STUDIES ON ELECTRICAL AND THERMAL PROPERTIES OF CERTAIN SELECTED PHOTONIC MATERIALS

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CERTIFICATE

Certified that the research work presented in this thesis is based on the original workdone by Mr. Edwin Xavier under my guidance in the International School of Photonics and initially in the Department of Physics, Cochin University of Science and Technology and has not been included in any other thesis submitted previously for the award of any degree.

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PREFACE

Researchers have been engaged in developing newer and better materials which should have striking properties suitable for applications in different fields like industry and technology. An entirely modern research field called "Material Science" has emerged to develop noval materials with attractive structure and properties so as to enable the design and fabrication of new devices and systems. Along with the above mentioned experimental developments and discoveries, a large effort has gone into understanding of the properties of materials which include structural, electrical, magnetic, optical, thermal and mechanical behaviour. In this context characterization of these materials becomes extremely important as it throws light on the behavior of these substances under different conditions. Several tools and techniques have been employed in recent times for this purpose. Measurement of electrical and thermal properties acquire great importance in this scenario. Two key parameters viz: the electrical conductivity, dielectric constant give valuable informations on the properties and prospects of the sample under investigation. Photoacoustic technique is a comparatively noval approach and currently it has been used for the measurement of thermal and optical properties of many materials.

The conductivity of a solid dielectric depends mainly upon the mobility of ions and other charge carriers and on their concentration. A basic question in the measurement

of conductivity of dielectrics is whether the transport process is electronic or ionic. Because of the general similarity between the expressions for ionic conductivity and for electronic semiconduction in a dielectric, it is often difficult to distinguish experimentally between the two types of conduction mechanism. However, the activation energy calculation reveals the dominant factor responsible for conduction process. Phase transitions occurring in materials are also a striking phenomenon which have a direct impact on the electrical properties of solids. A phase transition leaves its own impressions on the key parameters like electrical conductivity and dielectric constant. The interest in the Photoacoustic (PA) effect as a new experimental tool to unravel the thermal and optical properties of solids grew appreciably in the last ten years. The basic mechanism of the photoacoustic effect is that a sample illuminated by modulated light and is heated periodically by nonradiative transitions following optical absorption. Indirectly these effects can be detected by taking the sample in an enclosed cell along with a sensitive microphone and measuring the sound wave generated in the coupling gas medium. The PA technique has been applied to a large range of problems, in particular to the study of the thermal properties of different materials. Using PA technique, thermal diffusivities of thin films, polycrystallines and single crystals have been determined precisely and such measurements provide the absolute values of thermal diffusivity of samples as a function of temperature. Among many techniques now available, the PA technique has been revived as a very useful and ideal technique for the thermal and spectroscopic investigation.

The present thesis attempts to summarise the work carried out in the above directions by the author during the past few years in the International School of Photonics and initially in the Department of Physics of Cochin University of Science and Technology.

The thesis contains 8 chapters which are divided into two parts **A** and **B**. Part A includes three chapters which describe the detailed investigations carried out in pure single crystals pressed pellets of Ammonium Dihydrogen Phosphate and Ammonium Iodate using dc electrical conductivity and dielectric constant measurements. Special attention has been paid to reveal the mechanisms of electrical conduction in various phases of these samples and those associated with different phase transitions occurring in them. Part B contains the remaining five chapters in which the details of the measurement of thermal diffusivity on Phthalocyanines, axis-wise measurement of thermal diffusivity in single crystals of Potassium Dihydrogen Phosphate ,thermal diffusivity of metallic thin films and the over all conclusions are presented.

In the first chapter a general introduction is provided to give an overview of the importance of the study of electrical conduction ,dielectric properties and phase transition in solids and their theoretical aspects. This chapter also describes, the technique generally employed to study the mechanisms of electrical conduction as well as the different experimental system employed for these investigations.

