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Ion transport in Au^+ doped/undoped KDP crystals with KI/NaI as additives

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Abstract. Undoped KDP and KDP crystals containing KI/NaI with/without gold doping were grown by slow evaporation technique. All the grown crystals were *g*-irradiated using ^{60}Co source. Electrical conductivity measurements were carried out on all these crystals perpendicular to the unique direction before and after *g*-irradiation. The present results show that the conductivity of KDP crystals increases with the addition of KI/NaI and with gold doping as well as upon rise in temperature. Computed values of activation energies from the conductivity measurements are given. For all the grown crystals, dielectric constant is measured as a function of frequency.

Keywords. Impurity added KDP crystals; slow evaporation; gold doping; dielectric constant; electrical conductivity; activation energy.

1. Introduction

Electrical conductivity of ionic crystals has been the subject of many investigations. Such studies yield useful information regarding the mobility and production of lattice defects in these materials. At any temperature, the Gibbs free energy of a crystal is minimum when a 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). Earlier reports on KDP crystals doped with oxalate and chloride impurities have shown increase in conductivity that has been explained as due to the replacement of $(H_2PO_4)^{-1}$ ions by $(C_2O_4)^{-2}$ and Cl^{-1} ions (Shanmugham *et al* 1985; Udupa *et al* 1997).

We have made an attempt to modify KDP crystals by means of adding KI/NaI in definite ratios and doping with gold. Pure KDP and KDP containing KI/NaI with/without gold doping were grown by slow evaporation technique. In the present paper, results of our studies on electrical conductivity and dielectric constant of solution grown KDP crystals containing KI/NaI with/without gold doping have been reported.

2. Experimental

The samples used in the present study were grown from aqueous solution by slow evaporation at room temperature in the unstirred condition. KDP was added with KI/NaI in three different molecular ratios, viz. KDP : X (X represents KI or NaI) 10 : 0 (undoped KDP), 9 : 1 and 8 : 2.

Au^+ doped crystals were grown by adding a definite volume of tetra-auro chloric acid solution to the mixture of KDP and KI/NaI.

Grown crystals were found to be transparent and exhibited scalenohedral morphology. Crystals with high transparency and large defect free size were selected and used for electrical conductivity and dielectric measurements.

The crystals obtained were checked for XRD. EDAX data have been taken for the samples (shown in figures 1 and 2) to know the elemental composition, which indicates that the impurities have entered into the lattice of the KDP crystals.

2.1 *Dielectric measurements*

The extended portions of the crystals were removed completely and the crystals were ground to proper thickness and polished. Each sample was electroded on either side with air-drying silver paste so that it behaved like a parallel plate capacitor. A 4275A, Multi frequency LCR meter (Hewlett–Packard) was used to measure capacitance (*C*) of the sample as a function of frequency.

2.2 *Conductivity measurement*

Both undoped and Au^+ doped crystals were subjected to *g*-irradiation using ^{60}Co source to a dosage 5 Mrads. The conductivity measurements were carried out for both irradiated and non-irradiated crystals along *a*-direction

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using the conventional two-probe technique at various temperatures ranging from room temperature to 150°C. The conductivity values were fitted into the equation

$$s\ (T) = s_0 \exp(-E/kT),$$

where k is the Boltzmann's constant, T the absolute temperature, s_0 being a constant depending on the material and E the activation energy.

3. Results and discussion

(i) The variation of dielectric constant with frequency at room temperature for KDP, Au^+ doped KDP and KDP crystals containing KI/NaI with and without gold doping are shown in figures 3 and 4. It is observed that the dielectric constant (e) decreases with increase in frequency. Values of dielectric constant at 100 kHz and 1 MHz frequency for pure KDP, Au^+ doped KDP and KDP crystals containing KI/NaI with and without gold doping are given in table 1. KDP doped with KI has lower e than undoped KDP whereas KDP doped with NaI has higher e because of the change in the ionic sizes. Further, at high frequencies dipolar orientation effect is dominant whereas at low frequencies below 10^3 Hz ionic and electronic polarization are effective. The large value of dielectric constant is due to the presence of space charge polarization (Suryanarayana *et al* 1984).

(ii) The s values obtained along the a-direction are within the experimental error. Figures 5–9 show the plots of log s (T) vs 1000/T for the pure and KI/NaI added KDP crystals with and without gold doping before and after g-irradiation when the field is along the a-direction.

