
0.500	20.0
0.632	24.0
0.778	28.0

$$*\%\, I_2 = \frac{\text{Mass of } I_2 \times 100\%}{\text{Mass of Copper(II) 4-aminobenzoate} + \text{Mass of } I_2}$$

3.2 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) of copper(II) 4-aminobenzoate and copper(II) 4-aminobenzoate doped with different amounts of iodine were recorded as potassium bromide (KBr) discs.

The samples were finely ground and then mixed with dry spectroscopic grade KBr powder. The mixture was transferred into a hydraulic die and pressed into a transparent disc by applying 8 tonnes of pressure for about 5 minutes. The disc was mounted on a cell holder of the spectrometer.

The instrument used is Paragon 1000 PC FT-IR Spectrometer. The basic setting of the FTIR is showed in Table 3.2.

Table 3.2 Setting for FTIR spectrometer.

Energy Monitor	9511 volts
Range Scanned	400 to 4000 cm^{-1}
Scan Type	Ratio
Number of Scan	20

3.3 Conductivity Measurements

The conductivity of copper(II) 4-aminobenzoate and copper(II) 4-aminobenzoate doped with different amounts of iodine were measured as compressed disc. A two-probe method [1] is employed for this purpose. The samples were initially finely ground and then pressed into disc of diameter approximately 13 mm and thickness less than 1mm using a manual hydraulic pump at 4 metric tonnes of pressure for ten minutes. One side of the disc was painted with silver to form a circular electrode (~10mm) and was left to dry under the heat of an electric lamp for 2 hours. Two circular silver electrodes (diameter~3mm) was painted on the other side, one to act as backup if the other was damage during measurement (Figure 3.1).

The diameters of the electrodes were measured using a travelling microscope and the thickness of the disc was measured using digital vernier calipers. The disc was placed on an aluminium sheet before it was placed on the sample holder.

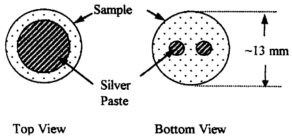

Figure 3.1 Configuration of electrodes

An aluminium sheet sample holder was designed to act as a base for placing the sample. A schematic diagram of the cryostat is shown in Figure 3.2 and the procedure to place the sample in the cryostat is as follows.

1. The clamp from the lower flange of the cryostat was removed and the main cryostat was disassemble from the vacuum jacket. To avoid damage of the wire connection, the upper clamp must not be removed.
2. The sample mounted on an aluminium holder was then screwed onto the platform at the tail of the cryostat.
3. Copper wire was connected to each electrode of the sample using silver paste. The other ends of the copper wires were connected to the terminals on the cold finger.
4. The main dewar was inserted back into the shroud and the clamp was re-installed to seal the vacuum jacket.
5. The two terminals on the cold finger of the cryostat were connected to a source measure unit (SMU).

The schematic diagram in Figure 3.3 shows the circuit connection from the SMU to sample.

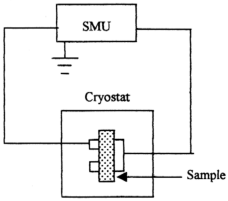

Figure 3.3 Circuit for current-voltage measurement

3.3.1 Room Temperature Conductivity

Room temperature conductivity measurements were taken at atmospheric pressure. All the measurements for conductivity were performed via Metrics software. Measurement for current was done for voltage range from 0-100V for both forward and reverse polarity.

After the measurement, the constant voltage of 60V was applied to the sample for 120 minutes to empty the trap levels in the sample. Another set of measurement was again taken for the forward and reverse polarity.

3.3.2 Low Temperature Conductivity

The set up for the conductivity measurement at low temperature and room temperature is quite similar. For low temperature measurement, the sample was cooled using liquid nitrogen. For greater insulation, a vacuum system consisting of a rotary and a diffusion pump was used to reduce the pressure in the vacuum jacket.

After the disc was placed onto the sample holder in the cryostat, the vacuum jacket pressure was pumped down to reduce the pressure to approximately 1.0×10^{-4} torr or less by using the rotary pump followed by the diffusion pump. After evacuation, the vacuum valve was closed. Periodic re-evacuation is necessary when the liquid hold time become unacceptably short.

A fixed voltage was chosen to be in the ohmic region of the I-V data at room and liquid nitrogen temperature. The variation of current with temperature was measured at the chosen fixed voltage which is 60V in this case.

3.3.3 Annealing Process

The furnace (Carbolite Furnaces Type STF 15/75) was calibrated to ensure that the position where the sample was placed is consistent with the temperature given by the furnace. This was done by plotting a graph of temperature versus position. The position where the graph shows a plateau is the position where the temperature is consistent with the temperature given by the furnace.

Copper(II) 4-aminobenzoate and copper(II) 4-aminobenzoate doped with 20% iodine were annealed in nitrogen ambient from 50^0C up to a maximum temperature of 200^0C for 30 minutes each time in step of 50^0C. The temperature was measured using a digital multimeter (TK 211 2A).

The powder was cooled in nitrogen. It was then pressed into disc using a manual hydraulic pump at 4 metric tonnes of pressure for ten minutes for conductivity measurements.

Reference

1. Sathya Prasanna, Sastry B. S. S. and Radhakrishnan T. P., *Indian Journal of Pure & Applied Physics*, **36**, 748, (1998)