Chapter 2

Experimental Technique
2.1 Introduction

Methods of measuring dc and ac electrical conductivity of single crystal are detailed and presented in this chapter. DC electrical conductivity can be measured using electrometer and ac conductivity & dielectric properties of the crystal can be measured using an impedance analyzer. A Keithley programmable electrometer (model 617) is used with internal source for dc measurements and Hioki impedance analyzer (model 3532), having frequency range 42 Hz to 5 MHz, is used for the ac conductivity measurement. The conductivity cell used for these measurements is discussed in detail. Method of growing a single crystal is also discussed. For the growth of the crystal, a constant temperature bath with digitally programmable temperature controller is used. Since conductivity and dielectrics are anisotropic properties that should be measured in all possible directions, large single crystals should be grown. Growing large single crystal with optical quality is a tedious process. Another objective is the identification of the crystallographic planes. The crystallographic planes can be identified using a well-known method named “stereographic projection”. In this thesis a detailed description is given, how the crystallographic planes are identified using Stereographic projection. This can be cross-checked by a computer program “Shape”.

2.2 Conductivity Measurement Methods

Conductivity measurement has widespread use in industrial applications that involve the measurement of conductivity on materials such as metals, crystals, amorphous materials etc. The unit of conductivity is Siemens/cm (S/cm), which is identical to the older unit of mhos/cm. In this section, methods for obtaining conductivity data on crystals are described. The use of conductivity measurements in research work is very important, and many excellent accounts of various measurement techniques
are already available [2.1], [2.2]. Various methods have been used to measure conductivity properties [2.3], [2.4], [2.5], [2.6] and are discussed in chapter 1. In this thesis the electrical properties of some glaserite crystals are studied.

2.2.1 DC electrical conductivity measurement

The conductivity of a material is measured in terms of its resistivity. Resistance is most often measured with a digital multimeter. Resistance in the gigaohm and higher ranges must be measured accurately. These measurements are made by using an electrometer, which can measure both very low current and high impedance voltage. Two methods are used to measure high resistance, the constant voltage method and the constant current method. In the constant voltage method a known voltage is applied and electrometer ammeter is used to measure the resulting current. In the constant current method, a constant current is forced through the crystal and the voltage drop across the crystal is measured.

![Resistivity measurement method](image)

**Figure 2.1:** Resistivity measurement method.

The basic configuration of the constant voltage method is shown in figure 2.1. In this method a constant voltage is applied in series with the crystal sample and an electrometer. Since the voltage drop across an
electrometer is negligible, essentially all voltage appears across the crystal sample. The resulting current is measured by the electrometer and the resistance is calculated using the Ohm’s law. The resistivity is calculated from the geometry of the electrode and the thickness of the sample. For accurate measurements, the high impedance terminal of the electrometer is always connected to the high impedance point of the circuit to be measured. If not, erroneous measurements may result. This test procedure is described in detail in ASTM [2.7].

2.2.2 Alternating current bridge method

Alternating current measurements are widely used to overcome certain difficulties in dc measurements. Among these are polarization effects in ionic conductors and electrolytes, barriers at internal surfaces and contact resistance. Assuming that the sample is represented by a parallel combination of capacitance and resistance, the values of series resistance and capacitance then describe the unknown directly. Current supply for the bridge is often an ac oscillator or signal generator with frequencies from 20Hz to 20MHz. In the simplest arrangement as shown in figure 2.2 (a 2-electrode cell), a voltage is applied to two flat plates immersed in the solution, and the resulting current is measured from Ohm's Law, the conductance = current/voltage. Actually there are many practical difficulties. Use of dc voltage would soon deplete the ions near the plates, causing polarization, and a higher actual resistance. This can be mostly overcome by using ac voltage, but in that case the instrument designer must correct for various capacitance and other effects. Modern sophisticated 2-electrode conductivity instruments use complex ac waveforms to minimize these effects.
The ac impedance method can be applied also to ionic conducting materials giving more information about the nature of conductivity. In this work there is also another advantage in using the ac impedance method: because the samples were cut into specific directions to measure the conductivity in that direction. Due to relatively small and nearly rectangular (1 mm x 1 mm x 2 mm) samples, the most convenient way to measure the conductivity is to place the sample between two electrodes.

