Research Article

Electrical And Thermo Electrical Properties Of Adp And Kdp Crystals

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Abstract : ADP and KDP single crystals were prepared under growth from aqueous solution method. Large crystals of KDP, ADP were grown using Holden crystallizer. The structure of ADP and KDP were found using XRD study with morphology. The electrical conductivity is measured for ADP and KDP crystals, which shows that conductivity is minimum at 303K for ADP in the range from 303 – 463K, similarly for KDP conductivity is minimum at 330K in the range from 303K to 463K. The activation energies were found along 'a' and 'c' axes which are found to be from 0.2 to 1.87 eV. Seebeck Coefficient is found to be negative in the Temperature ranges between 335 -345K.

Keywords: Single Crystals, ADP & KDP crystals, Electrical Properties, Seebeck Coefficients.

I **INTRODUCTION**

Crystalline solids plays very important role in fabrication of devices for science and Technology. Thereby a lot of industrious and effort putting on development of crystal growth and their techniques. Single crystal occupies significant role as modern devices like t rectifiers, transistors, lasers, polarizers, lasers, computer memory, strain gauges, modulators , etc . The role of crystal of crystal growth explores past and now changes novel technological application. Some crystals like silicon, quartz, garnets, KDP,ADP etc. Are large quantities grown annually. Because of their important properties such as piezoelectricity, pyroelectricity, KDP and ADP have been in used in many application. Some of their applications are: stabilization or control of frequencies in radio transmitters and receivers, frequency selection in electric filter circuits, frequency standards of very high accuracy. Single crystals of ADP have been utilized extensively as electromechanical transducers. KDP and ADP KDP and ADP are frequently uses in Nd-doped laser systems [1] as frequency doubling, frequency tripling and frequency quadrupling

And also in electro-optical modulators. KDP crystals are also used in the construction of continuously tunable generator of coherent light with an output of several watts and also used as a shutter reflector which performs the combined function of polarizer, an electro– optic modulator and analyzer and reflector. Pyroelectric property of KDP is used in the construction of detectors which is given by Hadni *et al* [2].Similarly ADP uses in optical modulator and in other acousto–optical devices due to their attractive electro–optical properties (Pockels effect) and also for construction of high-speed shutters, recording of sound waves, etc. Further, large crystals have been uses as appropriate x–ray monochromator plates. They have been used for the construction of Pockels cells. KDP crystals possess Kerr effect [3], so they have been used in Kerr cells. KDP can be used to increase energy output in laser fusion application as Q– switches and laser radiation converters.

II EXPERIMENTAL TECHNIQUES:

For KDP crystals growth, the central flask of system growth is filled up with well prepared, filtered KDP solution (about 1.2 liter) of strength 3 M at 51°C. The temperature of the system can be varied by the digital temperature controller (DTC). The surrounding glass beaker is filled with distilled water. The KDP solution is fast evaporated upto 12 days at 51°C. After that, a seed crystal of KDP with known dimension with a hole drilled at the center of gravity is hanged inside the solution with the help of a nylon thread/ platinum wire. Then we set a program in DTC which contains 3 segments. The first segment concerns with the decrement in temperature from 51°C to 45°C at the rate of 2^0C/h, the crystal being held for 6 hours. The second segment includes the decrease in temperature from 45^0C to 42^0C at the rate of 3^0C/h. In this range, the crystal is held for about 16 hours. In the third segment, we decreased the temperature in the growth chamber from 42^0C to 35^0C at the rate of 0.1^0C/h at duration of about 72 hours. The grown crystal was taken out after 10 days. The dimensions of the crystal are given by: length = 3.64 cm, breadth = 1.61 cm and height = 1.32 cm. Fig. 1 shows the KDP system grown crystals in which the above program represents the growth cycle for the crystal marked 1.

In the case of ADP also we have carried out the same growth process as mentioned above, but with some slight changes. The ADP solution (1.2 liter) of molarity 3.5 M at 50^0C, is fast evaporated upto a duration 10 days. With the known initial dimensions, the crystal is hanged inside the solution. The first segment contains the decrement in temperature from 50^0C to 46^0C at the rate of 1^0C/h. The second segment contains the decrement in temperature from 46^0C to 40^0C at the rate of 2 ^{0}C, whence it is hanged for 15 hours. The decrease in temperature is further carried out at the rate of 0.1^0C from 40^0C to 35^0C, whence it is hanged for 7 days. The

final dimensions as obtained: length = 4.51 cm, breadth = 1.18 cm, height = 0.99 cm of ADP are noticed. The grown crystal is as shown in Fig. 2.

