GROWTH AND HIGH TEMPERATURE PHASE CHARACTERISTICS OF PURE AND DOPED (KDP-ADP) CRYSTALS

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Abstract

The pure and doped Potassium Dihydrogen Phosphate (KDP) KH_2PO_4 and Ammonium Dihydrogen Phosphate (ADP) $NH_4H_2PO_4$ have been grown by slow evaporation technique from the supersaturated solution at room temperature. The pure and doped (KDP-ADP) crystals show a phase transition like phenomena named as high temperature phase transition at a characteristic temperature T_p. Upon heating above the T_p, the pure and doped (KDP-ADP) crystals experience a thermal dehydration. In order to investigate the nature of phase transition in MH_2PO_4-type crystals (M=K or NH_4), temperature-dependent resistivity measurements on mixed KDP-ADP crystals performed. *The activation energies of pure and doped (KDP-ADP) crystals were 0.45eV for KDP, 1.3eV for A-KDP, 1.17eV for K-ADP and 2.87eV for ADP.*

Keywords: high temperature**,** phase transition, dehydration**,** resistivity measurements.

Introduction

Crystalline solids play very important role in fabrication of devices for science and Technology (Y.Chaitanya *et al*.,2021). Ammonium dihydrogen phosphate (ADP) and potassium dihydrogen phosphate (KDP) having important applications and harmonic generation was solution grown by slow evaporation technique at room temperature (Kumaraman *et al.*,2008). The enormous advantages in the modern industry during the first few decades succeeded rapidly due to the increasing availability of high-quality single crystals of Semiconductors, Solid State Lasers, Piezo electrics, Ultra-violet and Infra-red sensitive materials crystalline film for microelectronics (Shaikh Kalim *et al*., 2015).

They are widely used as electro-optic modulator, Q-switch, and high-power laser frequency conversion material due to his magnificent performance as an active element in such devices: piezoelectric, ferroelectric and electro-optics (Shaikh Kalim *et al*., 2015). Among the applications of high temperature proton conductors are as solid electrolytes for humidity sensors, hydrogen sensors, fuel cells, hydrogen pumps and energy conversion. Ammonium Dihydrogen Phosphate (ADP) $NH_4H_2PO_4$ and Potassium Dihydrogen Phosphate (KDP) KH_2PO_4 belong to MH_2PO_4 type crystals MH_2PO_4 (where M = K, NH_4, Rb, Cs). Crystal structures of MH_2PO_4 family are isomorphous in room-temperature. In other words, the crystal structure of (KDP-ADP) at room temperature is tetragonal system (Guohui Li *et al.*,2005).

The chemical formula of the salt is pure and doped (KDP-ADP), it is composed of positive potassium ammonium ions (K-NH_4), negative phosphate ions (PO_4), and protons (H_2). Each ammonium ion consists of four hydrogen atoms covalently bonded to a nitrogen atom. Each phosphate ion consists of four oxygen atoms covalently bonded to a phosphorus atom. A phosphate ion carries the extra negative charge of three electrons, one of which it obtains from the ammonium part of the structure and two from the two other hydrogen atoms that furnish in this way two conducting protons (Fabricio Mendes Souza, 2017).

The super protonic conductivity study of the crystal plays important role in the class of solid electrolytes (A.SIERADZKI *et al*.,2011). Many authors have investigated the protonic conductivity or structural phase transition in crystal with short hydrogen bonds MH_2PO_4 family shows a phase transition like phenomena named as high temperature phase transition (HTPT) at a characteristic temperature T_p.

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Materials and Method

Crystal growth, the sample preparation, measurement of conductivity is the essential role in the present experiments work. Some details will be described because they are important in practice.

Crystal Growth and Observation on the Crystal

Most crystals grow from liquid solutions. The liquid is carrier of the atoms or ions necessary for the growth of the crystal, and may be water or a molten substance at room temperature. Chemical substance may dissolve in a particular liquid the solvent. The same solid substance may separate (crystallize) from the solvent when the temperature drops or when the liquid becomes saturated with the dissolve substance. The carrier liquid may be water, a molten salt, a molten metal, a molten rock or an organic solvent. Crystals grow from liquid is response to changes in temperature, pressure, or liquid composition. Many individual crystals may grow simultaneously if the nucleation rate is high. Single crystals of pure and doped (KDP-ADP) were grown by slow evaporation from aqueous solution containing 11.5 g of ADP and 23 ml, 1.5 g of KDP doped 11.5 g of ADP and 28 ml, 1.3 g of ADP doped 13.6 g of KDP and 29.8 ml and 13.6 g of KDP and 27.2 ml of distilled water.

