
J. V. Jovita**, A. Ramanandb, P. Sagayarajb

a Department of Physics, Queen Mary’s College for Women(A), Chennai- 600 004
b Department of Physics, Loyola College, Chennai – 600 034

*Corresponding author: Tel: 044-22601427, Mobile: 9444107954.
Email: jovitaqmc@gmail.com

Abstract

Three organic crystals, 4-Methylanilinium phenolsulfonate, 2-Amino-5-nitropyridinium trifluoroacetate and 2-Amino-4-methylpyridinium tartrate monohydrate were grown by slow evaporation solution technique from the organic compounds. Dielectric properties such as dielectric constant, dielectric loss, and AC conductance of these crystals at various temperatures and frequency range 100Hz to 1MHz were studied. The activation energy of these crystals was also calculated.

Key words: Organic crystals, Dielectric constant, Dielectric loss, AC conductance, Activation energy

1. Introduction

Organic crystals have been great source of intrigue for researchers for more than three decades because of their versatility and extensive use in variety of application. This can be attributed to the dielectric properties of the organic materials, which depends on the temperature and the frequency of the organic crystals. Composites are fabricated from organic filler materials possessing very high dielectric constant, dispersed in an electrostrictive polymer matrix. This composite can exhibit very high net dielectric properties while retaining the flexibility, so that this can be used in artificial muscles, smart skins and microfluidic systems for accurate drug
delivery (Zhang et al, 2002). Low dielectric constant materials are an important component of microelectronic devices and organic crystals which have low dielectric constants are very much sought after for variety of applications (Paul, 2003). A thorough examination of the sensor capabilities and proof-of-concept demonstration has been carried out in a wide range of application scenarios ranging from cytological studies in a microfluidic lab-on-chip environment to cancer detection and treatment in tissues. The purpose of the sensor, that analyzes dielectric properties of cells, is to monitor several separated cell samples simultaneously for changes in the concentration, the cell’s developing cycle stage or their vitality, for example, to monitor their specific reaction after drug exposure in a semi-automated way (Puentes, 2011). The research of the microwave engineering group in this field is focused on developing planar microwave sensors arrays for analysis and treatment in biomedical applications. All studied sensors have in common that they transduce the dielectric properties of materials under test in their direct vicinity into an electric signal.

A study of the dielectric properties of solids gives information about the electric field distribution within the solid (Anderson, 1964). The frequency dependence of these properties gives a great insight into the material’s applications. Dielectric properties are correlated to the electro-optic property of the crystal. The organic crystals namely 4-Methylanilinium phenolsulfonate (MAPS), 2-Amino-5-nitropyridinium trifluoroacetate (ANPTFA) and 2-Amino-4-methylpyridinium tartrate monohydrate (AMPTM) were synthesized by slow evaporation solution method and their synthesis, growth, structure, morphology and the characters such as spectral, optical, thermal, mechanical, conductivity and biological properties are reported (Jovita et al, 2013a-c, 2014a-c). The dielectric properties of MAPS, ANPTFA and AMPTM single crystals, such as dielectric constant, dielectric loss, and AC conductance with respect to various temperatures and in the frequency range 100Hz to 1MHz were studied and the activation energy was calculated and reported herein.

2. Experimental details

The organic crystals namely MAPS, ANPTFA and AMPTM were synthesized by slow evaporation solution method. The compound 4-Methylanilinium phenolsulfonate was synthesized from 4-methylaniline and 4-hydroxybenzenesulfonate. The compound 2-Amino-5-nitropyridinium
trifluoroacetate was synthesized from 2-Amino-5-nitropyridine and trifluoroacetic acid. The compound 2-Amino-4-methylpyridinium tartrate was synthesized from 2-amino-4-methylpyridine and tartaric acid. The dielectric measurements were carried out in the frequency range 100Hz to 1MHz in the various temperature ranges using HIOKI 3532-50 model HITESTER LCR meter for the organic MAPS, ANPTFA and AMPTM crystals. The dielectric constant, dielectric loss, and the ac conductivity of the MAPS crystals were carried out at the temperatures 323°K, 373°K and 413°K. For ANPTFA and AMPTM crystals the dielectric measurements were carried out at temperatures 333°K, 373°K and 333°K, 343°K respectively.

3. Results and discussions

3.1 Dielectric constant of MAPS, ANPTFA and AMPTM single crystals

The different polarization mechanisms in solids can be understood from the study of dielectric constant as a function of frequency and temperature. The action of an electric field brings the charges of the molecules of the dielectric into a certain ordered arrangement in space. The study of dielectric constant of a material gives an insight into the nature of bonding in the material. The relative dielectric constant $\varepsilon_r$ is $\varepsilon_r = \frac{Cd}{\varepsilon_0 A}$. Where, $A$ is the area of the sample, $d$ is the thickness of the sample, $\varepsilon_0$ is the permittivity of the free space. The dielectric constant of a substance is a property of the constituent ions. In general, the four major contributions to the dielectric constant would be the extrinsic nature of the material, the electronic polarizability, the ionic polarizability and the deformation of the ions (Smyth, 1965).

The plots of dielectric constant vs. frequency of MAPS single crystals at temperature 323°K, ANPTFA single crystals at temperatures 333°K & 373°K and for AMPTM crystals at temperatures 323°K, 373°K and 413°K are shown in Figure 1(a), (b) and (c) respectively.