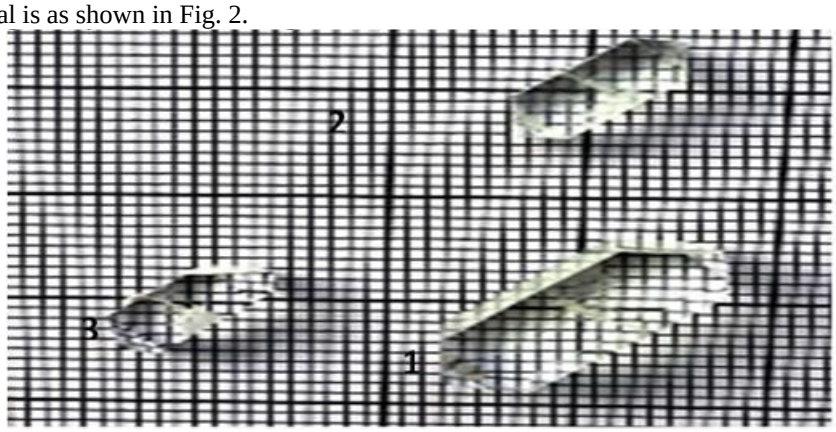

Fig. 1 Some typical grown crystals of KDP taken out of the system (1 unit = 2 mm)

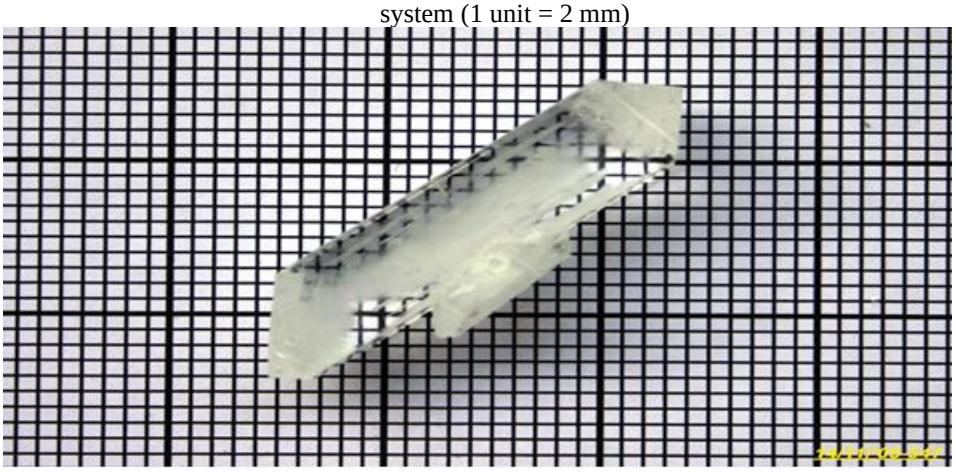

Fig. 2 A typical grown crystals of ADP taken out of the system (1 unit = 2 mm)

III RESULTS AND DISCUSSION

The direct measurement of resistance was carried out by MEGGER−Megohmmeter MM29 from THORN EMI Instruments, UK.

The D.C electrical conductivity measurements have been carried out on ADP crystals for *a-axis* and *c-axis*. The graphical plots of conductivity σ vs 1/T are shown in Figs. 1&2. For *a-axis*, the conductivity decreases initially after 305 K upto 330 K and shows minima at 330 K and then raises slowly upto 380 K and rapidly after 380 K. This can be seen more clearly from the plot between $\ln\boldsymbol{\sigma}_{dc}$ vs 1/T shown in Figs.3,4.

Beyond a temperature of 430 K, the material becomes to decompose and this is shown in graph by the abnormal conductivity behaviour at such higher temperatures. The conductivity measurements calculated for *c-axis* also gives the same effect. This is due to, temperature range from 305 to 380 K the variable composition phase of ADP occurs following the reaction of de ammoniation [4],

$$NH_4H_2PO_4 \rightarrow H_3PO_4 + NH_3 \uparrow$$

Further, the first minima of conductivity, ammonia is evolved from ADP in the range from 325 to 335 K, and that ammonia neutral molecules appear to be find within the crystals of ammonium chloride [5-10] and ammonium perchlorate [11],this can be understand that due to proton vacancies are formed in the ammonium lattice by incipient associated with the formation of H_3PO_4 and NH_3. The first step in the tis decomposition process causes breaking of ammonium hydrogen bond and the transfer of the proton directly to the neighbouring phosphate ion by electrostatic attraction. Hence, the minima in lnσ versus 1/T plot is an artifact of this kind of kinetic origin. Such an situation also has been observed by Mari *et al*. [12] in $HTaWO_6$. H_2O following the reaction by dehydration. This type of behaviour c is shown by the two regions I and II (range from 305 to 330 K and 330 to 380 K). The quick rasise in conductivity after 380 K shows to be related with the connection of structural phase transition [13] also this shows in the region III (380 to 420 K). From the conductivity graphs, it is shows that the conductivity is anisotropic with $\sigma_{c\text{-}axis} > \sigma_{a\text{-}axis}$.

