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Electrical conductivity measurements on gel grown KDP crystals added with some ammonium compounds

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Abstract. Pure and impurity added [with NH_4Cl, NH_4NO_3, $NH_4H_2PO_4$, $(NH_4)_2CO_3$ and $(NH_4)_2SO_4$] KDP single crystals were grown by the gel method using silica gels. Electrical conductivity measurements were carried out along both the unique axis and perpendicular directions at various temperatures ranging from 28 to 140°C by the conventional two-probe method. The present study shows that the conductivity in KDP crystals, for all the five dopants considered, increases with the increase in impurity concentration and temperature. Activation energies were also determined and reported.

Keywords. Impurity added KDP crystals; gel method; electrical conductivity; activation energy.

1. Introduction

Potassium dihydrogen orthophosphate, KH_2PO_4 (abbreviated as KDP) crystals have created considerable interest among several research workers. Pure and impurity added KDP crystals were grown from aqueous solutions and also in gel media by different workers (Varma *et al* 1983; Henisch 1988; Rashkovich 1991; Udupa *et al* 1997). KDP belongs to the scalenohedral (twelve sided polyhedron) class of tetragonal crystal system. It has a tetramolecular unit cell having the dimensions (Wyckoff 1960) given as $a = b = 7{\cdot}448$ Å and $c = 6{\cdot}977$ Å. KDP is ferroelectric well below room temperature and the curie temperature T is 123 K (Subbarao 1973). KDP is soluble in water and the molecular weight is 136·09 (Dean 1979).

In KDP type of crystals the possible type of point defects which help the electrical conduction process are the ionization defects, viz. $(HPO_4)^{2-}$ and H_3PO_4 produced as a result of proton jump from one phosphate group to another along the same bond (George 1989). The electrical conduction in KDP crystals has been established to be protonic (Keeffe and Perrino 1967; Shanmugham *et al* 1982). The conductivity value of KDP crystals increased when added with oxalate (crystals grown by the gel method) (Shanmugham *et al* 1985) and chloride (crystals grown by the slow evaporation method) (Ramasubramanian and Mahadevan 1991) impurities. This was explained by considering the replacement of $(H_2PO_4)^{-1}$ ions by $(C_2O_4)^{-2}$ and Cl^{-1} ions. It was also found that the activation energy values for KDP crystals do not vary much when added with oxalate impurity of various concentrations (Shanmugham *et al* 1985). It has been observed (Udupa *et al* 1997) that the KDP system has become complex after ion irradiation and it shows irregular behaviour with regard to conductivity property.

At any particular temperature, the Gibb's free energy of a crystal is minimum when a certain fraction of ions leave the normal lattice. As the temperature rises, more and more defects are produced which, in turn, increases the conductivity (Jain and Dahake 1964). In the high temperature (intrinsic) region, the effect of impurity on electrical conduction will not change appreciably whereas in the low temperature (extrinsic) region, the presence of impurity in the crystal increases its conductivity. The electrical conduction in dielectrics is mainly a defect controlled process in the low temperature region. The presence of impurities and vacancies mainly determine this region. The energy needed to form the defect is much larger than the energy needed for its drift (Shanmugham *et al* 1985; Udupa *et al* 1997). The conductivity of the crystal in the higher temperature region is determined by the intrinsic defects caused by the thermal fluctuations in the crystal.

We have, in the present work attempted to study the effect of ionic impurities [ammonium compounds with and without the common ion $(H_2PO_4)^{-1}$ added heavily (impurity added in the KDP solution used for the growth of crystals with impurity concentration ranging from 2000 to 10000 ppm, i.e. 0·2 to 1·0 mole%)] on the electrical conductivity at various temperatures ranging from 28 (room temperature) to 140°C of KDP crystals grown by the gel method. A report of our work is presented and discussed.