First, the required quantities of KDP and ADP were added to distilled watered by stirring. The temperature was slowly increased until all of the salt dissolve for preparing the saturated solution. The solution is heated and a saturated solution of (KDP-ADP) was prepared for 30 minutes at 32 ºC. The perfect little seed crystals were hung in a saturated KDP-ADP solution. Beautiful water clear tetragonal crystals of 1-2 cm diameter were obtained within 2 and 3 months, they were dried and placed in a seal bottle. The photographs of pure and doped (KDP-ADP) crystals are shown in Fig. 1, 2, 3 and 4.

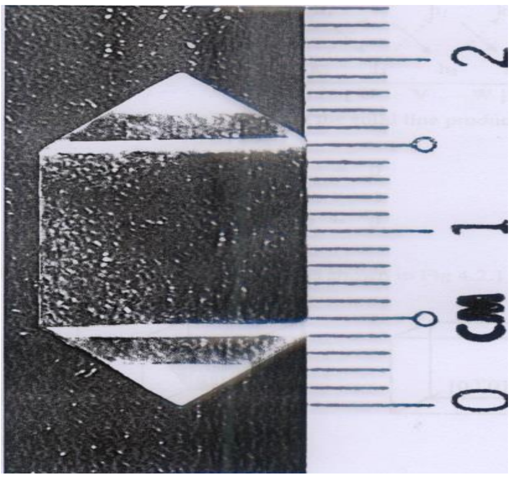

Figure 1 Photograph of KDP grown crystal

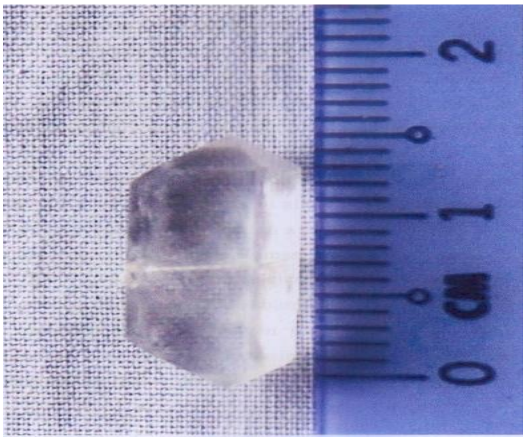

Figure 2 Photograph of A doped KDP grown crystal

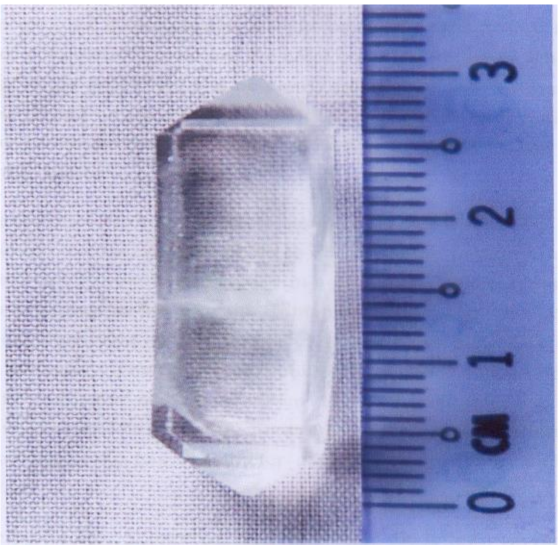

Figure 3 Photograph of K doped ADP grown crystal

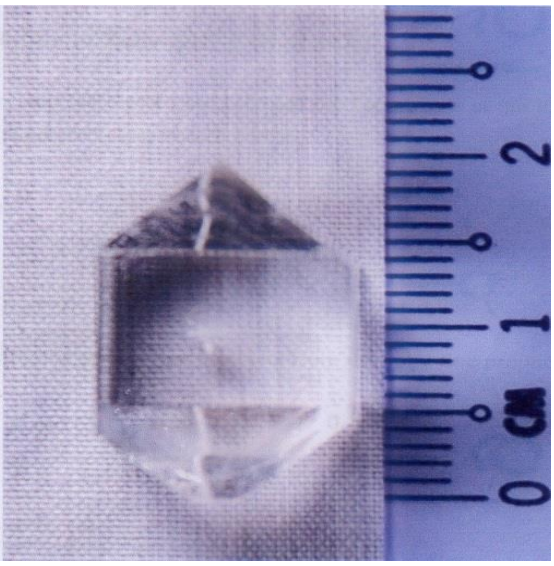

Figure 4 Photograph of ADP grown crystal

Temperature Dependent Conductivity Measurement

The sample was sandwiched between two copper plates that serve as two electrodes. To obtain better electric conduction, silver paste was applied evenly on both surface of the sample. The sample was placed in a sample holder that was immersed in a heating steel cell. Thermal conducting mica shield is used between the sample and the chamber to have a good thermal conductivity and to protect from electrical conduction. Arrangement and experimental set-up for conductivity measurement are shown in Fig. 5 and 6.

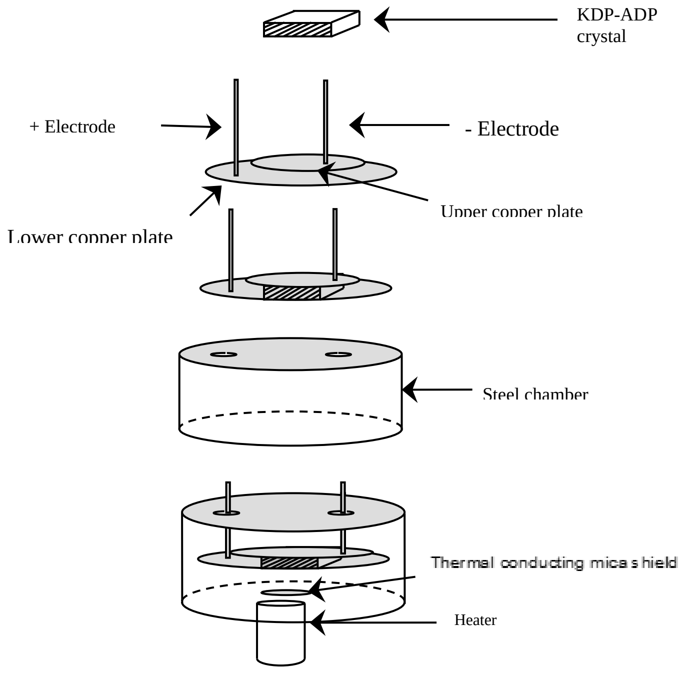

Figure 5 Arrangement for resistivity measurement

