

Electrical Conductivity and Dielectric Studies of Various Glaserite Crystals: A Review

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Abstract – The electrical conductivity mechanism is proposed as due to hopping of highly mobile charge carriers. Frequency dependent conductivity studies reveal the hopping mechanism in these crystals which obeys Jonschers power law. Electrical conductivity and dielectric studies of three glaserite crystals (Ferroelastic) namely Tripotassium sodium disulphate ((K₃Na (SO₄)₂ or KNS), Tripotassium sodium dichromate ((K₃Na (CrO₄)₂ or KNCr) and Tripotassium sodium diselenate ((K₃Na (SeO₄)₂ or KNSe) were investigated along the crystallographic axes in the temperature region from 303 K to 430 K. Ferroelastic crystals has potential applications in electromodulators, ferroelastic grating and many others. Moreover the ferroelastic crystals under investigation are stable and have high melting point.

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INTRODUCTION

Glaserite (also called apthitalite) has been considered to be either a stoichiometric compound K₃Na(SO₄)₂ forming a solid solution with Na₂SO₄ or a compound NaKSO₄ forming solid solutions with Na₂SO₄ as well as with K₂SO₄. Crystallization of glaserite during isothermal evaporation at 25°C of Southern Tunisian natural brines, when the density of 1.282 was reached has been reported. Apthitalite from Kilauac (Hawaiian Islands) has also been reported and they suggested that the composition is undoubtedly variable, but has been commonly regarded as (K,Na)₂SO₄ with K₂O:Na₂O = 3:1.

The glaserite structure has been originally determined by Gossner and confirmed later by Bcllanaca and Pontonnier et al. (2002). The glaserite structure and its deformed derivatives have been found or can be predicted for (A, C)₂BX₄ solid solutions with cations A = Na, Ag, Mg, Ca, Cd; cations C = K, Rb, Cs, Ti, NH₄, Sr, Ba, Eu and with tetrahedral complexes BX_a = BcF₄, SO₄, SeO₄, CrO₄, MoO₄, WO₄, PO₄, VO₄, AsO₄, SiO₄, GeO₄, etc. Moore. P. B (2003) considered that the formal composition of glaserite could be written as M (3) M(2) M [TO₄]₂. In K₃Na(SO₄)₂, Na atoms occupy the M(j) and K atoms the M(2) and M(3) sites. K. Okada and J. Ossaka (2000) showed that K atoms first fill

the M(3) sites then go to M(2) sites. The electronic structure of SO₄²⁻ ions has been calculated by Bishop et.al.(2006). However the magnetic symmetry of the SO₄²⁻ centers reported are orthorhombic and molecular symmetry is low. It is assumed that the ratio between

the radii of the cations is the governing factor responsible for the formation of glaserite like structure. In glaserite, the cations and anions are arranged in two types of columns in a hexagonal arrangement one containing only cations, Na⁺ and K⁺ (type I) and the other both cations and anions, K and SO₄²⁻ (type II).

Since the ions in each column are tightly bound along this direction, the structure has been considered as hexagonal packing of rods. Glaserite has cation: anion ratio of 2:1. Although many of the glaserite related structures do not satisfy this condition, the discrepancy can be accounted for by imputed ionic vacancies along selected columns, thus the structures of calcium tripotassium hydrogen phosphate CaK₃H(PO₄)₂ and a - tricalcium phosphates has been reported as glaserite. The glaserite like structure are stable for compounds in which the difference between the radii of the M⁺ and M³⁺ cations [$\Delta r(M^+ - M^{3+})$] occupying the M, X and Y positions is in the range $0.59 \leq \Delta r(M^+ - M^{3+}) \leq 0.89 \text{ \AA}$. However, compounds that are characterized by $\Delta r(M^+ - M^{3+}) < 0.59 \text{ \AA}$ and have glaserite like structure are also known. Thus $\Delta r(M^+ - M^{3+})$ for Na₃Fe(PO₄)₂ (Glaserite Structure type) is 0.38 \AA . After the Na₃Fe(PO₄)₂ structure was studied, Morozov et al. (2001) found that the stability range of glaserite structure could be expanded up to $0.375 \leq \Delta r(M^+ - M^{3+}) \leq 0.89 \text{ \AA}$. The electron irradiation induced transformation of apatite to perovoskite via glaserite structure has been reported. The schematic

representation of the condensed model of glaserite is shown in figure 1.

