Electrical resistivity measurements on gel grown KDP crystals doped with KCl, KNO3, NaCl and NaNO3

Beaulah Shanthini, C Anitha, C Mahadevan+ and C Balasingh

Department of Physics, Scott Christian College, Nagercoil-629 003,
India

+S T. Hindu College, Nagercoil-629 002, India

Abstract : Pure and impurity added (with KCl, KNO₃, NaCl and NaNO₃) KDP single crystals were grown by the gel method using silica gels. Electrical resistivity measurements were carried out along both the unique axis and perpendicular directions at room temperature by the conventional two-probe method The present study shows that the impurities with no common ion is able to create more defects along the perpendicular direction (*a*-direction) than those with a common ion

Potassium dihydrogen orthophosphate (abbreviated as KDP), KH_2PO_4, belongs to the scalenohedral (twelve sided polyhedron) class of tetragonal crystal system. It has a tetramolecular unit cell having the dimensions [1] given as $a = b = 7.448$ Å and $c = 6.977$ Å. KDP is ferroelectric well below room temperature and the curie temperature T_c is 123 K [2]. KDP is soluble in water and the molecular weight and density respectively are 136.09 and 2.338 g/cc [3].

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 [4–6]. 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 [7]. The electrical conduction in KDP crystals has been established to be protonic [8,9]. The resistivity value of KDP crystals decreases when added

with oxalate (crystals grown by the gel method) [10] and chloride (crystals grown by the slow evaporation method) [11] 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 [10]. It has been observed [6] 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, decrease the resistivity [12]. 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 decreases its resistivity. The electric 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 [6,10].

We have, in the present work, attempted to study the effect of ionic impurities (with and without the common ion K^+) added heavily (impurity added in the KDP solution used for the growth of crystals with concentration ranging from 2000 to 10000 ppm) on the electrical resistivity at room temperature (*i.e.*, at a particular temperature of 32°C in the extrinsic region) of KDP crystals grown by the gel method. A report of our work is presented and discussed.

KDP crystals were grown in silica gels prepared from sodium metasilicate (SMS) by the reduction of solubility method. Analytical reagent (AR) grade samples of KDP, potassium chloride (KCl), potassium nitrate (KNO_3), sodium chloride (NaCl) and sodium nitrate ($NaNO_3$) along with double distilled water and ethyl alcohol were used.

KDP was added with KCl, KNO_3, NaCl and $NaNO_3$ separately (as impurities) 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 the 2.5 *M* solution of KDP. SMS solutions with two different densities, *viz.* 1.06 and 1.08 g/cc were used.

SMS solution of density 1.06 or 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 (20 ml in each tube) (or diameter 2.5 cm) and was allowed to set at room temperature. Gelation occurred in about 15 to 20 hours. 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 12 to 15 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 resistivity measurements. The extended portions of the crystals were removed off and the opposite faces were polished and coated with good quality graphite to obtain a good ohmic contact.

The resistivity measurements were carried out along both a- and c-directions for all the fourty-two crystals grown using the conventional two-probe technique at a particular temperature of 32°C. The resistance of the crystals were measured using a 1000 Megohm meter. The dimensions of the crystals were measured using a travelling microscope (L.C. = 0.001 cm). The resistivity (ρ) of the crystal was calculated using the relation

$$\rho = RA/d,$$

where R is the measured resistance, d is the thickness of the sample and A is the area of the face in contact with the lead (electrode).

Results obtained in the present study are given in Table 1. Resistivities obtained in the present study are of the same order with those obtained by previous authors for the KDP

Table 1. Results of electrical resistivity measurements

Impurity	Molecular ratio	Resistivity ($\times 10^6$ Ω-m) along			
		(SMS density 1 06 g/cc)		(SMS density · 1 08 g/cc)	
		c-direction	a-direction	c-direction	a-direction
Pure KDP	1 . 0 000	0 6431	0 2948	0.6017	0 3600
KCl	1 0 002	0 4109	0 2546	0 3541	0 3227
	1 0 004	0.3360	0.2183	0 2683	0 2496
	1 . 0.006	0 2276	0.1744	0 2172	0 1769
	1 0 008	0.1779	0 1575	0 1595	0.1435
	1 0.010	0.0891	0.0768	0 0961	0 0960
KNO$_3$	1 . 0.002	0.4269	0 1921	0 3892	0 2475
	1 . 0.004	0.3945	0.1435	0.2007	0 1960
	1 · 0 006	0 1144	0 0600	0 1541	0 1343
	1 : 0.008	0.0542	0 0395	0.1342	0 1095
	1 : 0.010	0 0438	0 0259	0 0852	0 0520
NaCl	1 : 0.002	0.3891	0.2461	0.3456	0.2733
	1 0.004	0.2721	0 1785	0.2308	0 2213
	1 : 0.006	0.2006	0 1483	0.1897	0 1814
	1 : 0.008	0.1475	0 0653	0 1378	0 1232
	1 . 0.010	0 0817	0.0587	0.0770	0.0723

Table 1. *(Cont'd.).*

Impurity	Molecular ratio	Resistivity ($\times 10^6$ Ω-m) along			
		(SMS density : 1.06 g/cc)		(SMS density : 1.08 g/cc)	
		c-direction	a-direction	c-direction	a-direction
NaNO$_3$	1 · 0.002	0.4348	0.0805	0.4108	0.2430
	1 . 0.004	0.4145	0.0513	0.2206	0.1597
	1 . 0.006	0.3360	0.0450	0.2193	0.1118
	1 . 0.008	0.0771	0.0315	0.2073	0.0950
	1 · 0.010	0.0332	0.0160	0.0968	0.0385

crystals ($\times 10^6$ ohm-metre) [6,10–11,13]. It can be seen that the electrical resistivity decreases (consequently, electrical conductivity increases) with the increase in impurity concentration (in the solution used for the growth of crystals).

The resistivities are more along the c-direction than those along the a-direction (*i.e.*, perpendicular to the c- or unique axis direction). This is in correspondence with the results obtained by the previous authors [10,13]. Density of the SMS solution used for the growth of crystals has some effect. For all the dopants considered, the resistivity along a-direction increases with the increase in SMS density. The resistivity along the c-direction decreases with the increase in SMS density for the chloride impurities while no systematic variation observed for the nitrate impurities. This gives a rough idea that the KDP crystals grown with SMS density of 1.08 g/cc are less defective than those grown with SMS density of 1.06 g/cc.

Resistivities for the NaCl added KDP crystals are considerably less than those observed for the KCl added KDP crystals along both the a- and c-directions. Resistivities for the NaNO$_3$ added KDP crystals are considerably more and less respectively along c- and a-directions than those observed for the KNO$_3$ added KDP crystals. This shows that the impurities with no common ion are able to create more defects along a-direction than those with a common ion. However, along c-direction, the nitrates and chlorides behave oppositely. Reason for this is not understood.

Pure and impurity added KDP single crystals were grown and resistivities were measured along both the c- and a-directions at a temperature of 32°C. The present study indicates that the resistivity decreases with the increase in impurity concentration. The resistivities are more along the unique axis direction than those along the perpendicular (a-) direction. The impurities with no common ion are able to create more defects along a-direction than those with a common ion.

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