Figure 6 Experimental set-up of resistivity measurement

Results and Discussion

High Temperature Phase Transitions of KDP-ADP Crystals

Single crystals of $NH_4H_2PO_4$, $K_{0.1}(NH_4)_{0.9}H_2PO_4$, $(NH_4)_{0.1}K_{0.9}H_2PO_4$ and KH_2PO_4 were grown by slow evaporation of aqueous solutions at room temperature. The electrical conductivity measurement was performed in the temperature range between 333 K and 673 K.

Electrical Conductivity Measurement Results

The results of temperature-dependent conductivity measurement on (KDP-ADP) crystals are shown in Fig. 7, 8, 9 and 10.

Two distinct regions are separated by a knee at 365 K for ADP, at 372 K for KDP, at 381 K for A-doped KDP and at 383 K for K-doped ADP. The knees at those temperatures may be attributed to water in the surfaces of the samples at those temperatures.

A sharp change is found in the conductivity at 430 K. Upon heating above the characteristic temperature T_P, the crystal of the KH_2PO_4 type experiences a thermal dehydration taking place on the surface of the sample. The behavior of ADP at 430 K may be interpreted by the chemical reaction

$$2(NH_4)H_2PO_4(s) \rightarrow (NH_4)_2H_2P_2O_7(s) + H_2O\,(v) \qquad (1)$$

(Where s and v denote solid or vapor state, respectively).

Similarly, for KH_2PO_4,

$$2KH_2PO_4(s) \rightarrow K_2H_2P_2O_7(s) + H_2O\,(v) \qquad (2)$$

The onset temperatures of the dehydration described by Eq (1) and (2) are about T_P = 430 K for ADP and T_P = 434 K for KDP and dehydration takes place at reaction sites distributed on the surface of the grains. Above those temperature further decomposition of the samples proceeds also in the bulk.