The disadvantage in the ac impedance system is due to the errors caused by the contact resistance between the electrodes and the sample. However, when relatively high frequencies are used (such as 1 KHz) the effect of the contact resistance is negligible.

In ac conductivity measurements a sinusoidal voltage is applied and the current passing through the sample is measured. As a result impedance $Z^*$ is a complex presentation of the ratio of voltage and current maxima (figure 2.3 a).

$$Z^* = \frac{V_{\text{max}}}{I_{\text{max}}}$$
Figure 2.3: a) In the ac impedance method a sinusoidal voltage is applied and the current passing through the sample is measured. b) Impedance spectrum presented in complex plane. $Z'$ and $Z''$ represents the real and imaginary components of impedance $Z^*$. 

Figure 2.4: The $Z'$, $Z''$ or resistance-reactance curve for a resistor and capacitor connected in parallel. The arrow shows the direction of the increasing frequency.

The result may also be represented in a complex plane with $Z^* = Z' - jZ''$ (figure 2.3 b). In the ac impedance measurement the impedance is measured as a function of frequency. The impedance spectrum is typically presented in the $Z'$ - $Z''$ - complex plane. It is possible to construct an equivalent electrical circuit consisting of resistors and capacitors, which have the same frequency response as the measured material (for example figure 2.4). These equivalent circuits give further information on the conduction processes in the material.
Figure 2.5: An example of conductance, G, as a function of frequency.

It is possible to distinguish three regimes from the conductivity versus frequency plots (figure 2.5) [2.8]. The first regime is in the low frequency I and can be attributed to the electrode polarization. In the middle frequency regime II the conductivity is frequency independent corresponding to dc conductivity. In the high frequency regime III the conductivity versus frequency plot obeys Jonscher’s Universal Power law [2.9].

2.3 The Conductivity Cell

For the measurement of ac and dc conductivity a conductivity cell was used. The conductivity cell was designed in such a way that, it must well fit into the temperature circulator bath which was used as the temperature controller (Julabo, Labortechnik GmbH, Germany, model FP 50). The essential parts of the conductivity cell are shown in figure 2.6. The metallic outer case is 22 cm in length. The top lid is removable and is made vacuum tight by using a rubber “O” ring of 10 cm diameter. BNC pins are fixed in this lid for four-probe measurement. The bottom of the outer vessel is brazed to a thick copper plate in order to get good thermal contact with the bath liquid. A metallic tube is welded at the outer case, and can be connected to the vacuum chamber so that the cell can be evacuated. The sample holder is inserted through the top of the cell.
The sample holder (figure 2.7) consists of four small threaded rods with plates fixed to these rods using nuts. The bottom plate is made of copper so that a good thermal contact can be attained when it is placed in the conductivity cell. The sample is placed in between two graphite electrodes, well insulated from the outer chamber. The sample along with electrode is held in between two glass plates with help of a spring-loaded arm fixed at the top of the sample holder. A thin film platinum resistor Pt 100, model CRZ 2005 (Hayashi Denko Japan) is inserted into the copper plate by drilling a small hole in it. The change in the resistance with temperature was noted. The temperature coefficient of the RTD is positive. An approximation of the platinum RTD resistance change over temperature can be calculated by using the constant 0.00385 $\Omega^0C$ [2.10]. This constant is easily used to calculate the absolute resistance of the RTD at any temperature.

$$\text{RTD} (T) = \text{RTD}_0 + T \times \text{RTD}_0 \times 0.00385$$

where RTD(T) is the resistance value of the RTD element at a temperature $T^\circ C$, RTD$_0$ is the specified resistance at $0^\circ C$ and T is the ambient temperature of the RTD. The value of RTD$_0$ for a Pt 100 platinum resistance is 100.
**Figure 2.6:** Details of the conductivity cell.

