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Effect of dichromate addition on the electrical properties of KDP crystals

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ABSTRACT

With an aim of discovering new useful materials KDP single crystals added with potassium dichromate ($K_2Cr_2O_7$) in six different molecular ratios have been grown from respective aqueous solutions by the free evaporation method. Dielectric measurements were carried out on all the six grown crystals with a fixed frequency of 1kHz at various temperatures ranging from 50-150°C along a- and c- directions by using the parallel plate capacitor method . The chromium atom content determined through AAS method confirms the presence of chromate ion in the crystal. The present study indicates that the dielectric parameters increase with the increase in temperature, but do not vary systematically with respect to impurity concentration. Also it indicates that 0.4 mole% dichromate addition to KDP leads to low ε_r value dielectrics.

Keywords: Growth from solution, Potassium compounds, Dielectric materials, Characterization, Doping, Impurities, Single crystal growth.

INTRODUCTION

Potassium dihydrogen orthophosphate (KDP) KH_2PO_4 continues to be an interesting material both academically and industrially. KDP is a representative of hydrogen bonded materials which possesses very good electro-optic and nonlinear optical properties in addition to interesting electrical properties. Due to the interesting properties, structural phase transitions (at Curie temperature 123K) and ease of crystallization, KDP and its isomorphs have been the subject of a wide variety of investigations for over 50 years. The demand for high quality large single crystals of KDP increases due to the application as frequency conversion crystal in inertial confinement fusion [1-2]. KDP belongs to scalenohedral class of tetragonal crystal system [3].

The piezo- electric property of KDP crystal makes it useful for the construction of crystal filters and frequency stabilizers in electronic circuits. KDP is used as a tuning element in laser operation of eletro-optic devices is based on the Pockel's effect in which the change in dielectric constant $\Delta\varepsilon_r$ is a linear function of the applied field [4]. Micro electronics industry needs replacement of dielectric materials in multilevel interconnect structures with new low dielectric constant(ε_r) material as an interlayer dielectric (ILD) which surrounds and insulates interconnect wiring. Lowering the ε_r value of the ILD decreases the RC delay, lowers power consumption and reduces "cross-talk" between interconnects [5].

KDP and its deuterated analog DKDP (KD_2PO_4) are widely used to control the parameters of laser light such as pulse length, polarization and frequency through the first- and second- order electro-optic effects [6]. Pure and impurity added KDP single crystals have been grown from aqueous solutions and also in gel media and characterized by different workers. Some important and interesting results have already been reported on several properties of impurity added KDP single crystals [7, 8].

The second harmonic generation (SHG) efficiency is found to be appreciably increased by the addition of alkali halides as impurities [9]. The DC electrical conductivity is found to be reduced by the addition of NaCl and NaBr as impurities [10]. In order to explain the effect of impurities it is required to have data for diverse additives for various properties. Some substances when doped to KDP may yield KDP with low ε_r value, 0.6 mole% urea addition to KDP illustrates this. At 40°C, ε_r =2.86 along a- and 3.17 along c-directions only. This prompted a research programme to be carried out in our laboratory on the nucleation, growth and physical properties of pure and impurity (various types) added KDP single crystals. The nucleation studies led to three empirically formulated rules related to the variation of nucleation parameters with impurity concentration[11].

In the present study we have investigated the effect of $K_2Cr_2O_7$ (Potassium dichromate) as an impurity on the dielectric properties of KDP single crystals grown from aqueous solutions, by the free evaporation method. The results are reported herein.

MATERIALS AND METHODS

2. Experimental

Analytical reagent grade (AR) samples of KH_2PO_4 and $K_2Cr_2O_7$ along with double distilled water were used for the growth of single crystals by the free evaporation method. KDP was added with potassium dichromate in six different KDP: $K_2Cr_2O_7$ 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. Supersaturated aqueous solution of the salt (2.5 M) was prepared in a100 ml beaker (corning glass vessel) and allowed to equilibrate at the desired temperature. The crystals were grown in the unstirred condition. The supersaturated solutions were prepared at a slightly higher temperature, and then cooled naturally to 34°C and volume was 20ml, for all the crystal growth experiments. Small crystals appeared in the beginning due to free evaporation and grew larger in considerable finite time. Best crystals were selected from this and used for various measurements.