The computed values of the activation energy, E, for pure and impurity added crystals are given in table 2. It can be seen from the figures that the electrical conductivity has increased with addition of KI/NaI and with irradiation. The conductivity graphs exhibit the usual intrinsic and extrinsic regions. Conductivity at high temperature > 310 K (range 310–400 K) is intrinsic, which is due to the thermally created vacancies as well as the variation of their mobility with temperature. The low activation energy suggests that oxygen vacancies are responsible for conduction in this region. Extrinsic region i.e. the low temperature region < 310 K is a structure-sensitive region.

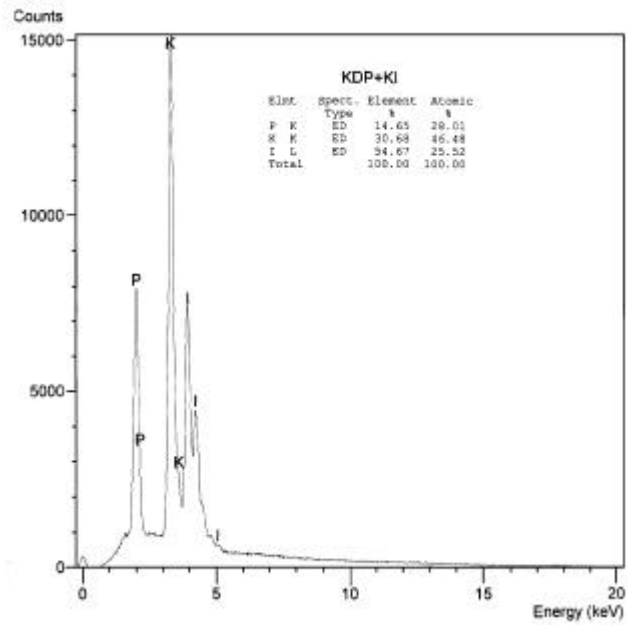

Figure 1. EDAX data of $(KDP)_{0.8}$ $(KI)_{0.2}$ crystals.

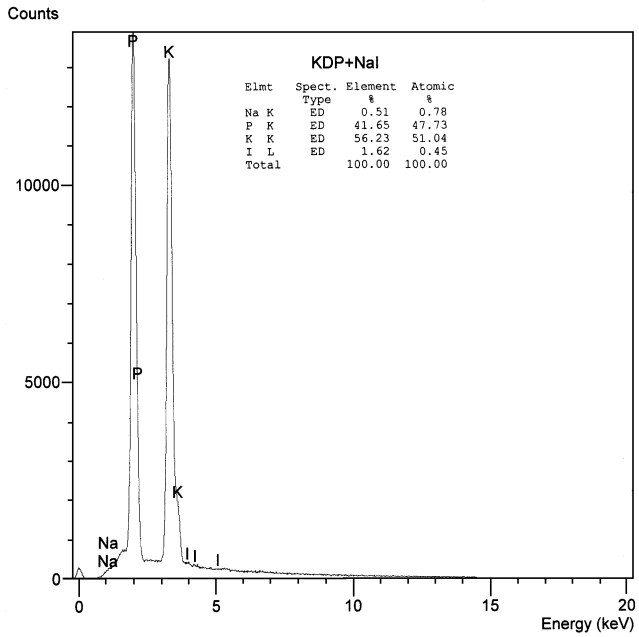

Figure 2. EDAX data of $(KDP)_{0.8}$ $(NaI)_{0.2}$ crystals.

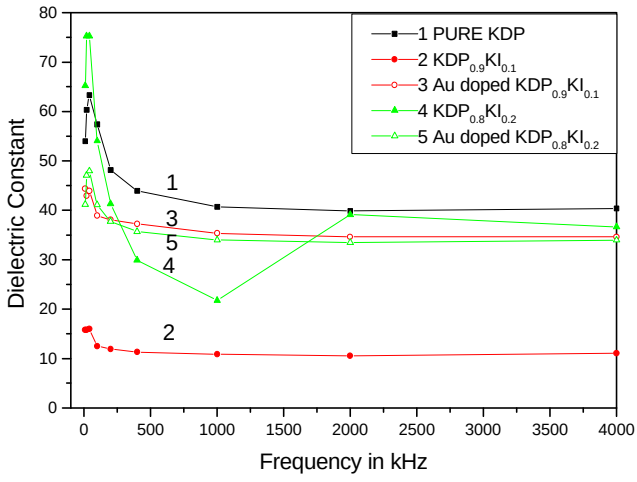

Figure 3. Variation of dielectric constant with frequency in KDP crystals containing KI with and without gold doping.