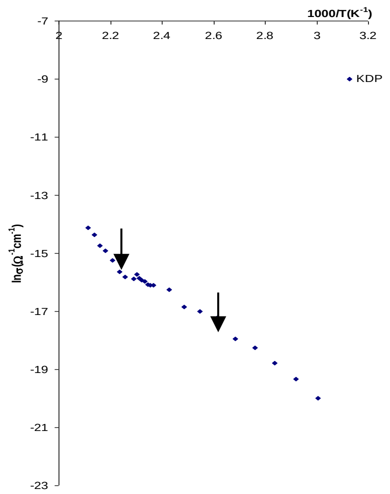

Figure 7 Temperature dependent electrical conductivity of KDP crystal

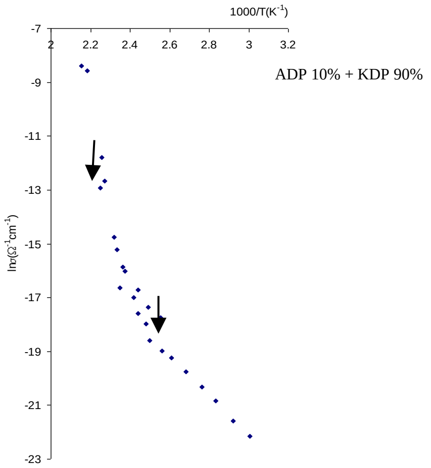

Figure 8 Temperature dependent electrical conductivity of A doped KDP crystal

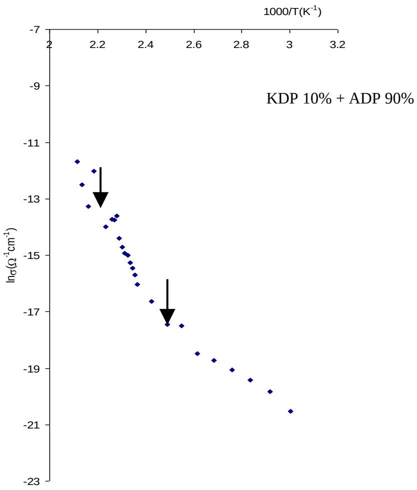

Figure 9 Temperature dependent electrical conductivity of K doped ADP crystal

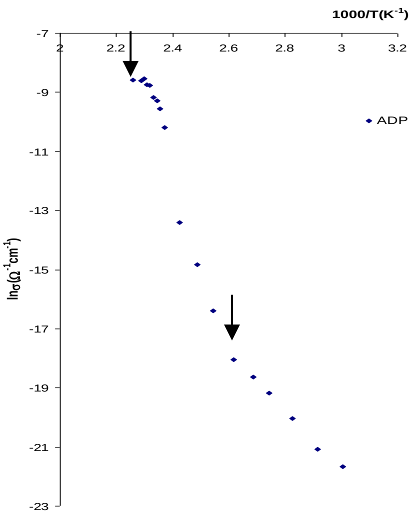

Figure 10 Temperature dependent electrical conductivity of ADP crystal

In the nearly temperature interval (365 K ≤ T ≤ 439 K), the value of ln σ changes with the temperature 1000/T for (KDP-ADP) crystals shown in Fig (11 - 15).

The electrical conductivities of (KDP-ADP) crystals have been investigated and in all the temperature dependence of the conductivity followed Arrhenius relations: $\sigma = \sigma_0 \exp[-E_a/kT]$ where σ is the conductivity, σ_0 is the pre-exponential factor, E_a is the activation energy for conduction, k is the Boltzmann constant and T is the absolute temperature.

$$\ln \sigma = - E_a/kT + \ln \sigma_0$$

$$\ln \sigma = -(\frac{E_a}{1000\,k} \cdot \frac{1000}{T}) + \ln \sigma_0$$

Comparing this equation with the experimental linear equation y = mx + c, the value of slope will give the value of ($-E_a/1000$ k). From Fig 11, the activation energy E_a can be obtained from the least-square method on the slope of ln σ versus 1000/T.

$$-(\frac{E_a}{1000\,k}) = m$$

$$-(\frac{E_a}{1000\,k}) = - 5.2045$$

$$E_a = 5.2045 \times 1000 \times 1.38 \times 10^{-23}\ \text{J}$$

$$= 0.45\ \text{eV}$$

Similarly, form Fig. 12, 13 and 14, the activation energies can be obtained.