2. Experimental

KDP crystals were grown in silica gels prepared from sodium metasilicate (SMS) by the reduction of solubility

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method. Analytical reagent (AR) grade samples of KDP, ammonium chloride [NH_4Cl], ammonium nitrate [NH_4NO_3], ammonium dihydrogen orthophosphate [$NH_4H_2PO_4$], ammonium carbonate [$(NH_4)_2CO_3$] and ammonium sulphate [$(NH_4)_2SO_4$] along with double distilled water and ethyl alcohol were used.

KDP was added with NH_4Cl, NH_4NO_3, $NH_4H_2PO_4$, $(NH_4)_2CO_3$ and $(NH_4)_2SO_4$ separately each in six different KDP : impurity molecular ratios, viz. 1 : 0·000 (pure KDP), 1 : 0·002, 1 : 0·004, 1 : 0·006, 1 : 0·008 and 1 : 0·010. The impurity was dissolved in 2·5 M solution of KDP.

SMS solution of density 1·08 g/cc was added to 2·5 M KDP solution in the volume ratio 1 : 4 (SMS : KDP). Thus prepared gel solution was then transferred to test tubes (of diameter 2·5 cm) (20 ml in each tube) and was allowed to set at room temperature. Gelation occurred in about 15 h. Then it was kept as such for one day for gel ageing. After that an equal volume of ethyl alcohol was added slowly above the gel and the test tubes were tightly closed with rubber corks to prevent evaporation of alcohol. Alcohol reduces the solubility of KDP which first precipitate at the gel alcohol interface. Diffusion of alcohol into the gel was followed by formation of nuclei which then grew larger. Completion of crystallization took about 15 to 20 days.

Scalenohedral morphology was exhibited by all the crystals grown. Crystals with high transparency and large defect-free size (> 3 mm) were selected and used for the electrical conductivity measurements. The extended portions of the crystals were removed completely and the opposite faces were polished and coated with good quality graphite to obtain a good ohmic contact.

The conductivity measurements were carried out along both the unique axis (*c*-) and perpendicular (*a*- and *b*-) directions for all the twentysix crystals grown using the conventional two-probe technique at various temperatures ranging from 28 to 140°C. The resistance of the crystals were measured using a thousand megohmmeter. The observations were made while cooling the sample. The dimensions of the crystals were measured using a travelling microscope (L.C. = 0·001 cm). The conductivity (σ) of the crystal was calculated using the relation

$$\sigma = \frac{d}{RA},$$

where R is the measured resistance, d the thickness of the sample and A the area of the face in contact with the electrode. The σ values were fitted into the equation

$$\sigma T = \sigma_0 \exp(-E/kT),$$

and the activation energy (E) values were calculated. Here k is the Boltzmann's constant, T the absolute temperature and σ_0 a constant depending on the material.

When the crystals are grown in gel media, there is a possibility that the conductivity and related properties are different for different crystals even though they are grown in the same container. It would be better if there is a possibility to estimate quantitatively the concentration level of the impurity that is present in each crystal. But, it is very difficult to do so since the impurities considered in the present study are ammonium compounds without any metal atom. Hence, in order to understand qualitatively (atleast) whether the added impurity has entered into the KDP lattice or not, we carried out the density measurement by using the floatation technique.

3. Results and discussion

It was observed that the difference in densities of crystals grown in the same container was very small and negligible. Average densities are given in table 1. The value observed for pure KDP (2·344 g/cc) compares well with that reported in the literature (2·338 g/cc) (Dean 1979). For all the five impurities considered in the present study, the observed decrease of density of KDP crystal caused by the impurities indicates that the impurities have entered into the lattice of KDP crystals. Moreover, it can be seen that the density decreases further with the increase in impurity concentration of the aqueous solution of KDP used for the growth of crystals.

The σ values obtained along the two directions (*a*- and *b*-) perpendicular to the unique axis (*c*-direction) are, within experimental error, the same. Figures 1–5 show the plots of ln(σT) against 1000/T for the pure and impurity added KDP crystals when the field is perpendicular (along the *a*-direction) to the unique axis. Figures 6–10 show the plots when the field is parallel to the unique axis. The values of the activation energy E for pure and impurity added KDP crystals are given in table 1.