The investigations carried out on an important photonic materials viz: Ammonium Dihydrogen Phosphate single crystal in the temperature range 100 K to 400 K using dc electrical conductivity measurements are presented in the second

chapter. The results obtained show that this material undergoes a drastic change at 147 K with a hysteresis of 1.1 indicating a first order phase transition at this temperature unlike other ionic crystals in this category. The directional change which is observed for the first time in the conductivity plot undoubtfully confirm that, the crystal exhibit pyroelectric behaviour at the phase transition point. This observation is in good agreement with the possible coexistence of two phases at low temperature transition point in ADP crystals. Electrical conductivity at low temperature could be resulting from protonic motion in addition to a small contribution due to impurity dominated extrinsic conduction.

Chapter III presents the results of dc electrical conductivity and dielectric constant measurements carried out in Polycrystalline Ammonium Iodate in the temperature range 300 K to 420 K. Both the above properties exhibit anomalous variations at 363 K thereby confirming the occurrence of a first order phase transition in this material. The variation of dielectric constant as a function of temperature for different frequencies has also been investigated. The activation energy values in this material indicates that protonic conduction is the dominant mechanism responsible for the electrical conductivity of this material.

Chapter IV, which is listed in the Part B, gives a summary of photoacoustic theory in solids. Photoacoustic effect has been employed fairly extensively to obtain information on thermal properties of materials. A model which has been extensively used to explain the PA effect is that of Rosencwaig and Gersho here afterwards refered to as RG theory. Rosencwaig has given expressions for the pressure

amplitude as measured by the microphone which can then be simplified depending upon the thermal characteristics of the sample.

During the last decade, several methods have been developed to determine thermal diffusivities with high precision. The most widely used method is based on the photoacoustic effect. It includes both front surface excitation and rear surface excitation. The fifth chapter describes the thermal diffusivity measurements in metal free Phthalocyanines, Metal phthalocyanines and iodine doped Metal phthalocyanines using front surface excitation technique. Phthalocyanines and its metal complexes play a key role in the field of molecular semiconductors. Its structure corresponds to the porphyrins, of which class chlorophyll is a member. Recently Metal Phthalocyanines have emerged as a noval class of materials for optical, electrophotographic and photovoltaic applications. The are also expected to serve as active materials for molecular electronic devices such as electrochromic displays and chemical sensors. Recent reports shows that organic dyes such as phthalocyanines are very good material for optical data storage applications in the place of metallic substances because of their chemical stability and feasibility for synthetic engineering. Because of its high thermal and chemical stability, Phthalocyanines have become the focus of recent research. The results indicates that doping with iodine enhances the thermal diffusivity in a substantial manner in Metal Phthalocyanines. Photoacoustic technique provides a very convenient method for obtaining the thermal conductivities along the different crystallographic axes for small sample.

In the sixth chapter, axis wise measurements of thermal diffusivity carried out for the first time in single crystals of Potassium Dihydrogen Phosphate (KDP) have been described. The anisotropy in thermal conductivity of KDP crystal has been demonstrated using photoacoustic technique. It has been found that thermal diffusivity decreases with temperature along a/b as well as c- axes. Thermal diffusivity measurements in thin films using rear surface illumination method have been described in the seventh chapter. It describes the fabrication details and performance of the cell used for this purpose. Thin films of Indium ,Aluminium, Silver and CdS prepared from vacuum coating technique have been used for measurements. Thermal diffusivity values obtained using this cell shows close agreement with the previously reported values for standard materials.

The last chapter provides an over all summary and conclusion of the whole work presented in the thesis.

Part of the investigations contained in this thesis has been presented in conference or published / communicated in the form of following papers.

1. Electrical conductivity, Dielectric constant and phase transition in NH_4IO_3,
   Edwin Xavier, R.Navil Kumar and C.P.G.Vallabhan
   Solid State Ionics:Materials and applications, **1**, 711 (1992).

2. Investigation of low temperature phase transition in $NH_4H_2PO_4$ using dc conductivity measurements.
   Edwin Xavier, R.Navil Kumar and C.P.G.Vallabhan.
   Proceedings of the Solid State Symposium, BARC, Bombay,
   33C, 321 (1991).