In order to understand whether the added impurity has entered into the KDP lattice or not, we made the AAS studies. Crystals with high transparency and large surface defect -free (ie without any pit or crack or scratch on the surface, tested with a travelling microscope) size (>3mm) were selected and used for the dielectric measurements. The capacitance (C_{crys}) and dielectric loss factor (tanδ) were measured using the conventional parallel plate capacitor method with a fixed frequency (f) of 1kHz using an LCR meter (Systronics make) at various temperatures ranging from 50-150°C along both the a- and c- directions while cooling the sample. The dielectric constant (ε_r) and the AC conductivity (σ_{ac}) were calculated in a way similar to that followed by Mahadevan and his co- workers [7,8,12].

RESULTS AND DISCUSSION

Figure1 shows the sample crystals grown. Scalenohedral morphology is exhibited by all the crystals grown. All the crystals are found to be stable, colourless and transparent. The pure KDP crystals are colourless. The mild orange –yellow coloration of KDP crystal caused by the $K_2Cr_20_7$ impurity increases for the higher dopant ratio and the coloration indicates that the impurity molecules had entered into the lattice of KDP crystals .The AAS studies carried out confirm the presence of chromate ions in the crystal .Table 1 provides the chromium content with dopant concentration.

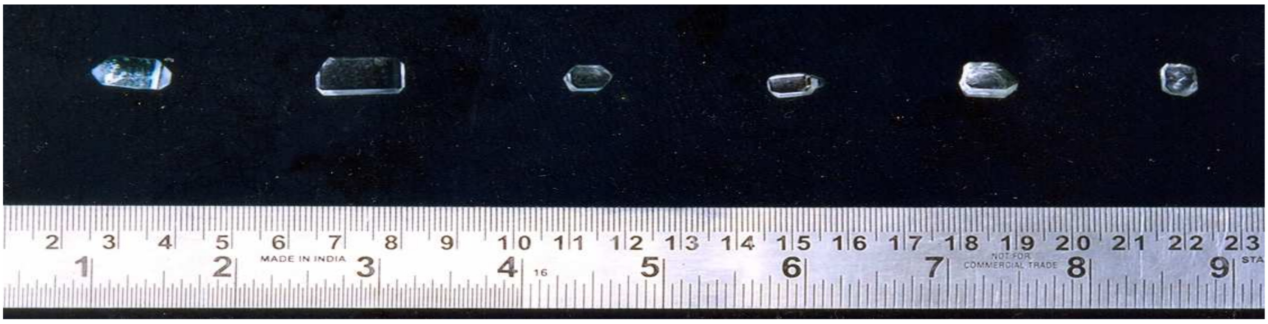

Figure1: Photgraph of the sample crystals grown [From left: Pure KDP and 0.2, 0.4, 0.6, 0.8 and 1.0 mol% chromate added KDP]

Table 1: The chromium atom contents measured using AAS values

KDP : $K_2Cr_2O_7$ ratio	Cr content (μ_g/g)
1:0.002	15
1:0.004	30
1:0.006	41
1:0.008	90
1:0.010	96

The dielectric constants observed in the present study are provided in Figure 2(a,b). The ε_r value increases with the increase in temperature in the case of all the six crystals grown in the present study. This is similar to that observed for pure and urea added KDP single crystals reported earlier [7].

The dielectric constant of a material is generally composed of four types of contributions viz, ionic, electronic, orientational and space charge polarizations. All of these may be active at low frequencies. The nature of variation of dielectric constant with frequency and temperature indicates the type of contributions that are present in them. The dipole orientational effect can be seen in some materials at high frequencies and ionic and electronic polarization below 10^3 Hz. The large value of ε_r at low frequency and low temperature is due to the presence of space charge polarization which depends on the purity and perfection of the sample [13,14]. It is understood that the space charge polarization is not dominating in the system considered in the present study.

Udupa et al [15] found that the dielectric constant decreases with increase of temperature at all frequencies they considered. Also they observed an appreciable increase in the value of ε_r after impurity addition and ε_r decreases with increase of frequency. Results obtained by Mahadevan et al [16] with some ammonium compound impurities show that the temperature and impurity concentration have complicated influences on the dielectric constant.