Conductivities obtained in the present study are of the same order with those obtained by previous authors for the KDP crystals (× 10^{-6} mho/metre) (Harris and Vella

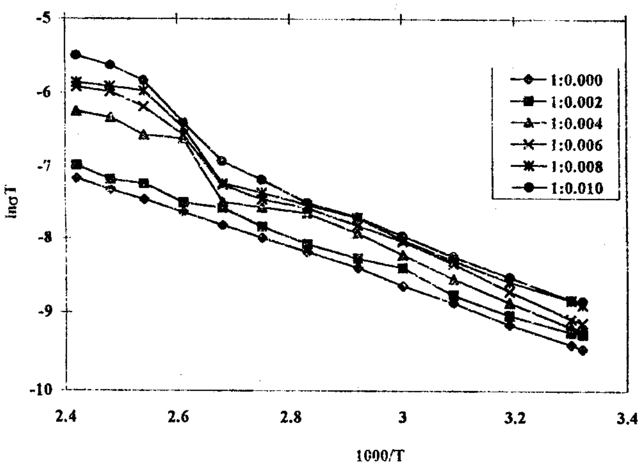

Figure 1. Variation of ln σT with 1000/T for NH_4Cl added KDP crystals along *a*-direction.

1966; Shanmugham *et al* 1985; Ramasubramanian and Mahadevan 1991; Udupa *et al* 1997).

It can be seen that, for all the impurities considered in the present study, the electrical conductivity increases with the increase in impurity concentration and temperature. This is similar to that observed for oxalate doped KDP crystal (Shanmugham *et al* 1985). The defect concentration will increase exponentially with temperature and consequently the electrical conduction also increases. The addition of impurity further increases the electrical conduction in the temperature region considered.

The electrical conduction in KDP crystals has been established (Keeffe and Perrino 1967; Shanmugham *et al* 1982) to be protonic. In KDP type of crystals the possible type of point defects which help the electrical conduction process are the ionization defects, viz. $(HPO_4)^{2-}$ and (H_3PO_4), produced as a result of proton jump from one phosphate group to another along the same bond (George 1989) and L and D defects. The conduction region considered in the present study seems to be connected to mobility of vacancies. The low activation energies observed suggests that oxygen vacancies may be responsible for conduction in this region.

If the probability of occupation of an interstice is f, then the probability of finding a vacant neighbour site is $(1-f)$. Even for very high concentrations, of the order of 10^{20} cm^{-3}, f does not exceed 10^{-2} so that in real cases with concentration of interstitials of the order of 10^{15} to 10^{20} cm^{-3}, $(1-f) \approx 1$ (Bunget and Popescu 1984).

Jaccard and his co-workers (Granicher *et al* 1957; Jaccard 1959) have shown that proton conduction may be accounted for by motion of protons accompanied by a *D* defect (excess of positive charge). Migration of these defects may only modify electric polarization and may not

Table 1. Activation energies and densities of pure and impurity added KDP crystals.

	System (impurity in mole%)	Density (g/cc)	Activation energy, E(eV) along	
			a-direction	*c*-direction
(a)	Pure KDP	2·344	0·220	0·216
(b)	NH_4Cl added KDP			
	0·2	2·341	0·222	0·211
	0·4	2·332	0·291	0·269
	0·6	2·309	0·309	0·277
	0·8	2·249	0·300	0·279
	1·0	2·178	0·325	0·311
(c)	NH_4NO_3 added KDP			
	0·2	2·330	0·217	0·233
	0·4	2·321	0·213	0·242
	0·6	2·313	0·213	0·242
	0·8	2·280	0·211	0·267
	1·0	2·240	0·210	0·266
(d)	$NH_4H_2PO_4$ added KDP			
	0·2	2·334	0·222	0·235
	0·4	2·295	0·220	0·234
	0·6	2·250	0·223	0·233
	0·8	2·201	0·222	0·239
	1·0	2·141	0·222	0·236
(e)	$(NH_4)_2CO_3$ added KDP			
	0·2	2·333	0·221	0·285
	0·4	2·324	0·230	0·338
	0·6	2·315	0·234	0·360
	0·8	2·294	0·255	0·385
	1·0	2·259	0·260	0·401
(f)	$(NH_4)_2SO_4$ added KDP			
	0·2	2·339	0·219	0·237
	0·4	2·331	0·218	0·240
	0·6	2·322	0·217	0·232
	0·8	2·299	0·215	0·247
	1·0	2·246	0·213	0·244