The electrical conductivity measurements on KDP crystals have been taken in the range 303 to 473 K, since these crystals melt after 463 K. The D.C conductivity measurements for ADP crystals have been taken in the range 303 to 463 K, since these crystals decompose and become milk-white and opaque after 453 K.

We have also carried out D.C electrical measurements for KDP on *a-axis* and *c-axis*. The graphical plots between conductivity (σ_{dc}) and temperature are shown in Figs 5,6. The graphical plots between $\ln\sigma_{dc}$ vs temperature are shown in Figs.7,8. From these graphs, we are inclined to conclude that the conductivity is anisotropic in nature with $\sigma_{c\text{-}axis} > \sigma_{a\text{-}axis}$. For the *a-axis*, the conductivity decreases up to about 330 K and for *c-axis*, the value is slightly increased i.e. at about 345 K. This initial decrease in conductivity is due to the fact that the whole experiment is carried out in humid air and no vacuum is used. So, this explain that the decrease in conductivity is on the surface adsorbed water. This decrease is shown by the region I. We observed a transition at about 380 to 400K for both the axes. This must in some way has relation with the rotation of $H_2PO_4^-$ group. According to Slater [14] there are six possible ways of the hydrogens with around oxygens of a PO_4group. 4 arrangements are identical but two are different in which two hydrogens attached to a PO_4 group are either both on the 'upper' side of the group or both on lower side of the group making $H_2PO_4^-$ group an electrical dipole. Hence , we imagine that a proton rotation of the H_2PO^-group would give rise to a dielectric anomaly along the *a* or *b-axis* and would facilitate proton transport along *c- axis.* At this particular temperature (~380 to 400 K) not appearing any structural changes. The tetragonal symmetry is maintained and a possible change in the space group might take place from *I42d I4₁md* [15]. This is indicated by regions II and III. The region IV indicates a plateau region from a temperature range 455 to 465K. After this plateau region due to pretransition behavior, there is rapid increase in the conductivity. After this region, there is phase changes from tetragonal to monoclinic as suggested by Itoh etal [15]. Over the transition, a large stress is creates in the crystals, which results in the breaking of the crystals and KDP transparent colorless single crystal becomes opaque and milky whitw.