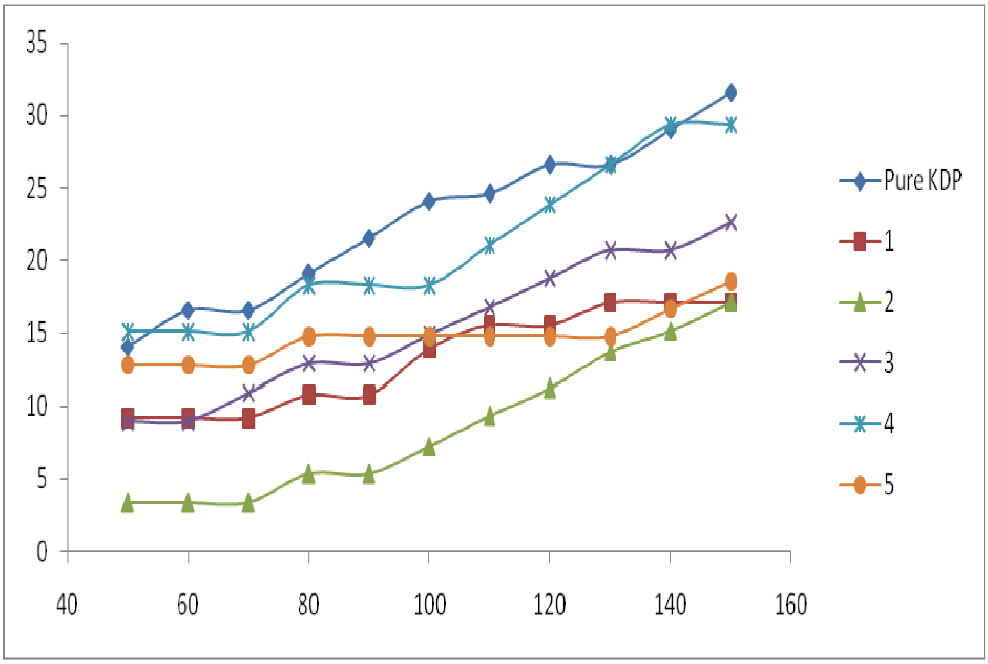

Figure: 2a. Dielectric constants along a-direction for Pure KDP, and for various KDP: $K_2Cr_2O_7$ ratios 1- 1:0.002, 2-1:0.004, 3-1:0.006, 4-1:0.008, 5- 1:0.010

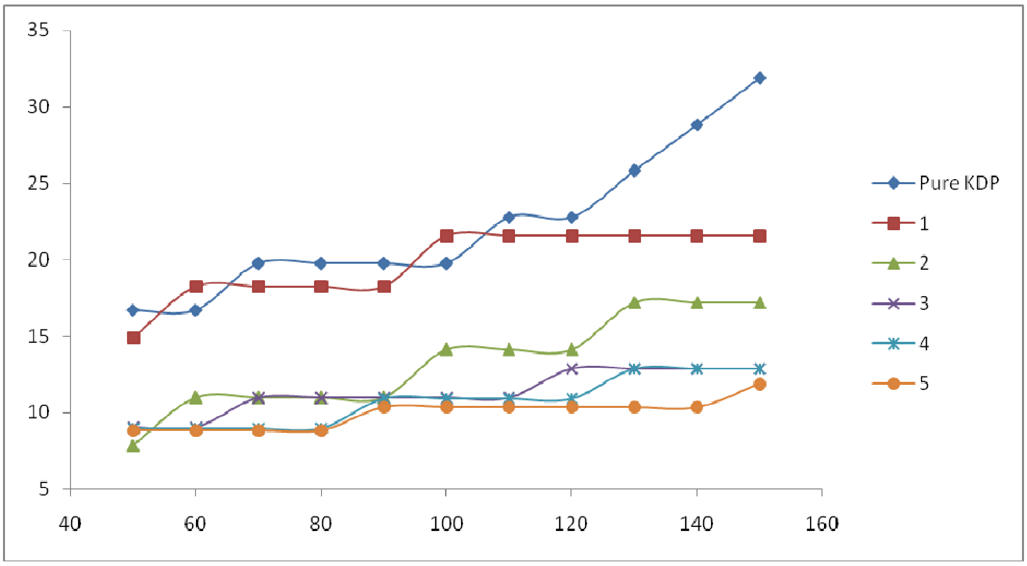

Figure: 2b. Dielectric constants along c-direction for Pure KDP, and for various KDP: $K_2Cr_2O_7$ ratios 1- 1:0.002, 2-1:0.004, 3-1:0.006, 4-1:0.008, 5- 1:0.010

Udupa etal [15] explained that the decrease of ε_r with increase in temperature may be due to the dehydration process of water molecules (acquired during the growth). There is ion dipole interaction between dipole moments of water molecules and the effective lattice charges. Thermal energy makes the water molecules free and finally dehydration of those molecules will take place as temperature increases.