Figure 1 Dielectric constant vs. frequency of (a) MAPS (b) ANPTFA (c) AMPTM crystals
The dielectric constant has high values in lower frequency region and decreases with increase in frequency. The large value of dielectric constant, at low frequencies is due to the excitation of bound electrons, lattice vibrations, dipole orientation and space charge polarizations (Arora et al., 2002, 2004, Kunjo Wakamura and Hiroyuki Uemori, 2010). The low value of dielectric constant, at high frequencies indicates the low power dissipation and that the crystal can be highly suitable for electro-optic applications. From the figure it is known that AMPTM single crystal has high dielectric constant compare to other two crystals.

3.2 Dielectric loss of MAPS, ANPTFA and AMPTM

The dielectric loss is a measure of the energy absorbed by a dielectric material. It is known that in a capacitor, the dielectric usually has a resistance $R$ and impedance $Z$ which are related to the phase angle. Assuming $R$ to be very large, $\tan \delta = 1/\omega RC$. Where, $\tan \delta$ is referred to as the dielectric loss. The dielectric loss depends very much on temperature and frequency (Arora et al, 2004). The dielectric loss, similar to that of dielectric constant strongly depends on frequency of the applied field. The plots of dielectric loss against frequency of MAPS single crystals at temperature 323°K, ANPTFA single crystals at temperatures 333°K & 373°K and AMPTM crystals at temperatures 323°K, 373°K and 413°K. are shown in Figure 2(a), (b) and (c) respectively.

![Figure 2 Dielectric loss Vs. frequency of (a) MAPS (b) ANPTFA (c) AMPTM single crystals](image-url)
The dielectric loss which is low at high frequencies reveals that the grown crystal is of good quality with lesser defects. The dielectric constant and dielectric loss of the crystal increase with temperature for a constant frequency due to the contribution of more number of dipoles and weakening of inter ionic forces of the crystal.

3.3 A.C. conductivity of MAPS, ANPTFA and AMPTM

The alternating current conductivity is calculated using the relation $\sigma_{ac} = \omega \varepsilon_o \varepsilon_r \tan \delta$, where “$\omega$” is the angular frequency, $\omega = 2\pi f$, $f$ is the frequency,” $\varepsilon_o$” is the permittivity of the free space, $\varepsilon_o = 8.854 \times 10^{-12}$ Farday/m, “$\varepsilon_r$” and “$\tan \delta$” are relative permittivity and dielectric loss respectively at frequency $f$.

The plots of A.C. Conductance against frequency of MAPS single crystals at temperature $323^\circ K$, ANPTFA single crystals at temperatures $333^\circ K$ & $373^\circ K$ for AMPTM crystals at temperatures $323^\circ K$, $373^\circ K$ and $413^\circ K$. are depicted in Figure 3(a), (b) and (c) respectively.

![Figure 3](image)

Figure 3 A.C. conductance Vs. frequency of (a) MAPS (b) ANPTFA (c) AMPTM single crystals.

The ac conductivity patterns show a stable plateau in the low frequency region and a steep increase at higher frequencies. It is observed that $\sigma_{ac}$ becomes independent of frequency after a certain value, where a plateau is observed.
and is the region of dc conductivity $\sigma_{dc}$. At low frequencies, random diffusion of charge carriers via hopping gives rise to a frequency independent conductivity. When the frequency is increased, the conductivity is found to obey a power relation (Rao and Smakula, 1965). The power law behavior is a universal property of materials that is related to the dynamics of hopping conduction which has widely been observed in crystalline solids (Suresh, 2012a, b).

### 3.4 Activation energy of MAPS, ANPTFA and AMPTM

By Arrhenius principle, the equation for the a.c. conductivity is $\sigma_{ac} = \sigma_{dc} \exp(-E_a/kT)$. Where, $\sigma_{ac}$ is the a.c. conductivity of the material, $\sigma_{dc}$ is d.c. conductivity of the material, $k$ is Boltzmann constant, $T$ is the absolute temperature and $E_a$ is the activation energy. The plot of $\log \sigma_{ac}$ and $1/T$ for grown crystals was drawn. The slope of the plot is equal to $E/k$ from which the activation energy $E$ can be calculated. The activation energy of the material of the grown crystals was calculated. The plots of A.C. Conductance Vs. frequency of MAPS single crystals at temperature 323°K, for ANPTFA single crystals at temperatures 333°K, 373°K and for AMPTM crystals at temperatures 323°K, 373°K and 413°K, are depicted in Figure 3(a), (b) and (c) respectively. The activation energy of MAPS thus calculated is 0.862 meV and that for ANPTFA and AMPTM are 3.09 meV and 0.1 meV respectively.
4. Conclusion

Dielectric studies on the three grown crystals showed normal dielectric behavior. The electrical conduction in dielectric study is mainly a defect controlled process at low temperature region. The increase in the conductivity with frequency may be due to reduction in space charge polarization at higher frequencies. By Arrhenius principle, the activation energy of MAPS, ANPTFA and AMPTM crystals were estimated as 0.862 meV, 0.31 meV and 0.1 meV respectively. These organic MAPS, ANPTFA and AMPTM crystals have application potential as dielectric materials.

References


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