change the charge at an electrode (Granicher *et al* 1957). The motion of defects occurs by some kind of rotation in the bond with defects. The speed of displacement $v = \nu a$, where a and ν are the distance and frequency respectively of the jump from one bond to the other. Utilization of the Nernst–Einstein equation with the diffusion coefficient given by

$$D = (1/2)\ \nu a^2 \exp(-E/kT),$$

where $a = 2{\cdot}8$ Å, while E equals the activation energy of conduction, has yielded in the case of pure KDP for the jump frequency $3 \times 10^{13}\ \mathrm{s}^{-1}$. This value was considered reasonable since it was close to $4 \times 10^{13}\ \mathrm{s}^{-1}$, found for oscillation frequencies of the P–O–H group in orthophosphates (Bunget and Popescu 1984).

If the sample crystal is placed in a stationary electric field (as in the present study) the carriers may be considered to be contained in an enclosure bounded by the capacitor plates. As the carriers may not leave the enclosure, they accumulate in the regions close to the plates which causes a concentration gradient to be formed and this gradient feeds a diffusion current. At equilibrium the diffusion current density equals that of the drift current. Charge accumulation is related to inhomogeneities of the material, the agglomeration of impurity ions by diffusion in the vicinity of electrodes or chemical changes in layers close to electrodes (Bunget and Popescu 1984).

The conductivities are more along the *a*-direction than those along the *c*-direction for all the impurities considered in the present study at low temperatures. This is in correspondence with the results obtained by the previous authors for their systems (Harris and Vella 1966; Shanmugham *et al* 1985). For the impurity $(NH_4)_2CO_3$ (for all the impurity concentrations) the conductivity along *a*-direction becomes less than that along *c*-direction beyond certain temperatures (70°C for 0·2 mole% and 30°C for other concentrations). For the impurity $(NH_4)NO_3$ the

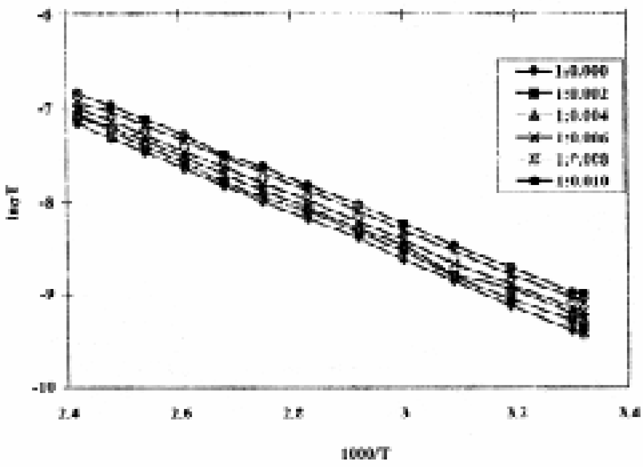

Figure 2. Variation of ln σT with $1000/T$ for NH_4NO_3 added KDP crystals along *a*-direction.