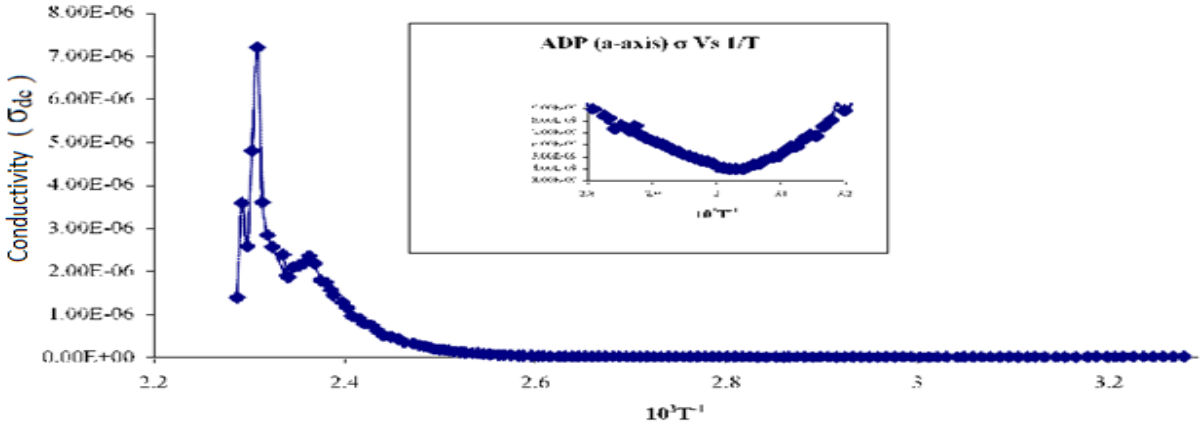

Fig.1 Plot of $\sigma_{dc} \rightarrow 1/T$ along *a-axis* for ADP crystals

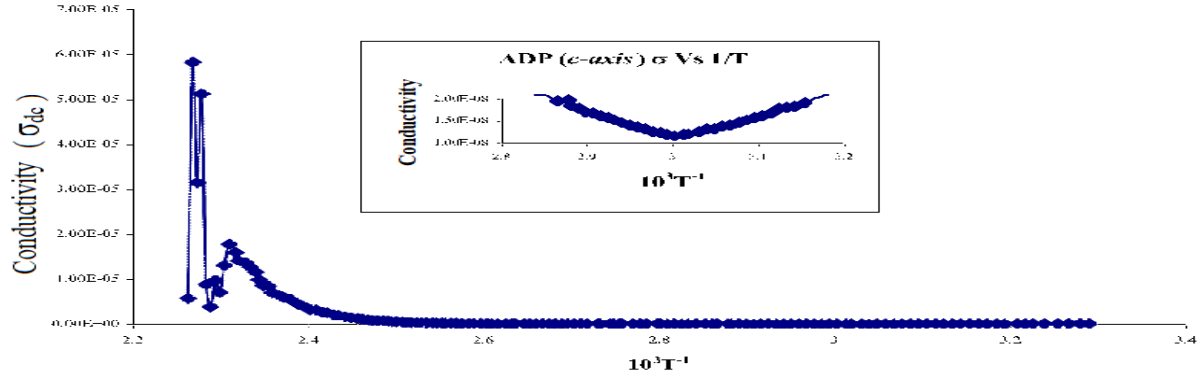

Fig.2 Plot of $\sigma_{dc} \rightarrow 1/T$ along *c-axis* for ADPcrystals

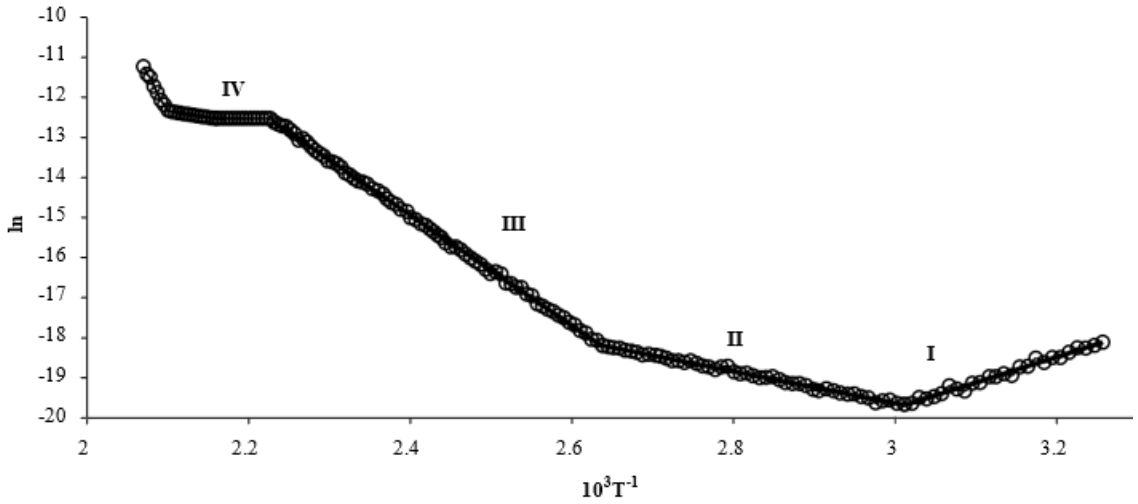

Fig.3 Plot of ln σ_{dc} → 1/T along *a-axis* for ADP crystals

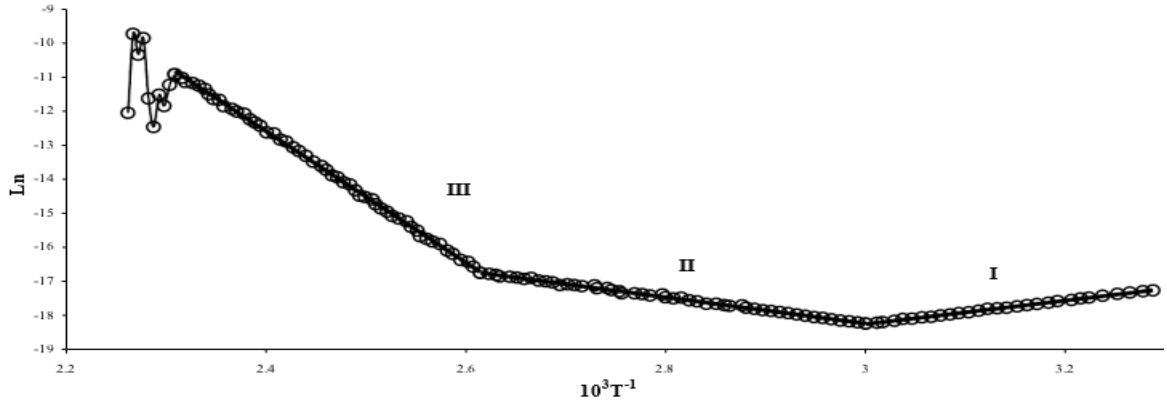

Fig.4 Plot of lnσ_{dc} → 1/T along *c-axis* for ADP crystals

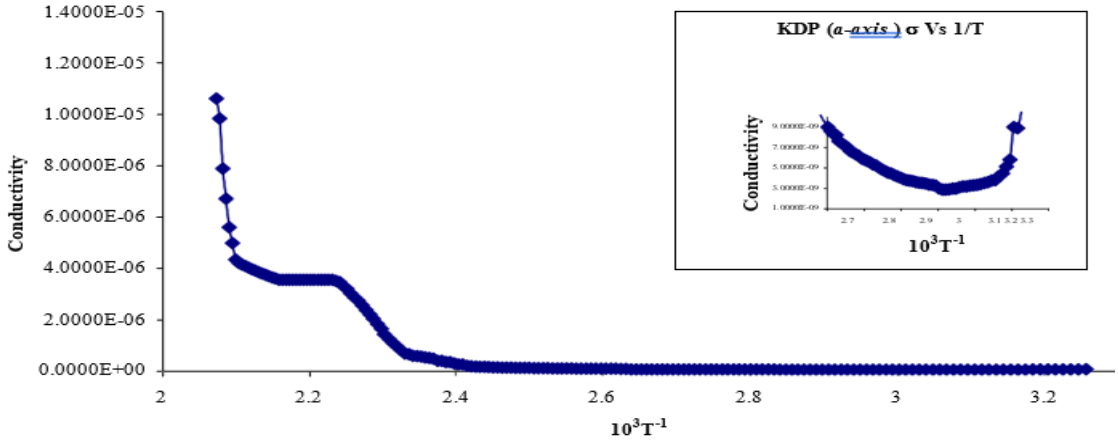

Fig.5 Plot of σ_{dc} → 1/T along *a-axis* for KDP crystals

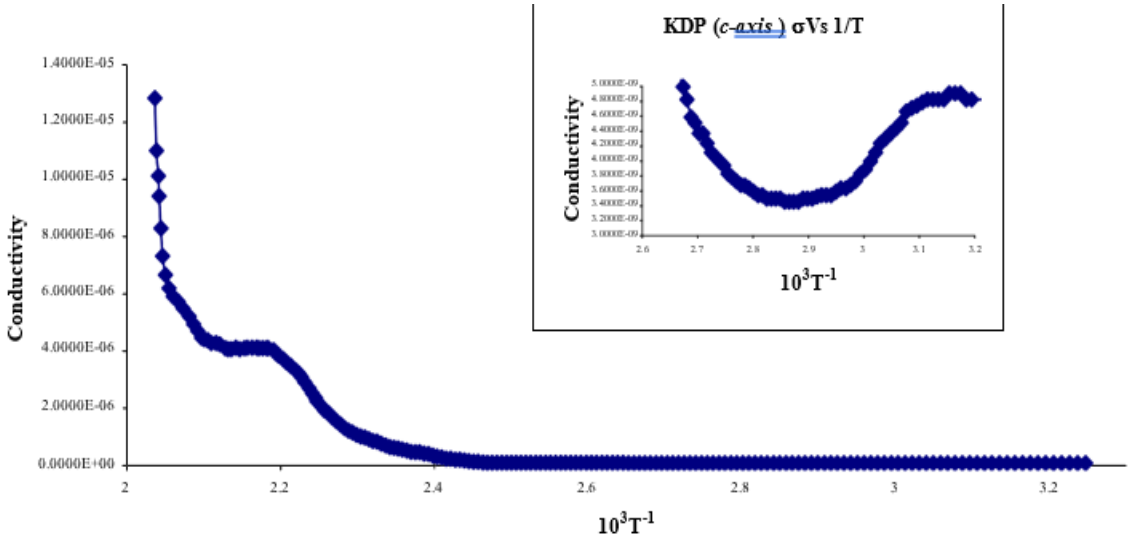

Fig.6 Plot of $\sigma_{dc} \rightarrow 1/T$ along *c-axis* for KDP crystals

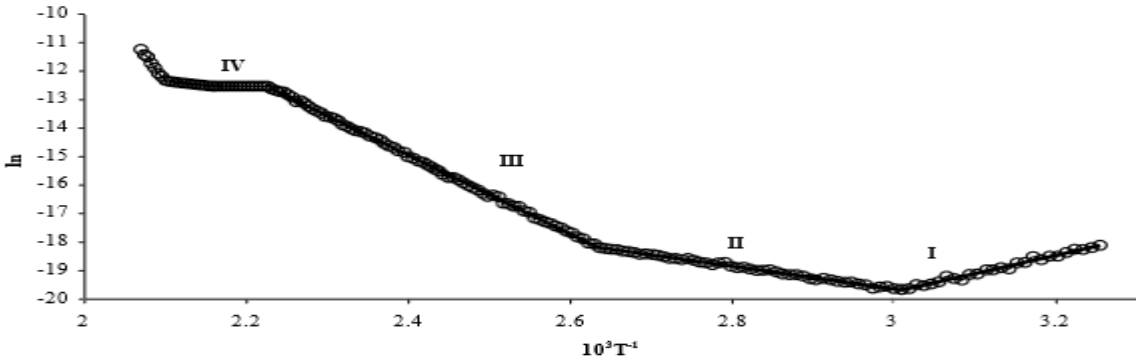

Fig. 7 Plot of $\ln\sigma_{dc} \rightarrow 1/T$ along *a-axis* for KDP crystals

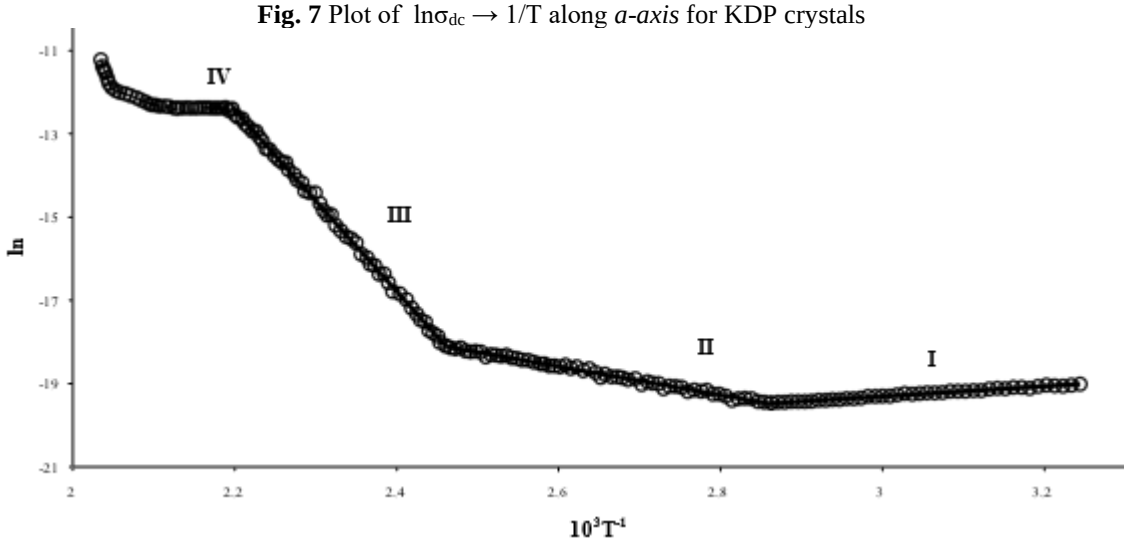

Fig.8 Plot of $\ln\sigma_{dc} \rightarrow 1/T$ along *c-axis* for KDP crystals

Activation Energies

Activation Energy is calculated using Arrhenius relation[16,17],

$$\sigma_{dc} = \sigma_0 \exp(E_a/kT) \quad (1)$$

where,

E_a = Activation energy (eV)