The onset temperatures of dehydration and activation energies for (KDP-ADP) crystals are listed in Table 1.

Table 1 Onset temperatures of the dehydration and activation energies for (KDP–ADP) crystals

Sr No.	Crystals	Onset Temperature(K)	Activation Energy (eV)
1	KDP	434	0.45
2	A-KDP	433	1.30
3	K-ADP	439	1.17
4	ADP	430	2.87

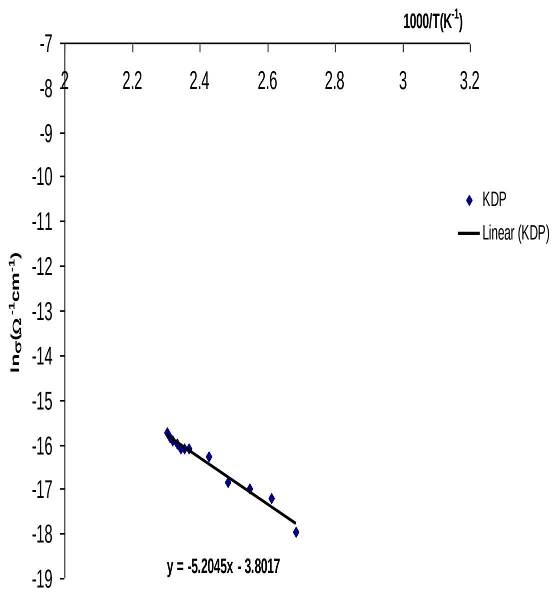

Figure 11 Temperature dependent electrical conductivity of KDP for (372 K ≤ T ≤ 434 K)

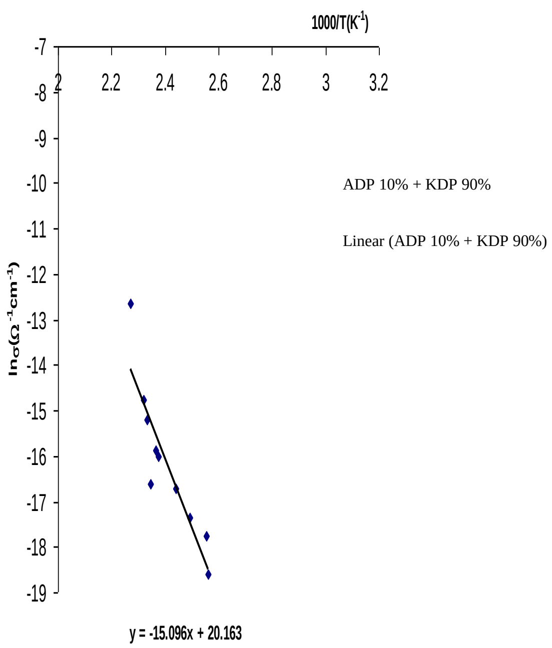

Figure 12 Temperature dependent electrical conductivity of A doped KDP for

(381 K ≤ T ≤ 433 K)

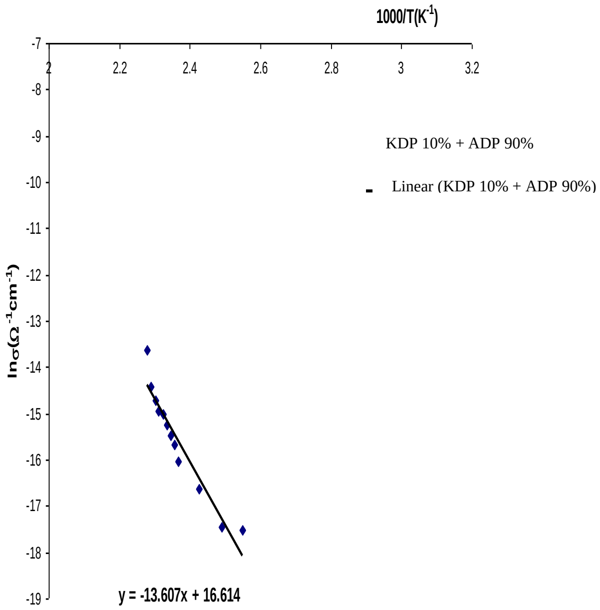

Figure 13 Temperature dependent electrical conductivity of K doped ADP for

(383 K ≤ T ≤ 439 K)