3. Photoacoustic detection of the low temperature phase transition in $NH_4H_2PO_4$. Edwin Xavier, R.Navil Kumar and C.P.G.Vallabhan., Proceedings of the Solid State Symposium, BARC, Bombay, **33C**, 304, (1991).

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8. Photoacoustic measurements of thermal diffusivity in metal phthalocyanines, Edwin Xavier, C.P.G.Vallabhan, Jayan Thomas and V.N.Sivasankara Pillai, Journal of Matieral Science Letters (communicated.)

9. A Study of low temperature phase transition in $NH_4H_2PO_4$ using dc conductivity measurements. Edwin Xavier, and C. P.G.Vallabhan. Journal of Material Science (communicated.)

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CONTENTS

PART - A Page No.

CHAPTER 1 : INTRODUCTION

PART - A

CHAPTER 1

INTRODUCTION .

1.1. ABSTRACT

This chapter presents an overview of ideas and concepts necessary for the exposition of the importance of the study of electrical properties of solids. It also describes a reasonably comprehensive theoretical basis of some of the thermodynamical aspects of phase transition process. The experimental techniques generally employed in the study of phase transitions are also specified in this section. The methods used to grow single crystals and the details of a metallic cell used for low and high temperature electrical measurements are also described in the present chapter.

1.2. A brief history of Photonic materials

Optics is an old and venerable subject involving the generation, propagation and detection of light. Three major developments, which have been achieved in the last thirty years, are responsible for the rejuvenation of optics and for its increasing importance in modern technology. These landmarks are the invention of the laser, the fabrication of low-loss optical fibers, and the introduction of semiconductor optical devices. As a result of these developments, new disciplines have emerged and new terms describing these disciplines have come into use: electro optics, optoelectronics, quantum electronics, quantum optics and light wave technology are some of the terms in this new technology. However, in recent years, the term photonics has become increasingly popular. This term, which was coined in analogy with electronics, reflects the growing tie between optics and electronics forged by the increasing role that semiconductor materials and devices play in optical systems. The term photonics is used broadly to encompass all of the aforementioned areas including the functions such as amplification, detection, frequency conversion, switching etc. in different regions of the electromagnetic spectrum.

The ancient achievements in developing materials inspire us to achieve new heights in the modern era especially when we consider many new elements which have been discovered and a variety of materials developed, by different combination of atoms and processes for use in our every day life and also for specific high technology applications. These include semiconductors used extensively in electronic devices and in all present day computers, superconductors, polymers, amorphous materials such as

amorphous silicon which is useful for solar cell applications, liquid crystals which are used in displays, quasi crystals, and more recently nanomaterials which could lead to technological breakthroughs such as nanostructured tunable lasers and materials where clusters rather than atoms would be the building blocks. All these developments have come from extensive and innovative research and from the progress in analytical and experimental techniques which are now developed to a level that even information with atomic resolution can be obtained using the high resolution electron and the scanning tunnelling microscopes (STM) and it has become possible to prepare structures atom by atom. Along with the above mentioned experimental developements and discoveries, a large amount of effort has gone into understanding of the properties of materials which include structural, electrical, magnetic, optical, thermal and mechanical behaviour. In the course of these experiments, researchers encountered certain interesting and important optoelectronic phenomena associated with materials, suitable for application in the field of photonics. Those materials are generally termed as " photonic materials" and the list of such materials is very lengthy. We have selected only a few of such materials, which are comparatively important, for our present investigation.

1.3. Importance of the study of electrical properties of the material.

Some of the electrical properties like electrical conductivity and dielectric constant have been used to characterize the materials and to study the phase transitions in them. The study of electrical conduction process in materials can yield a great deal of valuable information on the formation and migration of charge carriers in materials.

Basically electrical conductivity in materials is a defect controlled phenomenon and hence detailed investigation of the electrical properties of the materials is one of the best available methods for the study of defects concentration. Recently, the electrical conductivity and dielectric constant measurements have become accepted as a very sensitive method for the study of phase transition as well as for the study of defects in ammonium containing crystals [1-10]. Usually these electrical properties are investigated as a function of temperature or as a function of pressure.