Hence the addition of impurities further increases the electrical conductivity in the extrinsic region.

Conductivities obtained in the present study are in good agreement with those obtained by previous authors for the KDP crystals ($\times 10^{-6}$ mho/m) (Harris and Vella 1966; Shanmugham *et al* 1985; Ramasubramanian and Mahadevan 1991; Udupa *et al* 1997).

The electrical conduction in dielectrics is an impurity controlled process in the low temperature (structure-sensitive) region and a defect-controlled (thermodynamic) process in the high temperature region where defects are created which contribute to conductivity exponentially increasing with increasing temperature. The addition of impurity further increases the electrical conduction in the temperature region considered. It has been noticed from our studies that higher percentage of additives (NaI/KI) has not resulted in higher s compared to pure samples whereas lower percentage (viz. 0·1 mole wt or 10 mole%) of additives have caused higher values of s because ionic conductivity of alkali halides is lower than that of KDP crystals. Addition of higher concentration of alkali halides has resulted in lower s. Present experimental results are in line with the above arguments. Further, small quantity of Au^+ doped into KDP has shown an increase in s whereas in the presence of the additives, NaI/KI, its effect on s is not appreciable. This is because Au^+ present is very negligible compared to the amount of NaI/KI present. Also, effect of irradiation is to increase the defects and hence increase in s has been observed in the temperature region investigated.

In the case of KH_2PO_4, the most important contribution to an understanding of the structure is given by West (1930). The atomic arrangements in KDP are such that each P atom is surrounded by four O atoms at the corners of a regular tetrahedron. Each PO_4 group is linked with four other PO_4 groups by H bonds. The upper O of one PO_4 group is linked with the lower oxygen of the neighbouring PO_4 group by an H bond. Neutron diffraction studies revealed that each PO_4 group has two nearest Hs, and as a group they form (H_2PO_4) ions. The PO_4 group and the K ions are built up in such a way that K and P atoms alternate each other at a distance of $c/2$

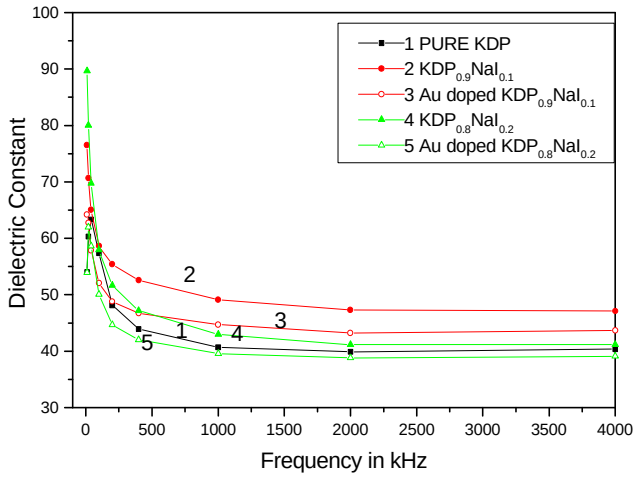

Figure 4. Variation of dielectric constant with frequency in KDP crystals containing NaI with and without gold doping.

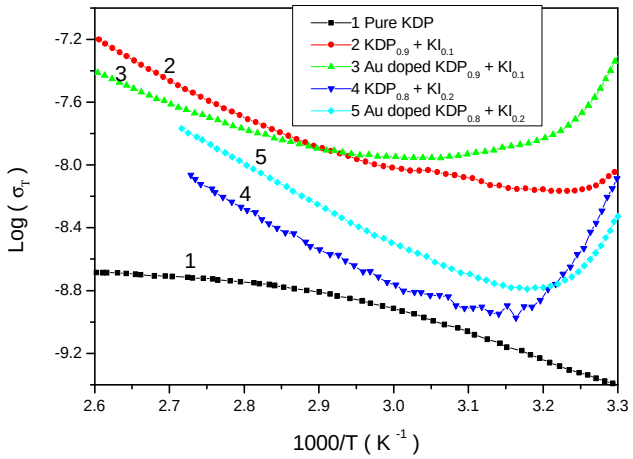

Figure 5. Variation of log(s_T) with 1000/T in KDP crystals containing KI with and without gold doping.

Table 1. Values of dielectric constant of pure and impurity added KDP crystals.