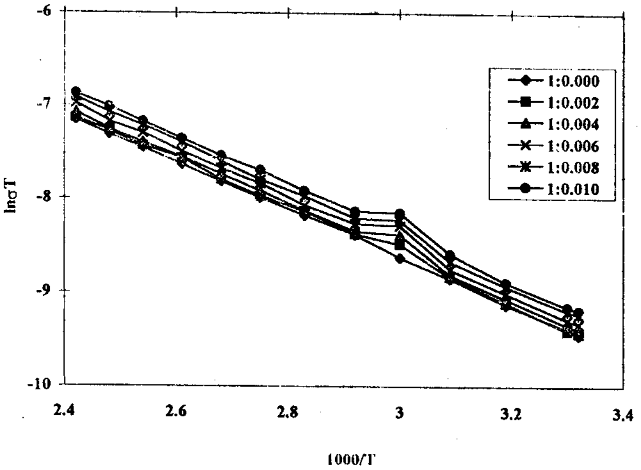

Figure 3. Variation of ln σT with $1000/T$ for ADP added KDP crystals along *a*-direction.

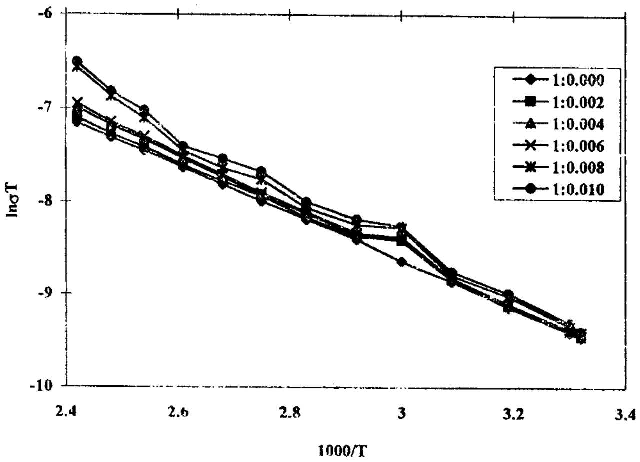

Figure 4. Variation of ln σT with $1000/T$ for $(NH_4)_2CO_3$ added KDP crystals along *a*-direction.

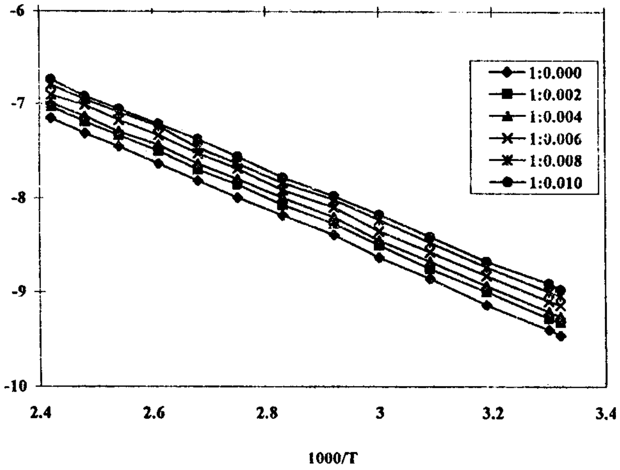

Figure 5. Variation of ln σT with $1000/T$ for $(NH_4)_2SO_4$ added KDP crystals along *a*-direction.

conductivity along *a*-direction becomes less than that along *c*-direction beyond 70°C and 60°C for 0·8 mole% and 1·0 mole% respectively.

At the lowest temperature considered in the present study (28°C), the conductivities of the pure and impurity added KDP crystals follow a particular order for all the impurity concentrations. However, the order is different for *a* and *c*-directions. For the *a*-direction, it follows:

σ [pure KDP] < σ [$(NH_4)_2CO_3$ added KDP]
< σ [$NH_4H_2PO_4$ added KDP]
< σ [NH_4NO_3 added KDP]
< σ [$(NH_4)_2SO_4$ added KDP]
< σ [NH_4Cl added KDP].