The obtained tanδ values in the present study are provided in Figure 3 (a,b). The tanδ values are found to increase with increase in temperature as in the case of dielectric constant which is similar to that observed by Goma et al [7]. Further, the low tanδ values observed indicate that the grown crystals are of good quality.

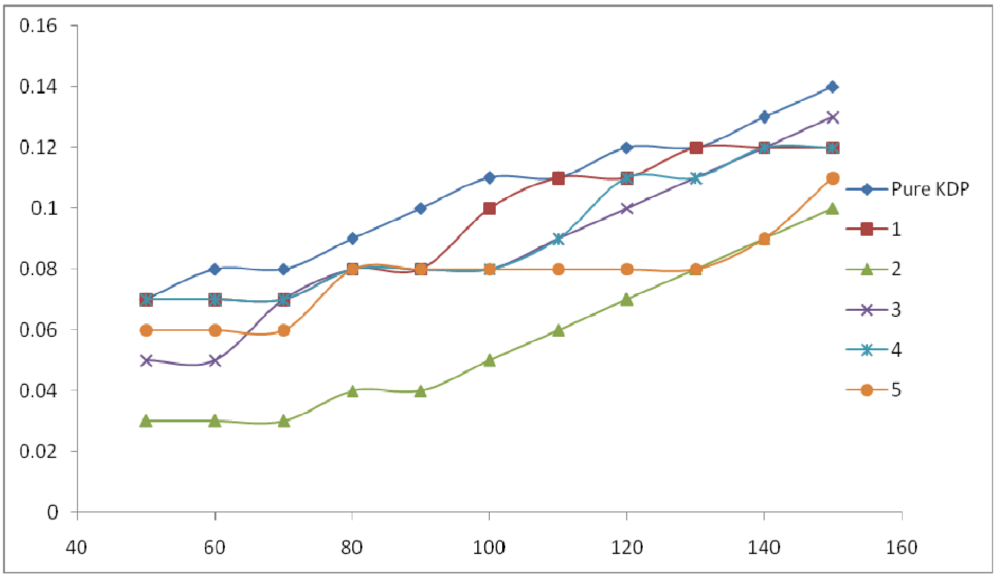

Figure: 3a. Tanδ along a-direction for Pure KDP, and for various KDP: $K_2Cr_2O_7$ ratios 1-1:0.002, 2-1:0.004, 3-1:0.006, 4-1:0.008, 5- 1:0.010

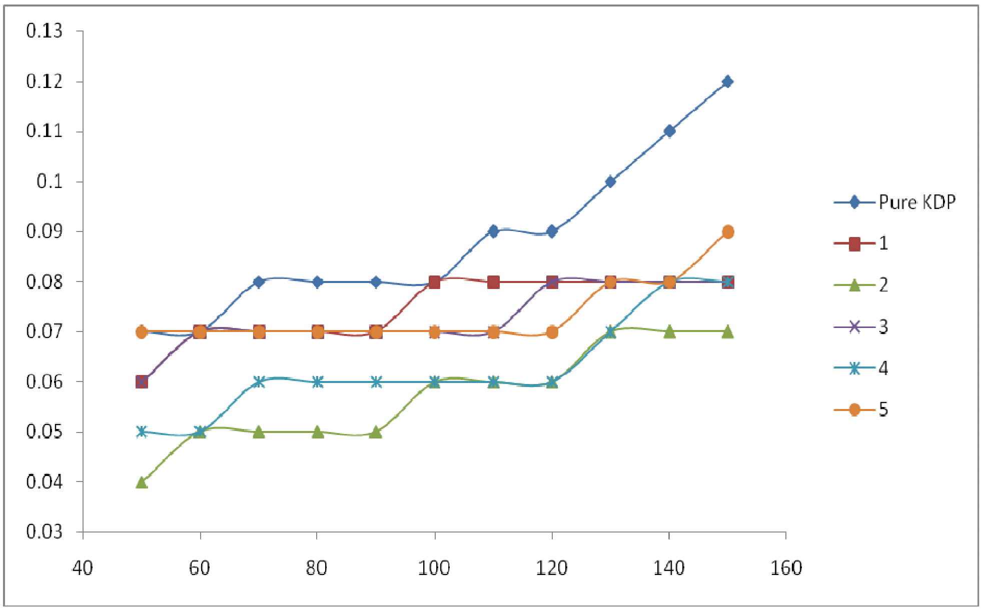

Figure: 3b. Tanδ along c-direction for Pure KDP, and for various KDP: $K_2Cr_2O_7$ ratios 1-1:0.002,2-1:0.004, 3-1:0.006, 4-1:0.008, 5- 1:0.010