	Dielectric constant (e) of KDP crystals added with 10 mole% of alkali halides		Dielectric constant (e) of KDP crystals added with 20 mole% of alkali halides	
Sample	At 100 kHz	At 1 MHz	At 100 kHz	At 1 MHz
Pure KDP	57·3877	40·6890		
Au^+ doped KDP	54·4281	36·0707		
KDP + KI	12·4990	10·8378	54·263	21·7347
Au^+ doped KDP + KI	38·9232	35·3457	41·1249	34·0060
KDP + NaI	58·6265	49·0909	57·9526	42·9681
Au^+ doped KDP + NaI	52·0709	44·7239	50·073	39·5597

along the *C*-axis. Each K is surrounded by eight Os and four of them nearer than the other four.

For electrical conduction it is proved (Keeffe and Perrino 1967; Shanmugham *et al* 1982) that K ion does not contribute much. The conduction is mainly due to the anions present viz. (H_2PO_4) ions. The H bond with the PO_4 group is in such a way that one H bond is associated with the upper O and the other H bond with lower O. This arrangement gives a favourable picture of the conduction mechanism.

As the temperature is increased, the spontaneous polarization decreases and becomes zero at and above the Curie temperature (123 K). This change is due to the change in the configuration of the PO_4 group. The H bonds, which are associated with either the upper two Os or lower two Os, at temperatures below the transition temperature, change their configuration in such a way that one H bond is associated with one of the upper Os and the other with one of the lower Os. This type of transformation of H bonds is called M defect. In a real crystal, the presence of M defect creates an H bond with two hydrogen at one end and an H bond with no hydrogen at the other end. These defects are known as D and L defects, respectively. Keeffe and Perrino (1967) introduced two more types of defects, $(HPO_4)^-$ and $(H_3PO_4)^+$, formed by self-ionization of H_2PO_4. These charges combine with the H_2PO_4, giving rise to an M defect. This M defect, in turn by intra bond jump annihilates itself and

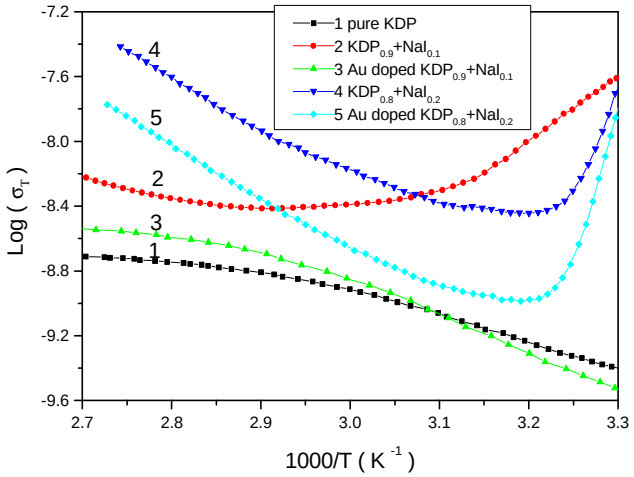

Figure 6. Variation of log(s_T) with 1000/T in KDP crystals containing NaI with and without gold doping.

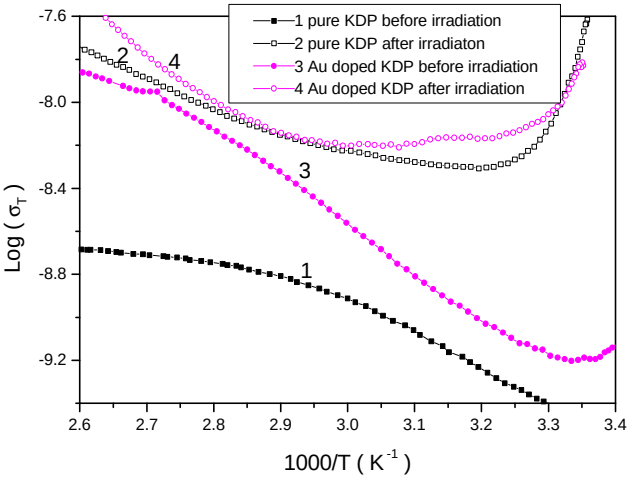

Figure 7. Variation of log(s_T) with 1000/T in pure KDP and Au^+ doped KDP crystals before and after irradiation.