1. BNC sockets  
2. To Vacuum pump  
3. Outer case  
4. Resting plate  
5. Copper bottom  
6. O Ring  
7. Sample Holder

**Figure 2.7:** A typical sample holder. Enlarged portion illustrates the sample can be mounted between two electrode plates.
2.4 DC Conductivity Measurements

The dc conductivity of the sample was measured using a Keithley (model 617) programmable electrometer with an internal source. In this setup the sample is considered as a resistance. Across the sample a voltage is applied and corresponding current was noted. Using Ohm’s law the resistance $R$ was calculated. From the resistance the resistivity $\rho$ was found out using the relation $R = \rho l/A$ where $A$ is the area of the sample and $l$ is the thickness. The conductivity is the reciprocal of resistivity.

2.5 AC Conductivity Measurements

Ac conductivity is given by [2.11], [2.12]

$$\sigma_{ac} = \omega \varepsilon_0 \varepsilon''$$

Where, $\omega$ is the angular frequency, $\omega = 2\pi f$.

$\varepsilon_0$ is the permittivity of free space,

$\varepsilon''$ is the imaginary part of dielectric constant, $\varepsilon'' = \varepsilon' \tan \delta$

where $\tan \delta$ is the loss tangent related to the phase angle $\theta$, $\tan \delta = |1/\tan \theta|$

$\varepsilon'$ is the real part of dielectric constant, $\varepsilon' = C d/A \varepsilon_0$

where $C$ is the capacitance, $d$ is the thickness and $A$ is the area of the sample. Capacitance $C$ and the phase angle $\theta$ are measurable quantities.

Then ac conductivity is

$$\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon' \tan \delta$$
2.5.1 Conducting an impedance spectroscopy (IS) experiment

The following precautions must be taken when doing the impedance spectroscopy (IS) experiment. When conducting IS at elevated/reduced temperatures the sample holder must be stable at the working temperatures, which can vary from -30°C to 180°C. Also the holder must be electrically inert and non-generative of any spurious currents or voltages. The holder has to be designed to hold the sample at an even pressure and with no movement during the experiment cycle. The sample holder must link the sample to the electronics, generating the signal and analysing the response. All electrical connections are made using insulated wires and kept to the minimum possible length. The cell apparatus should be fully electrically insulating. This will guard against external inductive effects. Such effects can have a significant impact on the results by altering the current and voltage produced by the sample. The leads used were of similar length to reduce differences in the resistance or any capacitance effects, and should be short as possible. The whole system was calibrated using known resistors to reduce the affects of any internal capacitance due to wiring or connections.

The accurate control of temperature is very important when performing an IS experiment. For this a Refrigerated Circulator Bath (Julabo GmbH, Germany, model FP 50) having temperature range from −50°C to + 200°C with temperature accuracy 0.01°C was used. Since the experimental temperature ranges from 30 °C to 150 °C, transformer oil was used as liquid in the bath.

Providing suitable contacts to the specimen is an extremely important aspect of conductivity measurements. These contacts should be appropriate to the material being studied, the conductivity range, the temperature range, temperature and currents required and other conditions of the measurements. Improper contacts may cause most serious problems
for dielectrics studies. So attention must also be paid to them in measuring
the dielectric constant, particularly if ac methods are employed.

The dielectric constant can be determined by measuring the
capacitance of a parallel plate capacitor with sample as the dielectric. The
sample is a 100 or 010 or 001-oriented slice of a single crystal. Different types
of electrodes are available to make electrical contact. These are gold,
platinum, silver, copper etc. Here in this work graphite is used as the electrode
for electrical contact and the advantage of using the graphite as an electrode is
discussed in chapter 1 (section 1.7). Graphite electrodes of size 0.5 mm x
0.5 mm are placed on both sides of the sample to form a capacitor.