The AC electrical conductivities (σ_{ac}) obtained are provided in Figure 4(a,b). The σ_{ac} values are found to increase with increase in temperature as in the case of ε_r and tanδ values similar to that observed by Goma et al [7] for urea added KDP single crystals. The conduction in KDP is established to be protonic [17,18] and mainly due to the anions [$(H_2PO_4)^-$ ions] and not the cations [K^+ ions]. The defect concentration will increase exponentially with temperature and consequently the electrical conduction also increases. The conduction region considered in the present study seems to be connected to mobility of vacancies. Oxygen vacancies may be responsible for conduction in this region.

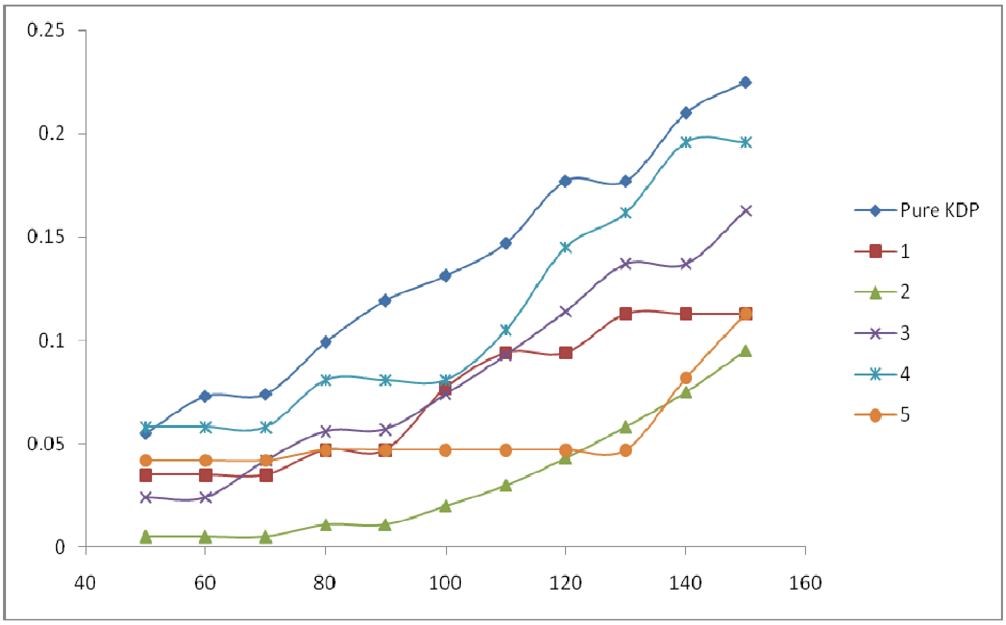

Figure: 4a. AC conductivities (x10^{-6}mho/m) along a-direction for Pure KDP, and for various KDP: $K_2Cr_2O_7$ ratios 1-1:0.002, 2-1:0.004, 3-1:0.006, 4-1:0.008, 5- 1:0.010

