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## Evaluation of the true electro-optic effect in some doped KCl crystals

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**Abstract.** The strain-optic contribution to the electro-optic effect in KCl doped with  $\text{Br}^-$ ,  $\text{Tl}^+$ ,  $\text{Cd}^{2+}$  and  $\text{Mn}^{2+}$  ions has been evaluated from the independent measurements of the photoelastic and the electrostrictive coefficients and the true electro-optic coefficients have been calculated. The relatively small electrostrictive elasto-optic contribution in these doped KCl systems has been discussed in the light of the change in the ionicity of the bonds between the impurity ions and the  $\text{Cl}^-$  ions. The possible application of the systems  $\text{KCl}:\text{Cd}^{2+}$  and  $\text{KCl}:\text{Mn}^{2+}$  at high (microwave) frequencies has been discussed in comparison with  $\text{KTaO}_3$ .

### 1. Introduction

The quadratic electro-optic (EO) effect in a material is most commonly described in terms of a fourth-rank **R**-tensor defined by the expression

$$\Delta \left( \frac{1}{n^2} \right)_{ij} = \sum_{k,l} R_{ijkl} E_k E_l \quad (1)$$

where  $(1/n^2)_{ij}$  represents the components of the impermeability tensor and  $E_k$  is the  $k$ th cartesian component of the applied electric field. An alternative description uses the field-induced crystal polarization  $P_k$  as the driving term, in which case

$$\Delta \left( \frac{1}{n^2} \right)_{ij} = \sum_{k,l} g_{ijkl} P_k P_l \quad (2)$$

where  $g_{ijkl}$  are the components of the polarization-optic (PO) coefficients. Such a description would be more appropriate since polarization is a property of the dielectric medium in which the effect occurs. The PO coefficients are remarkably constant from material to material and do not change substantially over a frequency range 0– $10^{15}$  Hz [1]. The EO and PO coefficients are simply related by appropriate linear susceptibilities. As a result we note the important qualitative rule that large EO coefficients are associated with large linear susceptibilities. It is for this reason that ferroelectric crystals have attracted such wide interest in electro-optics.

Regarding the quadratic EO effect, several perovskites (e.g.  $\text{BaTiO}_3$ ,  $\text{KTa}_x\text{Nb}_{1-x}\text{O}_3$ ) in their paraelectric phase show large effects for small applied electric fields, when operated near their ferroelectric transition temperatures ( $T_c$ ) [2, 3]. This is because near  $T_c$ , spontaneous polarization sets in and the lattice polarization becomes large. The

growth of these materials with sufficient uniformity, optical quality and electrical resistivity is extremely difficult. However, the material  $\text{KTa}_{0.65}\text{Nb}_{0.35}\text{O}_3$  (KTN) with Curie point near room temperature has been found suitable for many interesting applications [3].

From a device point of view, it is desirable to have materials with large electro-optic effect but with small dielectric constant [4]. Unfortunately, these two requirements contradict each other in the case of ferroelectrics, which is the only class of materials with a large EO effect, and the refractive indices of most of the materials are so large that it is difficult to provide optical matching from air into the material.

Alkali halides, having a refractive index of nearly 1.5, are suitable for this purpose. These crystals are optically isotropic in zero field and are not optically active, since they belong to cubic  $m\bar{3}m$  symmetry. Large single crystals can be grown easily and they are easily cut and polished. These crystals are transparent over a wide range of wavelengths. In spite of all these advantages, they suffer mainly from the fact that, being centrosymmetric, they exhibit the Kerr electro-optic effect only and have very small Kerr constants of the order of  $10^{-22} \text{ m}^2 \text{ V}^{-2}$  [5]. However, recent studies [6–12] showed that the Kerr constants could be enhanced by three to five orders of magnitude by doping with substitutional defects and have thus revived the interest in them. It should be noted that the measurement of the Kerr effect, in the systems studied in references [6–12], have been carried out at low frequencies.

In order to account for the fact that the crystal is deformed under the application of the electric field and the refractive index changes due to the deformation of the crystal, we now write equation (1) in a form that displays explicitly any strain-optic contribution to  $\Delta(1/n^2)_{ij}$  associated with the electrostrictive strain induced by the applied electric field. At low frequencies, the appropriate Kerr constant is the zero stress ( $\sigma = 0$ ) or the unclamped value represented with a superscript  $\sigma$  as  $R_{ijkl}^\sigma$ . At high (microwave) frequencies, below the optical vibrational modes and above all acoustic resonances, the crystal is effectively clamped and the appropriate Kerr constant is the zero strain ( $\eta = 0$ ) or the clamped coefficient and is represented with a superscript  $\eta$  as  $R_{ijkl}^\eta$ . Thus we write the change in the coefficient of the index ellipsoid as

$$\Delta \left( \frac{1}{n^2} \right)_{ij} = \sum_{k,l} R_{ijkl}^\eta E_k E_l + \sum_{m,n} p_{ijmn}^E \eta_{mn} \quad (3)$$

where  $\eta_{mn}$  are the elements of the strain tensor and  $p_{ijmn}$  are the components of the strain-optic tensor. Superscripts  $\eta$  and  $E$  denote that the coefficients are measured at zero strain and electric field respectively. The second term on the right-hand side represents the electrostrictive elasto-optic contribution to the electro-optic effect. This contribution can in some materials be of the same order of magnitude as that of the clamped coefficient [13, 14]. Therefore, the strain-optic effect is an important consideration in the discussion of the electro-optic phenomena, especially at low frequencies.