Conductive graphite paste is coated on either side of the crystal
sample before mounting the sample in the graphite electrode. This will
ensure that the area of the electrode is the effective area of the sample
crystal only and hence reducing any air capacitance. Silver paste cannot
be used because silver paste can diffuse into the crystal lattice, which will
affect the conductivity measurements. Figures 2.8 and 2.9 shows the
photographs of the dc conductivity measurement setup and a close up
view of the electrometer used. Figures 2.10 and 2.11 shows the
photographs of the ac conductivity measurement and a close up view of
the LCR meter used.

The sample is mounted in a graphite electrode block and kept inside
the vacuum chamber of the conductivity cell. By evacuating the chamber, all
air moisture is removed. Moisture solidifying on the sample when the
temperature is lowered would interfere with its electrical properties. Platinum
RTD is attached to a corner of the sample and connected to a digital
multimeter, which measures the sample temperature analogue of the
resistance. Capacitance and dissipation factor tan δ measurements are taken
using a digital LCR meter with an ac test signal of $1V_{\text{rms}}$ amplitude and 1 KHz frequency. A test fixture interfaces the sample leads to the LCR meter.

Figure 2.8: DC conductivity measurement setup.

Figure 2.9: Close up view of keithley electrometer.
Figure 2.10: AC conductivity and dielectric measurement setup.

Figure 2.11: Close up view of LCR meter.
2.6 Sample Preparation

The sample preparation techniques and the details of the instrument used for the crystal growth are described. The samples prepared were Tripotassium sodium disulphate (K₃Na(SO₄)₂ (or KNS), Tripotassium sodium dichromate (K₃Na(CrO₄)₂ (or KNCr) and Tripotassium sodium diselinate (K₃Na(SeO₄)₂ (or KNSe). These are water-soluble crystals and hence they are grown from their aqueous solutions.

2.6.1 Crystal growth from solution

Growth of crystals from aqueous solution is one of the important methods of crystal growth. The methods of crystal growth from low temperature aqueous solutions is extremely popular in the production of many technologically important crystals. The growth of crystals by low temperature solution growth involves weeks, months and sometimes years. Much attention has been paid to understand the growth mechanism of the process. Though the technology of growth of crystals from solution has been perfected, it involves meticulous work and much patience. A power failure or a contaminated batch of raw materials can destroy months of work. There are several methods for growing the crystals. Every method has its own advantages and disadvantages.

Growth from solutions [2.13], [2.14], [2.15], [2.16], [2.17], [2.18] is the most widely used method of growing crystals. It is always used for substances that melt incongruently, decompose below the melting point, or have several high-temperature polymorphous modifications. Even in the absence of above restrictions the crystal growth from solution is an efficient method. On the other hand, in contrast to other methods like growth from melt or vapour, in solution growth the crystals are not grown in a one-component system. The presence of other components materially affects the kinetics and mechanism of growth.
The methods of growing crystals from solutions are classified into several groups according to the principle by which super saturation is achieved.

1) Crystallization by changing the solution temperature. This includes methods in which the solution temperature differs in different parts of the crystallization vessel (temperature-difference methods), as well as isothermal crystallization in which the entire volume of the solution is cooled or heated.

2) Crystallization by changing the composition of the solution (solvent evaporation)

3) Crystallization by chemical reaction

The choice of the method mainly depends on the solubility of the substance and the temperature solubility coefficient $\delta C_0/\delta T$. For many crystals both the slow cooling technique and the constant temperature solvent evaporation technique can be successfully used.