1.4. Electrical conduction in dielectrics.

Knowledge of electrical conduction in materials is the fundamental basis for the development of the branch of physics called Material Science and Technology. Most of the solid state devices developed in the last three decades are based essentially on the motion of the electrons. After the discovery of fast sodium ion conduction in β-alumina and silver ion conduction in $MAg_4 I_5$(M=K,Rb,NH_4) in 1967 [11,12], ionic solids have been found numerous applications in fabricating solid state batteries, fuel cells, memory devices, display panels etc. Nowadays a large number of Physicists, material Scientist and Engineers are engaged to develop a high density solid state battery for vehicular traction and low density miniaturized batteries for device applications. In this respect, the role played by the superconducting materials is very important in the sense that, these materials are potentially important from the point of view of technical applications.

The foundations upon which our understanding of ionic conductivity are built were laid down before 1940 by the early work of Schottky [13],Wagner [14] and Mott and Littleton [15,16]. It was found that the transference of mass and charge occurring in alkali halide crystal is mainly by means of ionic processes. Later the subject of ionic conductivity was expounded at length by Lidiard [17-19], Fuller [20-25], Barr [26,27], Franklin [28] etc. In addition to these, some other notable works [29-35] can also be found in literature.

1.5. Simple theory of electrical conduction in dielectrics.

All materials conduct electricity to a greater or lesser extent, and all suffer some form of breakdown in a sufficiently strong electric field. For low field strengths the conduction process in most material is ohmic, but as the field strength is increased further some form of destructive irreversible conduction takes place. The conductivity of dielectrics may be either ionic or electronic or both. A basic question in measurements of the conductivity of dielectrics is whether the transport process is electronic or ionic. Because of the general similarity between the expressions for ionic conductivity and for electronic semi conduction in dielectrics, it is often difficult to distinguish experimentally between the two types of conduction. Ionic conductivity is simply due to the migration of positive or negative ions. This could arise in a dielectric in two different manners; in an ionic crystal such as an alkali halide the basic constituents are ions and physical imperfections alone can be responsible for mechanisms of current flow, while in a non ionic substance chemical imperfection

is required to supply the mobile species. The basic theoretical expression for all electrical conductivity is,

$$\sigma = \sum n_i e_i \mu_i \quad \text{----------} \quad (1.1)$$

where n_i is the density of carriers of the i^{th} species, and e_i and μ_i the corresponding charges and mobilities. In the usual analysis of experimental low field ionic conductivity, one write ,

$$\sigma = \sigma_0 \exp.(\Phi/kT) \text{----------} (1.2)$$

where σ_0 and Φ are experimentally determined (usually constants with in some given range of temperatures), k is Boltzmann's constant and T the absolute temperature. Since both the density and the mobility of the migrating species are usually temperature dependent, the single temperature dependent term in equation (1.2) combines the effect of temperature on both n_i and μ_i of equation (1.1). The field dependence of ionic mobility should be small, but the concentration of charge carriers could be strongly influenced by an electric field. The simplest understanding of electronic conduction in a solid dielectric arises from modifications to the quantum mechanical band theory of solids. This gives a picture of a dielectric in which a series of allowed electronic energy bands are completely occupied by electrons up to a certain level, and empty there after. The conduction band does not give rise to any conductivity since it contains no electrons, and neither

does the valence band conduct since there are no unoccupied states into which an electron can be accelerated by an applied field. This simple picture applies only to a perfect crystalline insulator at the absolute zero of temperature. But in real insulators at finite temperature, trapping levels are caused by the influence of foreign ions, vacant lattice positions, interstials etc. on the normal lattice field. In general only the conduction and valence levels are important in pure, strain free crystals at low temperatures. The relative importance of isolated levels increases with admixture of foreign ions, mechanical strain, and rise in temperature. In band theory the effect of an applied electric field is regarded as causing an acceleration of conduction electrons in the band; it may however be more correct to regard the electric field as causing transitions between adjacent but more or less localized states of the conducting electrons. This mechanism is referred to as hopping conduction, and the conducting electron is regarded as making its way through the dielectric in a series of discrete movements. Band conduction and hopping conduction are not regarded as the antithesis of each other; rather the latter is a more appropriate visualization than the former in the limiting case of narrow bands. These simple ideas of the electronic conductivity of dielectrics fail in a striking way for certain of the transition metal oxides. Regardless of the theoretical model which one may adopt to explain electrical conduction in the insulating transition metal oxides, the experimental data is adequately described in terms of an activation energy with the conductivity given by equation (1.2).,The basic theoretical steady state conduction equation is