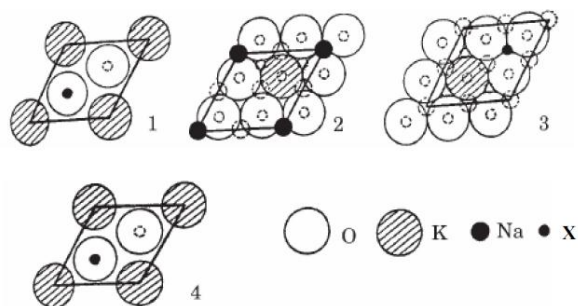


Figure 1: Schematic representation of the condensed model of aphtthalite (glaserite) ($K_3 Na (XO_4)_2$ where $X = S, Cr, Se, \text{ or } Mo$. numbers 1–4 refer to the adjacent sheets formed by O and K packing atoms.

Glaserites has the general formula $A_3C (8X_4)_2$, where A and $C = Na, K, Rb$ and BX_4 tetrahedra = $SO_4, SeO_4, CrO_4, MoO_4$ and WO_4 . The glaserite $K_3Na(SO_4)_2$ is the parent compound for many related compounds, which has been in the focus of intense work owing to their interesting crystal chemistry and importance in mineralogy. Among others $K_3Na(SeO_4)_2, K_3Na(CrO_4)_2, K_3Na(MoO_4)_2$ and $K_3Na(WO_4)_2$ are crystallizing in glaserite type structure. Glaserite crystals are in general very stable in air and having very high melting point. Many members of the glaserite family perform a phase transition from the trigonal to monoclinic form. The transition temperatures seem to be mainly depending on the size of the BX_4 tetrahedron. The main structural difference between the monoclinic and trigonal structure is in the tilting of the BX_4 tetrahedron and the co-ordination of the potassium ions. While in $K_3Na(WO_4)_2$, the transition is finished at around $275^\circ C$, the transition temperature in the corresponding molybdates, $K_3Na(MoO_4)_2$, with $240^\circ C$ is in the same range. The transition in the selenate, $K_3Na(SeO_4)_2$ is lower ($61^\circ C$), while in the chromate, $K_3Na(CrO_4)_2$ it is significantly lower at $-34^\circ C$. In the sulphate glaserite, $K_3Na(SO_4)_2$, the phase transition is found to be at $-203^\circ C$. The B-X bond lengths at room temperature and phase transition temperature of some glaserite compounds is shown in table 1.

Compound	B-X bond length (Å)	Phase transition temperature ($^\circ C$)
$K_3Na(SO_4)_2$ [1.16]	1.472	-203
$K_3Na(CrO_4)_2$ [1.28]	1.639	-34
$K_3Na(SeO_4)_2$ [1.27]	1.654	61
$K_3Na(MoO_4)_2$ [1.29]	1.773	240
$K_3Na(WO_4)_2$ [1.7]	1.848	~ 250

Table 1: B-X bond lengths at room temperature and phase transition temperatures of some glaserite compounds.

ELECTRICAL CONDUCTIVITY

The most important property characterizing the electrical properties of a crystalline solid is the electrical resistance R . The resistance R offered by a conductor to the flow of electric charge is found to be directly proportional to the length (l) and inversely proportional to the area of cross section (A) of the conductor. Therefore $R = \rho (l/A)$ where ρ is the proportionality constant called electrical resistivity. Then $(1/\rho)$ is the electrical conductivity σ . The basic unit of conductivity is Siemens (S) (or mho). Electrical conductivity is an inherent property of most materials, and ranges from extremely conductive materials like metals to very non-conductive materials like plastics or glass. The actual cause of the resistivity must be sought as a deviation from the periodicity of the potential in which the electrons move. It is on this concept that the modern theory of conductivity is based. Deviations from the periodicity of the potential causing resistivity may be due to (a) lattice vibration (b) lattice defects such as vacancies, interstitials and dislocations (c) foreign impurity atoms and (d) boundaries. It is interesting to note that Wein in 1913, before the development of wave mechanics, put forward the hypothesis that the resistivity in pure metals was due to thermal vibrations of the atoms in the lattice. The justification of this idea had to await the development of the band theory. In metals, electrons act as moving charge carriers. The electrical conductivity of a metal is defined by

$$I_x = \sigma E_x$$

where I_x is the current density resulting from an applied electric field E_x in the x-direction. In the case of anisotropic solids, the conductivity depends on direction and σ becomes a tensor.