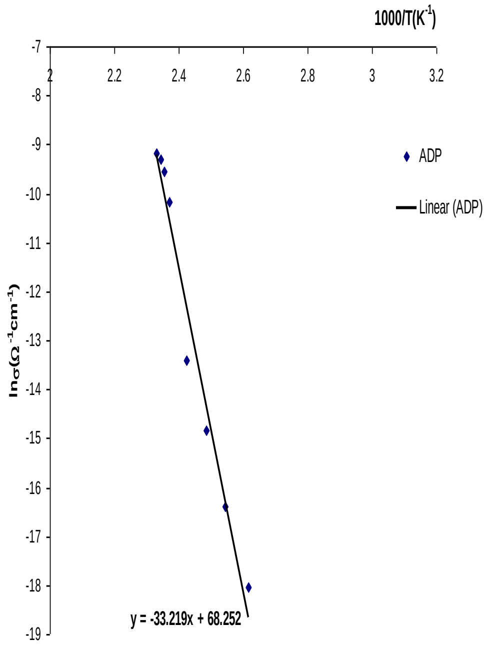

Figure 14 Temperature dependent electrical conductivity of ADP for (365 K ≤ T ≤ 430 K)

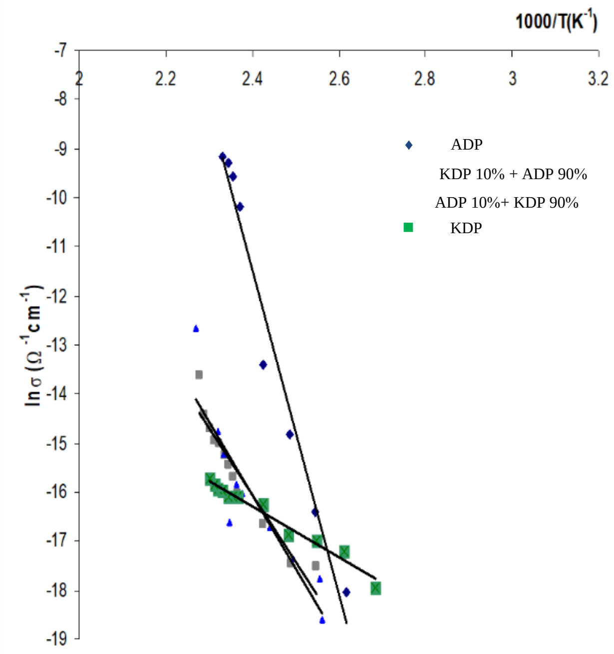

Figure 15 Temperature dependent electrical conductivity of (ADP-KDP) crystals for

(365 K ≤ T ≤ 439 K)

Conclusion

Single crystals of (KDP-ADP) were grown by slow evaporation technique. The electrical conductivity measurement results for (KDP-ADP) crystals suggest that T_P = 430 K for ADP, 434 K for KDP, 433 K for A doped KDP and 439 K for K doped ADP mark the onset of partial polymerization taking place on the surfaces of the samples, such that the phases above those temperatures are the mixed phases consisting of tetragonal ADP or KDP in the bulk of the samples and ammonium polyphosphate, $(NH_4)_2H_2P_2O_7$ or potassium polyphosphate, $K_2H_2P_2O_7$, at the surfaces of the samples. Electrical resistivities of the samples are found to be decrease with increasing temperature. The activation energies of pure and doped (KDP-ADP) crystals were 0.45eV for KDP, 1.3eV for A-KDP, 1.17eV for K-ADP and 2.87eV for ADP.

Acknowledgements

I would like to thank Dr Than Tun, Rector, Pathein University, for her kind permission and encouragements to carry out this work.

I would like to thank Dr Aye Ngwe, Professor and Head, Department of Physics, Pathein University, for his kind permission and encouragements to carry out this work.

Special thanks are due to Professor Dr Than Than Swe, Department of Physics, Pathein University, for his valuable guidance and helpful advice to carry out this work.

I would like to express my gratitude to Professor Dr Khin Myo Ma Ma Saw, Department of Physics, Pathein University, for her kind permission and encouragements to carry out this work.

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