$$j = \sigma E \text{ ---------- } (1.3)$$

where j is the current density, E, the electric field strength and σ the electrical conductivity defined by equation (1.1). The experimentally measured quantities are the current I and the voltage V. The simplest procedure to establish a connection between theory and experiment is to write,

$j = I/A$ and $E = V/d$ ----------(1.4)

where A is the cross sectional area and d, the thickness of the specimen. Since the breakdown path usually extends over only a tiny fraction of the cross sectional area, the current density in the break down channel is much higher than would be found by the application of equation (1.4) for prebreakdown current; it is therefore used for lack of anything better. The correct relation between voltage difference and field strength across the dielectric involves consideration of space charges.

1.6. Dielectric Constant.

The investigation of dielectric properties has provided an important approach to an understanding of the structure of matter, and, without some understanding of the relation of these properties to the structure of the materials, our extensive knowledge of dielectric behavior loses much of its significance. The so called static or low frequency dielectric constant will be examined first, since it has thus proved most useful in investigating structure and since understanding of the static constant is necessary for the treatment of the high frequency constant. The dielectric properties of a material are governed by the response of the material to an

applied electric field at the electronic, atomic, molecular and macroscopic levels. If an electric field is created in a dielectric material the dipole moments of separate kinetic elements or atomic groups will tend to orient in the field direction. If the external electric field is now removed then after a certain time the polarization of the sample will diminish to zero as a result of thermal motion of separate kinetic elements, and the system will return to its previous equilibrium state. Such a process of transition to equilibrium is called dielectric relaxation. It is characterized by the relaxation time τ. On the other hand if an alternating voltage is applied to the dielectric, the dielectric properties of the material will obviously depend on the relation between the frequency of the applied voltage ω and the dielectric relaxation time τ.The dielectric properties of the specimen can be characterized by the, complex dielectric constant,

$$\varepsilon^{*} = \varepsilon^{1} - i\,\varepsilon^{11} \text{ ---------- (1.5)}$$

where ε^{1} the real component of complex dielectric constant, and ε^{11} the imaginary component of complex dielectric constant (also called the dielectric loss factor),

The ratio $\varepsilon^{11} / \varepsilon^{1} = \tan\delta$----------(1.6)

is the dielectric loss tangent. It characterizes the phase shift between the alternating voltage applied to the capacitor between whose plates the sample is

placed and the current passing through the capacitor. If the dielectric relaxation can be described by a single relaxation time then,

$$\varepsilon^{1} = \varepsilon_{\alpha} + (\varepsilon_{0} - \varepsilon_{\alpha} / 1 + \omega^{2} \tau^{2}) \text{---------- (1.7)}$$

$$\varepsilon^{11} = (\varepsilon_{0} - \varepsilon_{\alpha})\, \omega\tau \,/\, (1 + \omega^{2} \tau^{2}) \text{- ----------(1.8)}$$

where ε_0 is the dielectric constant at $\omega = 0$.

ε_α, the dielectric constant at ω = infinity and,

$$\tan \delta = (\varepsilon_{0} - \varepsilon_{\alpha})\, \omega\tau \,/\, (\varepsilon_{0} + \omega^{2} \tau^{2}) \text{----------(1.9)}$$

If ε_0 the static dielectric constant, ε_r , the relative permittivity, ω, the angular frequency and tan δ the loss tangent, then, σ_{ac} can be found out by the equation,

$$\sigma_{ac} = \varepsilon_{0}\, \varepsilon_{r}\, \omega \tan \delta \text{----------(1.10)}$$