DIELECTRICS

Dielectrics are material with very few electrons to take part in normal electric conductivity. Dielectric materials have interesting electric properties because of the ability of an electric field to polarize the material to create electric dipoles. A dipole is an entity in which equal positive and negative charges are separated by a small distance. The electric dipole is given by $\mu = qdl$ where q is the charge and dl is the distance.

The simplest arrangement for measuring the components of the dielectric tensor occurs in the conventional thin parallel plate condenser. Here the electric field direction is dictated by geometry to the normal to the plates and the depolarization field is also in this direction. Hence the measurement essentially involves only a single direction. Maintaining the imposed electric field in the presence of the depolarization field, for example by fixing the potential on the capacitor requires additional charges on the

plates, and thus the dielectric slab increases the capacitance. The ratio of the capacitances of the system with either dielectric or vacuum between the plates is given by the ratio of the charge densities at constant voltage

$$D_n/\epsilon_0 E^0 = \epsilon_n/\epsilon_0$$

where E^0 is the applied electric field, D_n is the component of electric displacement vector (D) along E^0 and ϵ_n is the appropriate diagonal element of (ϵ_{ij}) in a coordinate system one of whose axes lines up with the electric field. Obviously D_n is larger than $\epsilon_0 E^0$.

If the direction of the field relative to crystal axes is known, μ_n can be expressed in terms of the components of the dielectric tensor in the crystal system by using the transformations. If the crystal axes are not known, we may choose an arbitrary system of coordinates to specify the dielectric tensor. In that case the slab directions for independent measurements could be along the x, y and z-axes and somewhere in each of the xy, the yz and the xz planes of this system. Once the schemes of the coefficients are known, it may then be examined for additional symmetry by transforming it to other frames of reference.

DIELECTRICS AND DIELECTRIC SPECTRA ANALYSIS

Dielectric materials-

Dielectric materials are basically insulators having the property of storing and dissipating electrical energy when subjected to electromagnetic field. The energy storing property leads to the fabrication of most important constituents of electrical circuit known as capacitors. The dielectric phenomenon arises from the interaction of electric field with different charged particle such as electrons, ions protons and electron shells, which goes to constitute the dielectric material. All dielectric can be subdivided into two-polar and non-polar dielectrics.

A dc field behaviour however provides information about the nature of charge carriers, their mobility, conduction mechanism etc. Whereas studies in ac field provide an information into the electrical nature of the molecular or atomic species, which constitutes the dielectric materials.

Dielectric spectroscopy measures the dielectric permittivity as a function of frequency and temperature. It can be applied to all nonconducting materials. The frequency range extends over nearly 18 orders in magnitude: from the μHz to the THz range close to the infrared region.

Dielectric spectroscopy is sensitive to dipolar species as well as localized charges in a material; it determines their strength, their kinetics and their interactions. Thus, dielectric spectroscopy is a powerful tool for the electrical characterisation of nonconducting or semiconducting materials.

Rather than focus on details of what happens inside the dielectric materials, electrical engineers often analyze dielectrics from a macroscopic perspective. Impedance spectroscopy (IS) is one such macroscopic approach. Conducting an IS experiment on a solid electrolyte system allows a number of characteristics to be determined. The characteristics of interest will depend on the nature of the system. If the system is a single crystal the bulk electrical property will be of interest. In polycrystalline form grain boundary and defect structures will form an interesting part of the spectrum. As IS is a study of interfaces, it is not only possible to gain some insight into the structure of the material but also know how the material is behaving at the surface.

The most commonly used technique for the measurement of dielectric properties is the measure of impedance in the frequency domain. For this type of experiment a single voltage is applied at varying frequencies and the resulting phase shift and amplitude of current are recorded. Phase and amplitude can be directly converted into the real and imaginary components for analysis.