For the *c*-direction it follows:

σ [pure KDP] < σ [NH_4NO_3 added KDP]
< σ [$NH_4H_2PO_4$ added KDP]
< σ [$(NH_4)_2SO_4$ added KDP]
< σ [$(NH_4)_2CO_3$ added KDP]
< σ [NH_4Cl added KDP].

At the highest temperature considered in the present study (140°C), the conductivities observed for the impurity added KDP crystals along the *c*-direction are minimum for the $NH_4H_2PO_4$ added KDP and maximum for the $(NH_4)_2CO_3$ added KDP for all the impurity concentrations considered. However, no systematic order is observed with that along the *a*-direction.

Though it is not possible to make an authentic statement with the observations made in the present study, it may be stated that while the NH_4Cl impurity is able to create more defects the $NH_4H_2PO_4$ impurity is able to create less defects among the impurities considered in the present study. Hence, the present study gives further evidence to the statement (Keeffe and Perrino 1967;

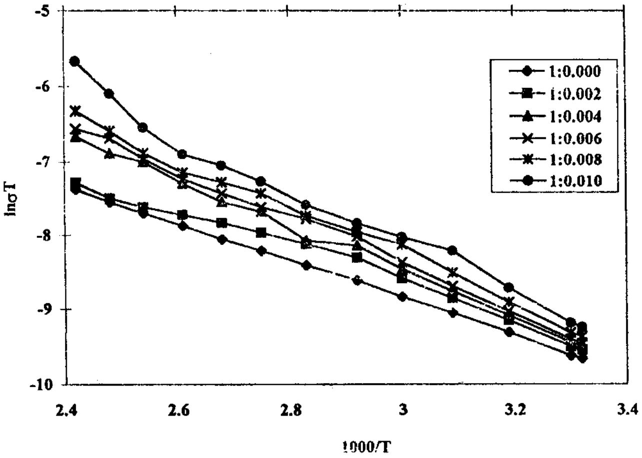

Figure 6. Variation of ln σT with $1000/T$ for NH_4Cl added KDP crystals along *c*-direction.

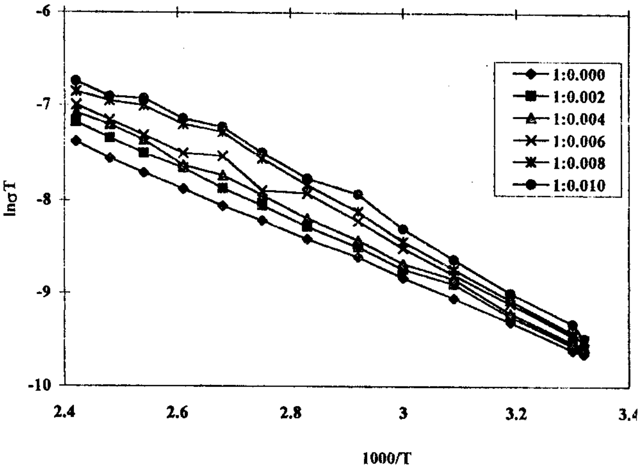

Figure 7. Variation of ln σT with $1000/T$ for NH_4NO_3 added KDP crystals along *c*-direction.

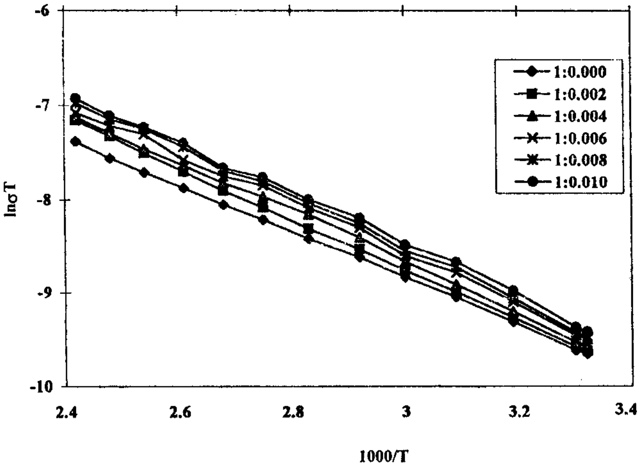

Figure 8. Variation of ln σT with $1000/T$ for ADP added KDP crystals along *c*-direction.