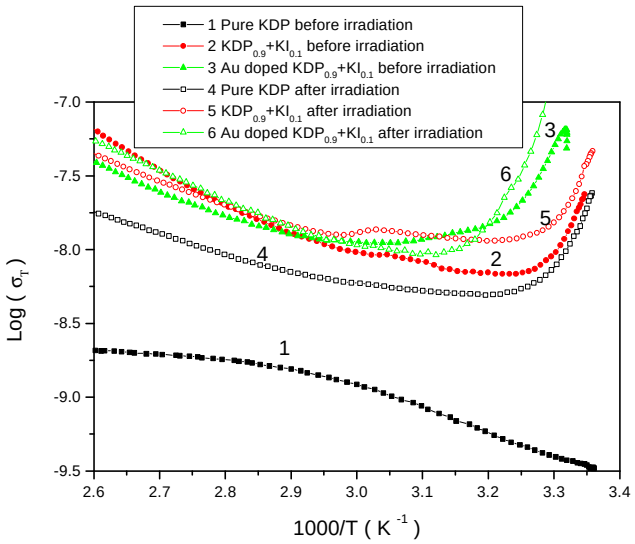

Figure 8. Variation of log(s_T) with 1000/T in KDP crystals containing KI with and without gold doping before and after irradiation.

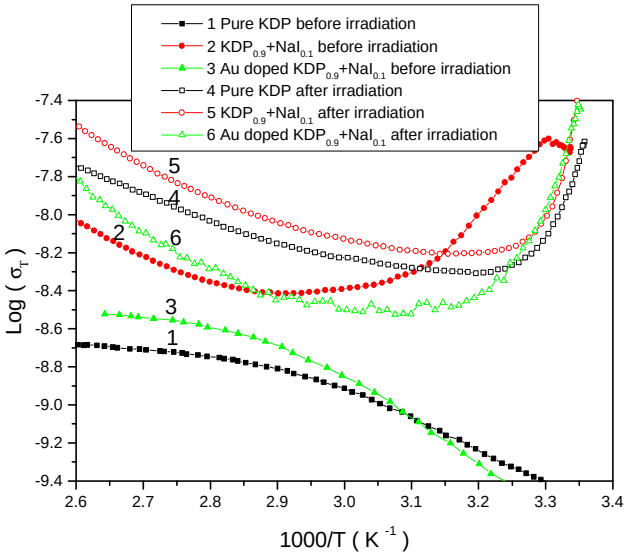

Figure 9. Variation of log(s_T) with 1000/T in KDP crystals containing NaI with and without gold doping before and after irradiation.

Table 2. Activation energies of pure and impurity added KDP crystals.

Sample	Activation energy, E (eV) of KDP crystals added with 10 mole% of alkali halides (before irradiation)	KDP crystals added with 20 mole% of alkali halides (before irradiation)	KDP crystals added with 10 mole% of alkali halides (after irradiation)
Pure KDP	0·3076		0·2309
Au^+ doped KDP	0·4368		0·4481
KDP + KI	0·4145	0·4440	0·3608
Au^+ doped KDP + KI	0·3421	0·4813	0·3349
KDP + NaI	0·2535	0·5536	0·2961
Au^+ doped KDP + NaI	0·3972	0·5518	0·4462

Accuracy = ± 0·0001 eV.

yields L and D pairs. These defects are responsible for the electrical conduction in KH_2PO_4 crystals.

The increase in conductivity of KDP crystals containing KI/NaI impurities can be explained by considering the replacement of $(H_2PO_4)^{-1}$ ions by I ions. This is in agreement with the results obtained by the previous workers in the case of doped KDP crystals (Harris and Vella 1966; Shanmugham *et al* 1985; Albin Sancta *et al* 2001).

Computed values of activation energies from the plots of s (T) vs 1000/T confirm higher values of activation energy in case of KDP crystals containing NaI/KI and also with Au^+ doping. In irradiated crystals still higher activation energies have been found. This increase in activation energy gives a clue regarding the diffusion of impurities to the regular position.

4. Conclusions

Pure and NaI/KI added KDP single crystals with and without gold doping were grown by slow evaporation technique.

EDAX data confirms that the impurities have gone into the lattice of the crystal.

Electrical conductivities were measured along the *a*-direction at various temperatures ranging from room temperature to 150°C.

The present study gives further evidence 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 addition of KI/NaI and also with gold doping. Also it confirms that the further increase in conductivity is due to the effect of radiation-induced defects.

Higher value of activation energy in case of KDP crystals containing NaI/KI, and also with Au^+ doping gives a clue regarding the diffusion of defects either to the regular position or to the interstice.

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