Dielectric relaxation-

The microscopic behavior of a dielectric material under an electric field can be attributed to the polarization phenomena of the charged particles, which constitutes the dielectrics. This may an extra nuclear electron, and positively charged nuclei, anion, and cations etc. The oppositely charged species with a reasonable bond between them will form a dipole which will behave as one unit. These dipoles under an electric field may undergo special translational or rotational displacement, which will be reflected in macroscopic behavior of dielectric. The polarization effect will also be dependent on the nature of the dipole and frequency of the applied field under an ac field but the polarization of the dielectric may not follow the field variation. This displacement due to polarization may persist even when the field is stopped. This gives rise to a decay time to attain the equilibrium and the phenomenon is known as relaxation. The decay time is known as relaxation time.

Interpretation of the dielectric behavior-

The Debye model is frequently used to explain the dielectric behaviour of materials. A good description of the experimental results is often obtained by using a distribution of relaxation times. The dielectric

behaviour of materials under an externally applied ac field has been the focus of numerous papers, in view of its high scientific and technologic importance. Measurements are made in a very wide range of frequencies and temperatures and for many types of materials. Jonscher made a very comprehensive review on the subject, and presented a model, the many-body model, for the dielectric spectroscopy. This model introduces the idea of correlated states in the material, arising from interactions between individual dipoles in an interactive system, which form a narrow half-filled band. The preferred orientations of the system can be represented by two potential wells, where their relative occupancy determines the total polarisation, and the application of the external field will excite these states making transitions between the two wells.

ELECTRODE MEASUREMENT PROPERTIES EFFECTS OF ON THE DIELECTRIC

Frequency dependent measurements of the ac conductivity have been recognised as an important tool for the study of ionic transport properties of the solids. For this, the conductivity data of solid electrolytes are generally analysed in terms of equivalent circuits composed of frequency independent resistances and capacitances. In most of the cases, the ac response cannot be simulated correctly by simple R-C circuits, e.g. the cases of depressed semicircles in the impedance formalism. To explain such deviation from the ideal behaviour various empirical functions have been formulated which are helpful to fit the experimental data. Most dielectric samples used for impedance measurements have some form of evaporated or otherwise applied metallic electrodes which may be relatively thin, say, of the order of $1\mu\text{m}$ or less. With samples of conductance and capacitance this may lead to effects which are not negligible and which may affect the shape of the characteristics, giving a false impression of the properties of the material in question.

In recent years Jonscher's universal law of dielectric response has been used to model the observed properties of the solid electrolytes. This approach considers theories of cooperative migration and when applied for simulation, needs frequency dependent elements in the equivalent circuits. A R Kulkarni and H S Maiti studied the electrolyte/electrode interface using various electrodes namely silver, graphite and lithium.

METHODS

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 kiethley 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 study a detailed description is given, how the crystallographic planes are identified using Stereographic projection. This can be cross-checked by a computer program "Shape".

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. Various methods have been used to measure conductivity properties. In this study the electrical properties of some Glaserite crystals are studied.

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.

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.

DC Conductivity Measurements-

The dc conductivity of the sample was measured using a Keithely (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 ρ 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.

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 ($K_3Na(SO_4)_2$ (or K_3NS), Tripotassium sodium dichromate ($K_3Na(CrO_4)_2$ (or K_3NCr) and Tripotassium sodium diselenate ($K_3Na(SeO_4)_2$ (or K_3NSe). These are water-soluble crystals and hence they are grown from their aqueous solutions.

CONCLUSION

This study deals with the topic of measuring dc and ac electrical conductivities and dielectric properties of three selected glaserite crystals namely Tripotassium sodium disulphate ($K_3Na(SO_4)_2$ or K_3NS), Tripotassium sodium dichromate ($K_3Na(CrO_4)_2$ or K_3NCr) and Tripotassium sodium diselenate ($K_3Na(SeO_4)_2$ or K_3NSe). These are purely ferroelastic crystals. The scope of this work involves calculation of bulk properties, knowing the nature and mechanism of conductivity, variations of dc conductivity with temperature, variations of ac conductivity with temperature and frequency, dielectric behavior at different temperatures and frequencies, detection of any phase transition present and determination of power law parameters and activation energies of the crystals under investigation which are reported for the first time.

Large single crystals are necessary for the electrical conductivity and dielectric measurements, since these properties are measured in all possible directions. These crystals are not readily available and hence they are grown in the laboratory by slow evaporation technique at constant temperature as a part of the present work.

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