Bi-directional rotation of the growing crystal and/or solution stirrer is very essential for perfection in growth. For a continuously growing crystal the substance has to be transported to the growing phase from the solution. In a motionless solution the delivery of the substance is by a slow diffusion process. In a pure diffusion regime the supersaturation differs over different areas of the phases. To reduce this non-uniformity of the supersaturation and nutrition of different areas of the phases, and for faster mass transport for increased growth rate, motion of the crystalline solution relative to one another must be ensured. In low-temperature aqueous solutions, rotation of the crystal in
solution or stirring is usually applied. Too vigorous stirring can lead to cavitations or turbulence, which may give wedge shaped crystals.

Seed crystals should be prepared with care; the quality of a crystal is usually slightly better than that of the seed. Particular care should be taken that the surface is not damaged. Spurious nucleation can be a major difficulty. If insoluble particles from the atmosphere are not contaminating the solution, the cause may be in the initial solution. Laboratory grade reagent can contain large amounts of insoluble residues and even high-grade materials may contain some. The care lies in filtering. Sintered filter tend to be more reliable than papers. Spurious nucleation is caused by temperature fluctuation and foreign solid particles in the solution. Spurious nucleation can be prevented for an extent, if dense immiscible liquid (carbon tetra chloride) is added to the solution. Sometimes changes of habit may be achieved by [a] Adding a habit-modifying agent [b] changing the temperature of growth [c] changing the pH of the solution [d] changing the solvent. For a given solute, there may be different solvents. The solvents must be chosen taking in to account the following factors to grow crystals from solutions. A solvent of choice is the one with [a] a good solubility for the given solute [b] a good temperature coefficient of solute solubility [c] less viscosity [d] less volatility [e] less corrosion and non – toxicity [f] small vapour pressure [g] cost advantage. It is known that the choice of solvent provides some control over crystal habit and this effect depends on the interaction of the surface of the crystal as it grows and the solvent molecules. Sometimes this is sufficient to result in the precipitation of a new crystalline phase. Also this effect is related to the influence of impurities or additives upon habit [2.19].
The possible difficulties and their remedies are the following.

[1] Veiling - It can be remedied by decreasing the growth rate, improving the stirring, improving the temperature stability.

[2] Spurious nucleation - It can be prevented by using purer starting materials, filtered solution improving temperature stability, eliminating turbulent stirring, placing a layer of dense immiscible liquid under the solution.

[3] Cracked crystals - It can be remedied by cooling more slowly at end of run and preventing solvent evaporation on removal from solution.


Among the various methods of growing single crystals, solution growth at low temperatures occupies a prominent place owing to its versatility and simplicity. After undergoing so many modifications and refinements the process of solution growth now yields good quality crystals for a variety of applications.

2.7 Constant Temperature Bath

In this section the details of the bath, which has been used for crystal growth at constant temperature by solvent evaporation method and digitally programmable temperature controller, used to grow crystals are discussed. The bath is a glass tank measuring about 24 inches in length, 12 inches in width and 12 inches in height, figure 2.12 illustrates the essential details of the bath. The tank is given 1cm thick heat insulating outer lining made of polyurethane foam. This is to prevent unnecessary heat loss from the tank and hence to reduce the
power required to keep the tank at a regulated temperature above room temperature. For the same reason, thin layer of paraffin oil is poured over the water inside the tank. There is a window with a foam shutter in front of the tank made in the foam lining for observing the growing crystal. Heater coils, which are sealed inside glass tube, are fitted at the sides of the tank so as to get uniform heating. This also prevents any electrical contact between bath water and heater coils. An IC (LM335) temperature sensor enclosed in an oil filled glass tube is kept in the water bath for temperature sensing. Stirring motors are fitted near left and right ends of the bath for uniform temperature distribution. The Photograph of the constant temperature bath is shown figure 2.13.