k = Boltzmann constant = 1.38 X 10^{-23} JK^{-1} ,

T = Absolute temperature (K).

yields the values of involved activation energies which can be calculated for different regions of ADP and KDP along

different axes. The values are given in table.

1. The disturbing results in higher temperature range i.e. the region III, may be due to an additional enthalpy term involving association or trapping [18]

Table.1 Activation energies calculated for ADP and KDP crystals

Regions on $\ln\sigma \rightarrow T^{-1}$curve	Activation Energy (eV)			
	ADP		KDP	
	a-axis	*c*-axis	*a*-axis	*c*-axis
I	0.45	0.3	0.6	0.2
II	0.35	0.34	0.35	0.31
III	1.65	1.67	1.19	1.87

SEEBECKEFFECT:

To measure the Seebeck coefficient of samples uses in the present examining as a function of temperature, which is from 298 K to 4033 K and ΔT to ±10 K combinly with better than ±1 K stability. This is a several limitation of the instrument. The problem generally facing in preparing thermoelectric power measurements is stray thermal emfs. In the present instrument these have been removed b by providing choice of selection of temperature gradient in the range from 1 to 10 K.

The variation of power of thermoelectric, S(T), determined as a function of 1/T is shown in Figs. 9 to 12 for ADP and KDP crystals along a-axis and c-axis. In general, we have seen in Seebeck coefficient with temperature as a linear fit rise . This is a typical behavior. At lower temperatures the mobility of ions is very low, entailing low thermoelectric power. The seebeck coefficient increases with temperature across both the habit planes studied. The coefficient is observed to be negative over the range of temperatures (335-345 K) studied revealing that electrons are the charge carriers which participate in the conduction of the crystals of KDP and ADP. As the temperature increases, many electrons jump from valance band to conduction band, creating many holes. In such high temperature zone, the holes too become majority charge carriers and participate in the conduction along with electrons. This can be seen in the high temperature range (~ ≥ 345 K). We have carried out the experiment in the temperature range from 480-500 K depending upon the nature of the crystal.