1.7. Protonic Conductors.

Protonic conductors assume significance in fuel cells, high energy density batteries and in sensors. This recent interest has initiated detailed investigation on thermally stable protonic conductors [36,37].The existence of proton as a conductor in a medium is not that simple as it appears to be. An unsolvated proton has a very small radius, such free protons are not found in materials under equilibrium

conditions. Hydrogen atom is covalently bond to electronegative atoms such as carbon, nitrogen or oxygen. Hydrogen has the rare capability for expanding its covalency forming additional bond (hydrogen bond) which is characterized by directional properties. Oscillations of the hydrogen atom in such situations would effectively lead to a shift in its equilibrium position. This is equivalent to the transport of a proton. Since the hydrogen bond has directional characteristics, transport of a proton across a hydrogen bond has different magnitudes along different crystal axes depending upon the lattice structure.

1.8. Mechanism of Proton Conduction.

1.8a. Liquid Transport.

Certain protonic conductors with layered structure contain intercalated water molecule. In these layered materials, water molecules present in the interlayer space form a liquid like network permitting high protonic conductivity [38]. In pellicular materials with absorbed moisture, the water present on the surface and in the interpellicular space can also act as a liquid transport medium [39].

1.8b. Proton Jump followed by reorientation of hydrogen bonds.

Proton jump is often possible by a process of tunneling through a hydrogen bond. In effect, a reorientation of the hydrogen bond occurs. This mechanism operates

in hydrated salts, ammonium salts and organic acids. The probable modes of transport are described below.

(i) Polyatomic ion migration (vehicle mechanism).

This conduction mechanism operates strongly in acidic media containing water where H_3O^+ species is dominantly present, e.g. H_3O^+ - β- alumina [40], phosphomolybdic acid etc. [41]. In these cases H_3O^+ species migrates, thus effectively transporting H^+ A layered configuration of the anions facilitates this type of vehicular transport. Since the transport involves migration of massive polyatomic ions, the activation energy of the process is fairly high.

(ii) Cooperative proton transfer (Grothus mechanism).

Conduction can also occur due to proton exchange across a continuous chain or network of hydrogen bonds. This occurs in some layered hydrates which are weakly acidic or basic. The activation energy in such cases will be due to the barrier for the reorientation of the hydrogen bond and will be low in magnitude.

1.9. Protonic Conduction in Ammonium Salts.

Electrical properties of ammonium salts such as NH_4Cl and NH_4Br have been extensively investigated by various workers [42-49]. Herrington and Staveley made a comparative study of the electrical conductivity of NH_4Cl, NH_4Br, NH_4I,$(NH_4)_2SnCl_6$ and NH_4PF_6. They concluded that protons play a dominant role in charge

transport in these ammonium salts. Later investigation on NH_4 Cl and NH_4 Br support the observations of Herrington and Staveley. Murti and Prasad [46] have probed phase transition using electrical conductivity measurements. They ascribed the excess conductivity observed at the phase transition to the release of protons from freely rotating ammonium ions. This well fit into the proton transport mechanism proposed by Herrington and Staveley .

A survey of the literature reveals that $NH_4H_2PO_4$ (ADP) is an ammonium compound thoroughly investigated by several research groups [51-56]. Harris and Vella [53] have unambiguously proved that ADP dissociates according to the scheme,

$$NH_4H_2PO_4 \longrightarrow NH_3 + H_3PO_4$$

This process was detected at all temperatures above 40^0 C. C.P.G.Vallabhan et.al. have investigated a number of ammonium salts like $(NH_4)_2SO_4$, $LiNH_4SO_4$, $NH_4H_2PO_4$, , $(NH_4)_3H(SO_4)_2$, $(NH_4)Cr_2O_7$ and $(NH_4)_2HPO_4$ by dc and ac electrical conductivity and ionic thermocurrent measurements [1-10].

1.10. Application of Protonic conductors.

An era of active research in solid state protonic conductors was opened up by the energy crisis in early seventies. From the energy point of view major application of solid state protonic conductors is as electrolytes in fuel cells meant for stand alone power systems, heavy duty automobile traction and electricity storage by the