The solution for crystal growth may be taken in a beaker of 500 ml capacity and can be kept dipped in the bath at a suitable depth by using a bench connected to the adjustable stand. The seed crystal was tied using thin nylon fiber and was hung in the solution. The solution was stirred properly. The stirrers are rotated by dc motors, which can rotate in both directions. The motor is driven by specially designed control circuit, which can periodically reverse the rotation direction. The description of the control circuit was detailed by L. Godfrey [2.20]. The circuit has a provision for adjusting the speed of rotation and also the period of time between rotation reversals can be changed. Further, there is a dead time before a rotation reversal during which no power is given to motor. This dead time is allowing the inertia to die out before reversal. In the absence of the dead time, a jerky movement can be produced which would strain the crystal.
Figure 2.12: A view of the constant temperature bath.

1. Glass tank
2. Heater coils
3. Bath stirrers
4. Solution stirrers
5. Beaker containing solution
6. Growing crystals
7. Temperature sensor
8. $M_1, M_2, M_3, M_4 & M_5$ Motors
9. $S_1, S_2 & S_3$ Adjustable stands

Figure 2.13: Photograph of the crystal growth setup.
2.8 Digitally Programmable Temperature Controller

The designed and constructed digitally programmable temperature controller [2.21] is used to maintain constant temperature of the bath with an accuracy of ± 0.05K (figure 2.14). There is also a provision to reduce the temperature in steps at any desired rate. This is achieved by combing digital and analog circuits. Counters are used in the digital section and OPAMPS are used in the analog section. Using digital to analog converters, voltage corresponding to each digital word is generated and fed to a summing circuit to produce the desired pulse for the solid state relay at a rate fixed by the counters. When the desired lower temperature is reached, the counters should stop counting to avoid thermal shock to the crystal. This is achieved by a combination of logic circuit to produce disable output for the counters, when the counting is completed. The provision to reduce the temperature in steps at any desired rate is used to grow crystals in the temperature reduction technique so that the growth rate of the crystals can be optimised. Good quality crystals can be grown within short duration.

![Photograph of the digitally programmable temperature controller.](image)

**Figure 2.14:** Photograph of the digitally programmable temperature controller.

2.9 Identification of the Faces Using Stereographic Projection

The stereographic net is used to identify the natural faces and axes of the crystal. By knowing the lattice parameters, crystal system and space group
one can construct a stereographic plot. These plots are made with the help of a computer programme ‘Jcrystal’. In this angles between the points in the net were computed and it is compared with measured interfacial angels of natural faces. From this comparison one can easily identify the faces.

Figure 2.15: Photograph of the crystal cutter.

Figure 2.16: Close up view of the goniometer in the crystal cutter.
2.10 Crystal Cutting and Polishing

After identifying the crystal faces the bulk crystal have been cut using a slow speed diamond wheel saw. This diamond saw consists of a thin metal blade with micron sized diamond powder embedded on the surface of the disc. The blade is fixed to a shaft driven by a speed controlled motor. The crystal to be cut is fixed (by gluing it) to a precision movable arm. This movable arm contains the goniometer, micrometer and a counter weight arrangements. The arm can be lowered so that the crystal rests on the rotating blade. The photograph of the crystal cutter is shown in figure 2.15. A close up view of the goniometer of the crystal cutter is shown in figure 2.16. A coolant continuously cools the blade. Liquid paraffin can be used as an effective coolant.

Figure 2.17: Photograph of the crystal polishing unit.
Parallel faces can be cut by adjusting the micrometer screw without disturbing the glued crystal. The cut samples have been polished well. For this a crystal-polishing unit is used (figure 2.17) which consist of a well-faced circular disc made of stainless steel. This disc is attached to a rotation mechanism driven by a speed controlled motor. A removable circular glass plate can be attached over the steel disc so that different grades of abrasive paper can be glued on to a circular glass plate for better result. Finally the crystal is polished well using a cerium oxide powder. Crystals with good optical quality have been prepared using these methods.
References


2.7 American Society for Testing Materials methods D257 titled “DC Resistance or conductance of insulating materials”.