In a nondegenerate material the equilibrium thermoelectric power due to electron diffusion can be written as [19,20]

$$S = -\frac{k}{e}\left[A + \frac{E_F}{kT}\right]$$

where k is the Boltzmann constant, e is the electronic charge and A = (5/2 – s) is the constant that changes from 0 to 4 involved on the scattering process connection. Suppose, A = 4 and 3 show charged impurity scattering and piezoelectric scattering respectively. E_F apart of the Fermi level from the bottom to conduction band. The observed thermoelectric power depended temperature can be qualitatively explained by analysis of the magnitude of dS/dT according with temperature also.

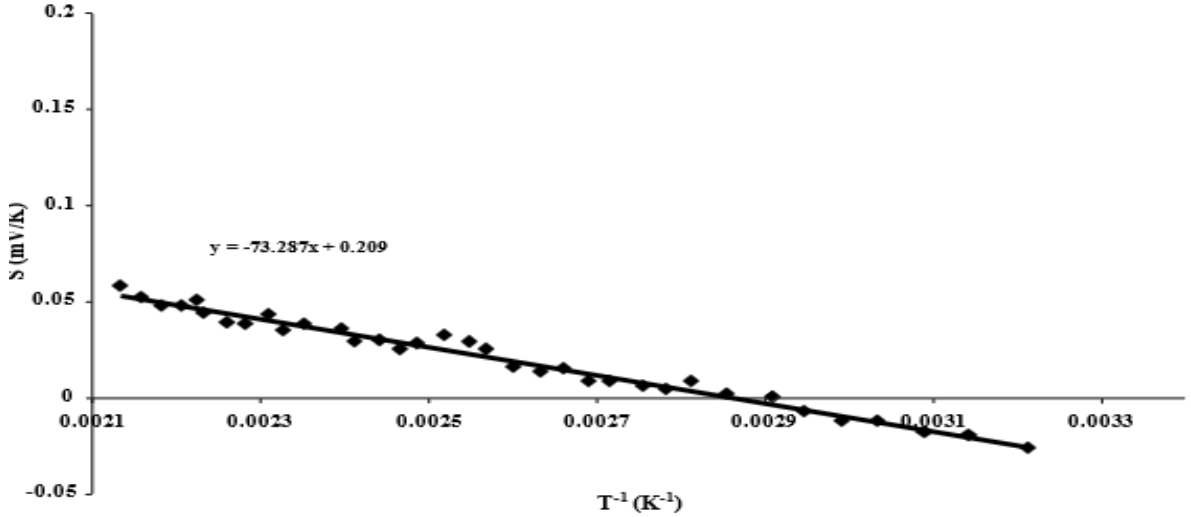

Fig.9 Variation of Temperature with thermoelectric power of ADP (*a-axis*) single crystals.

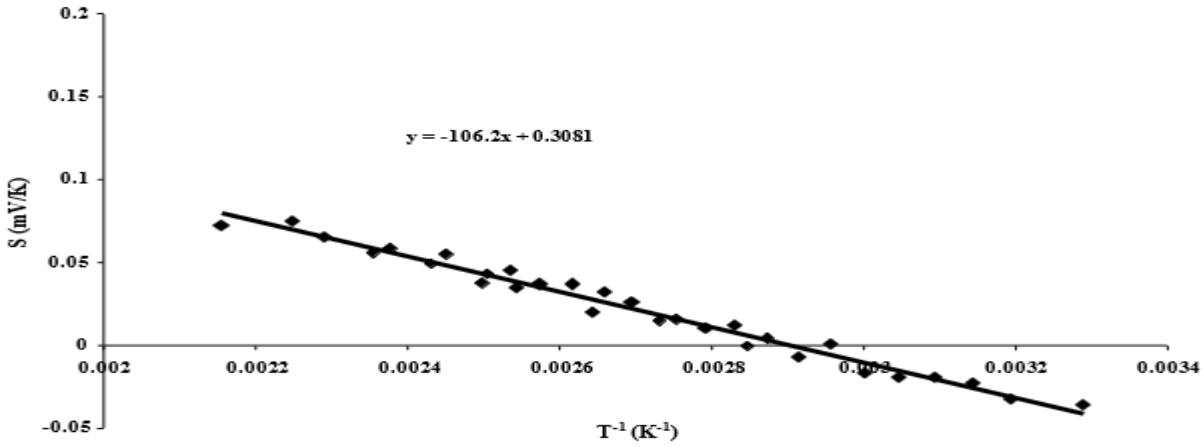

Fig.10Variation of thermoelectric power with temperature of ADP (*c-axis*) single crystals.