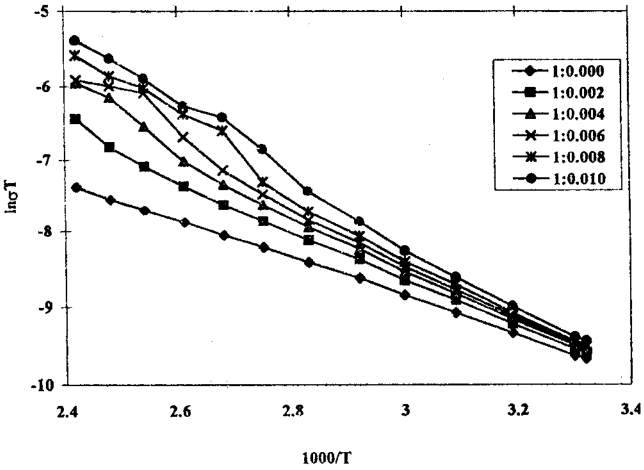

Figure 9. Variation of ln σT with $1000/T$ for $(NH_4)_2CO_3$ added KDP crystals along *c*-direction.

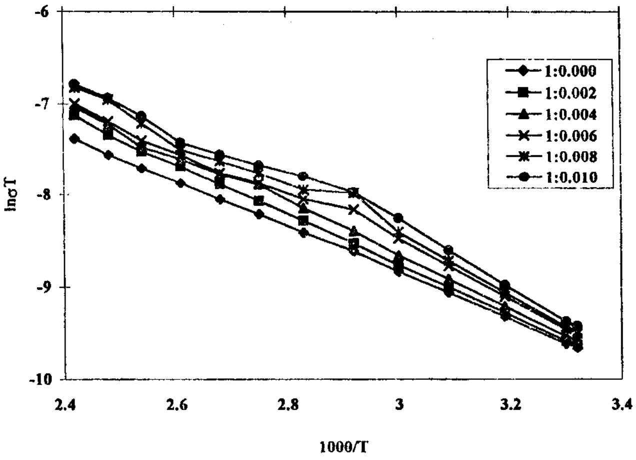

Figure 10. Variation of ln σT with 1000/T for $(NH_4)_2SO_4$ added KDP crystals along *c*-direction.

Shanmugham *et al* 1982) that the conduction in KDP is mainly due to the anions viz. $(H_2PO_4)^{-1}$ ions and not the cations viz. K^+ ions.

The *E* values (see table 1) increase with the increase in impurity concentration in the case of $(NH_4)_2CO_3$ and NH_4Cl impurities along both the *a*- and *c*-directions (*E* value for NH_4Cl added KDP in 0·2 mole% is slightly less than that for pure KDP along the *c*-direction). In the case of NH_4NO_3 and $(NH_4)_2SO_4$, the *E* values along the *a*-direction decrease with the increase in impurity concentration. The *E* values increase with the increase in impurity concentration along the *c*-direction in the case of $(NH_4)_2SO_4$ impurity. However, there is no systematic variation observed in the case of NH_4NO_3 (in the *c*-direction) and $NH_4H_2PO_4$ (in both the *a*- and *c*-directions) impurities.

4. Conclusions

Pure and impurity added (with five ammonium compounds separately) KDP single crystals were grown and conductivities were measured along both the *a*- and *c*-directions at various temperatures ranging from 28 to 140°C. Density measurement indicates that the impurities have entered into the lattice of KDP crystals. Also, the present study gives further evidence to prove that the conduction in KDP is mainly due to the anions and not the cations. The present study indicates that the conductivity increases with the increase in impurity concentration and temperature. At low temperatures, the conductivities are more along the *a*-direction than those along the *c*-direction.

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