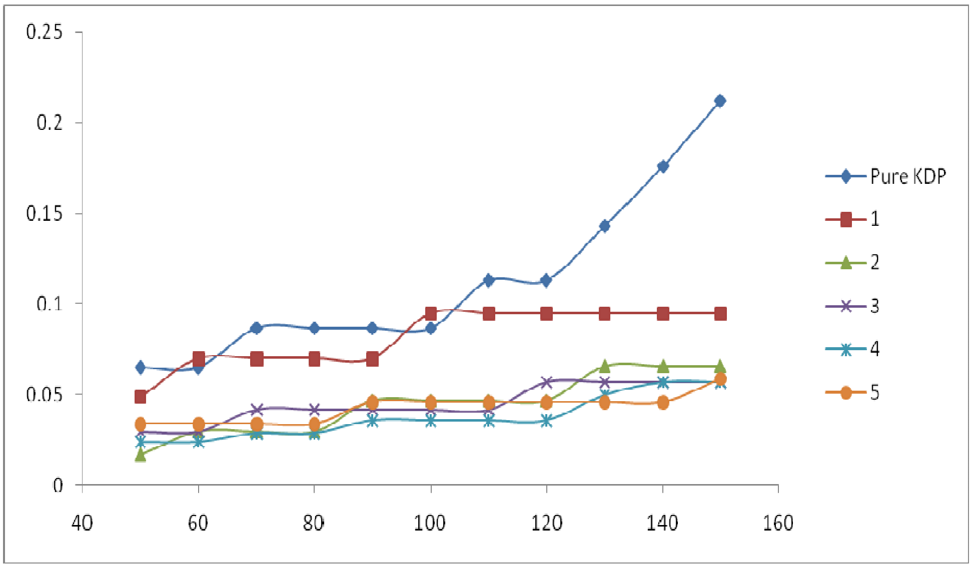

Figure: 4b. AC conductivities (x10^{-6}mho/m) along c-direction for Pure KDP, and for various KDP: $K_2Cr_2O_7$ ratios 1-1:0.002, 2-1:0.004, 3-1:0.006, 4-1:0.008, 5- 1:0.010

Variation of ε_r, tanδ and σ_{ac} valves with impurity concentration (taken in the solution used for the growth of single crystals) at 50°C are provided in Table 2. It is observed that these values do not vary systematically with impurity concentration. However, it can be seen that these values are minimum for the dichromate added KDP with impurity concentration 0.4 mole %. As the samples were annealed before making measurements this may not be due to absorbed water or polar contaminants. Also as this feature is found to be true for both a – and c –directions, surface finish condition, electrode self – adjusting orientation ohmic contacts or measuring errors may not be the reasons for this discrepancy.

In real crystals, concentration of interstitials is expected to be of the order of the 10^{15}-10^{20} cm^{-3}, i.e. upto a maximum of 1% (Here concentration of molecules is assumed as 10^{22} cm^{-3}) [17].

Potassium dichromate is expected to replace the $(H_2PO_4)^-$ ions in KDP as well as occupy the interstitial positions (sites). Increase in dichromate concentration may lead to high density of induced bulk defect states due to competition in getting replaced the $(H_2PO_4)^-$ ions or occupying the interstitial sites for the dichromate ions to occupy. Decrease in dichromate concentration may lead to high density of induced bulk defect states due to availability of unoccupied interstitial sites. 0.4 mole % may be the proper concentration for the dichromate ions to replace $(H_2PO_4)^-$ ions or to occupy the available interstitial sites in the KDP crystal structure. This may be the reason for the nonlinear variation of dielectric parameters with the impurity concentration observed in the present study.

Table 2. ε_r, tanδ, σ_{ac} values along both a- and c- directions of Pure and various KDP: $K_2Cr_2O_7$ ratios 1- 1:0.002, 2-1:0.004, 3-1:0.006, 4-1:0.008, 5- 1:0.010 at 50°C.

Ratio	ε_r along		tanδ along		σ_{ac} ($x10^{-6}$mho/m) along	
	a-direction	c- direction	a-direction	c- direction	a-direction	c- direction
Pure KDP	14.03	16.730	0.07	0.07	0.055	0.065
1:0.002	9.025	14.910	0.07	0.06	0.035	0.049
1:0.004	3.350	7.860	0.03	0.04	0.005	0.017
1:0.006	8.980	9.050	0.05	0.06	0.024	0.030
1:0.008	15.070	8.980	0.07	0.05	0.058	0.024
1:0.010	12.810	8.860	0.06	0.07	0.042	0.034

The present study, in effect, indicates that the dielectric parameters do not vary systematically with the impurity concentration. This may be attributed to the complex situation created by the dichromate ions in replacing the $(H_2PO_4)^-$ ions and occupying the interstitial sites. However, it is interesting to note that 0.4 mole % dichromate addition to KDP leads to a significant reduction of ε_r value (at 50°C, 3.35 along a- direction and 7.86 along c- direction) and consequently leads to low ε_r value dielectrics which is gaining more importance in microelectronics industry[7,8].

CONCLUSION

With the aim of discovering new useful materials, KDP single crystals were grown by adding potassium dichromate ($K_2Cr_2O_7$) as impurity by the free evaporation method in six different KDP: $K_2Cr_2O_7$ molecular ratios. Scalonohedral morphology was exhibited by all the grown crystals and the mild coloration (orange –yellow) and AAS measurement indicate that the impurity molecules have entered into the lattice of KDP crystals. The ε_r, tanδ and σ_{ac} values increase with the increase in temperature. Non observation of systematic variation of dielectric parameters with impurity concentration in the present study could be explained by considering the complex situation created by the dichromate in replacing $(H_2PO_4)^-$ ions and occupying the interstitial sites. In addition, the present study indicates that 0.4 mole % dichromate addition to KDP leads to low ε_r value dielectric crystal which is gaining more importance in microelectronics industry.

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