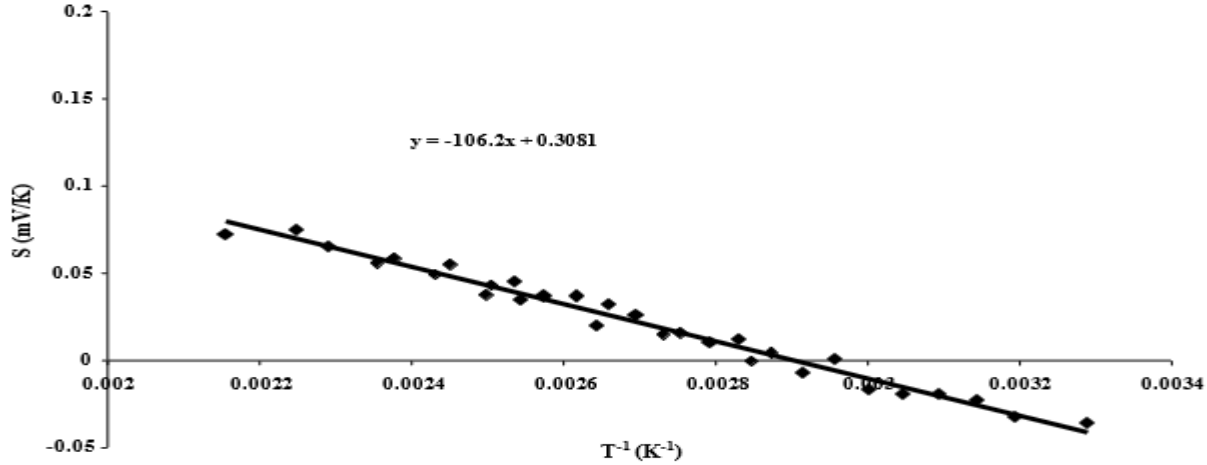

Fig.11 Variation of thermoelectric power with temperature of KDP (*a-axis*) singlecrystals

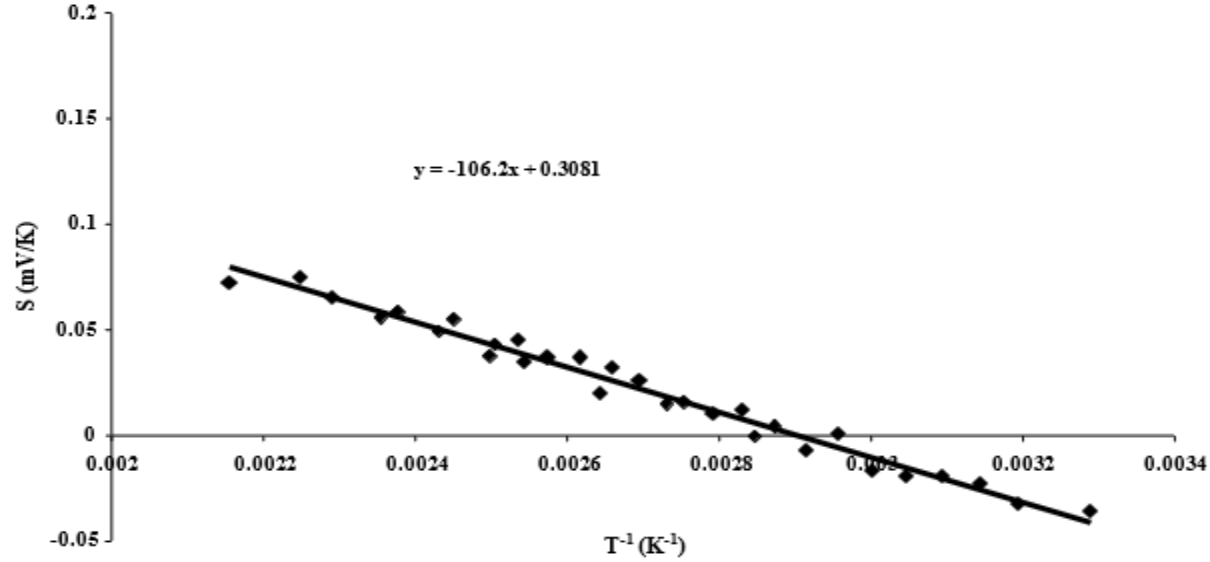

Fig.12 Variation of temperature with thermoelectric power of KDP (*c-axis*) singlecrystals

IV CONCLUSIONS

The electrical conductivity (σ_{dc}) values for ADP and KDP show that this parameter is anisotropic with $\sigma_{c\text{-}axis.} > \sigma_{a\text{-}axis}$. In case of ADP, minima (~330 K) in the conductivity occur due to deammoniation and the high temperature phase changes occurs at 420 K. In case of KDP, minima (330-345 K) in the conductivity is associated with the rotation of $H_2PO_4^-$ group and the high temperature phase transition occurs at ~ ≥ 455K.

Activation energies for different axis and for different regions are calculated in which the higher temperature gives disturbing results because of the enthalpy term involving association or trapping. From the thermopower measurements, values of E_F and A are determined, which indicate the type of scattering associated. The seebeck coefficient increases with temperature and is observed to be negative over the range of temperatures (335 K-345 K) revealing that electrons are the charge carriers and at higher temperatures the conduction is due to holes.

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