The strain-optic contribution can be evaluated by measuring the electro-optic coefficient at low as well as high frequencies. The high-frequency region is usually in the vicinity of 1 MHz depending upon the dimensions of the specimens. Another method of evaluating this contribution is by measuring independently the strain-optic coefficients,  $p_{ijmn}$ , and the electrostriction coefficients,  $d_{mnkl}$ .

Since the electrostriction coefficients are available for the systems  $\text{KCl}:\text{Br}^-$ ,  $\text{KCl}_{0.8}\text{Br}_{0.2}$ ,  $\text{KCl}_{0.4}\text{Br}_{0.6}$ ,  $\text{KCl}:\text{Cd}^{2+}$  and  $\text{KCl}:\text{Mn}^{2+}$  [15], it is enough if we determine the

photoelastic coefficients of these KCl-doped systems in order to evaluate the strain-optic contribution to the Kerr effect. Once the electrostrictive elasto-optic contribution is known, we can evaluate the true or the clamped EO coefficients of these systems. As the low-frequency Kerr constants of KCl: Mn<sup>2+</sup> are not available, we have performed EO measurements, as described in reference [12]. In addition to these systems, we have also studied KCl: Tl<sup>+</sup> (0.1 mol%), whose EO and the electrostriction coefficients have been determined in the same manner as indicated in reference [12] and [15] respectively.

A report of the measurements of the photoelastic coefficients and the evaluation and discussion of the clamped or true electro-optic coefficients is presented here.

## 2. Photoelastic measurements

The photoelastic effect in a material couples mechanical strain to the optical index of refraction. This effect occurs in all states of matter and in particular in crystalline media belonging to all symmetry groups. The principal source of photoelasticity for ionic crystals is the change of the polarizabilities of the ions induced by stress fields. This effect is described analytically by a fourth-rank stress-optic tensor  $q_{ijkl}$ , which couples the stress tensor  $\sigma_{kl}$  to the indicatrix,  $(1/n^2)_{ij}$ .

### 2.1. Theoretical considerations

Within the limits of Hooke's law, the change in the coefficients of the optical indicatrix is directly proportional to the applied stress as the following:

$$\Delta \left( \frac{1}{n^2} \right)_{ij} = \sum_{k,l} q_{ijkl} \sigma_{kl}. \quad (4)$$

Also, since the change in the optical indicatrix is proportional to the strain, we can write

$$\Delta \left( \frac{1}{n^2} \right)_{ij} = \sum_{k,l} p_{ijkl} \eta_{kl} \quad (5)$$

where  $p_{ijkl}$  are called strain-optical constants and  $\eta_{kl}$  are the components of strain. The components of the  $\mathbf{p}$ -tensor are dimensionless and the units of the  $\mathbf{q}$ -tensor are  $\text{m}^2 \text{N}^{-1}$ .

Therefore, in the presence of a stress field, the index ellipsoid becomes

$$\sum_{i,j} \left[ \left( \frac{1}{n^2} \right)_{ij} + \Delta \left( \frac{1}{n^2} \right)_{ij} \right] x_i x_j = 1. \quad (6)$$

For the  $m\bar{3}m$  crystal symmetry the three independent components of the  $\mathbf{q}$ -tensor are  $q_{1111}$ ,  $q_{1122}$  and  $q_{1212}$ . Following Nye [16] the non-vanishing components of the  $\mathbf{q}$ -tensor (expressed in shorthand notation) can be evaluated as follows.

(i) When the uniaxial stress is applied parallel to [100] direction the difference ( $q_{11} - q_{12}$ ) can be calculated using the relation

$$\Delta n = -\frac{n_0^3}{2}(q_{11} - q_{12})\sigma. \quad (7)$$

(ii) When the uniaxial stress is applied parallel to the [110] direction the component  $q_{44}$  can be calculated using the relation

$$\Delta n = -\frac{1}{2}n_0^3q_{44}\sigma \quad (8)$$

where  $n_0$  is the refractive index of the material in the zero-field condition. The convention followed here is that the compressive stress is negative and

$$q_{mn} = q_{ijkl} \quad (n = 1, 2 \text{ or } 3)$$

$$q_{mn} = 2q_{ijkl} \quad (n = 4, 5 \text{ or } 6).$$

The stress-optic coefficients are coupled to the strain-optic coefficients in the following way:

$$p_{ijkl} = \sum_{m,n} q_{ijmn}c_{mnkl} \quad (9)$$

where  $c_{mnkl}$  are the elastic constants. Therefore,

$$(p_{1111} - p_{1122}) = \sum_{m,n} (q_{11mn}c_{mn11}) - (q_{11mn} - c_{mn22}) = (q_{1111} - q_{1122})(c_{1111} - c_{1122}) \quad (10)$$

and

$$p_{1212} = q_{1212}c_{1212}. \quad (11)$$

## 2.2. Experimental details

The growth of single crystals and the determination of the concentration of the impurities have already been reported [12]. The concentration of the  $Tl^+$  ions in KCl has been determined from the intensity of the absorption band at around 250 nm. Crystals with parallel faces, oriented along [100] and measuring about  $10 \times 8 \times 4 \text{ mm}^3$ , could be cleaved from the grown crystals. The samples oriented along [110] direction have been cut and polished, taking (100) plane as the reference. The specimens thus cut are annealed at 600 K for about three hours and then quenched to room temperature on a copper plate. The presence of any strain is checked by examining the samples between the crossed polarizers.

The experimental arrangement, as far as the optics is concerned, is the same as that used for the determination of the Kerr electro-optic constants [12]. Here, in place of the electric field, uniaxial stress is applied to the crystals and the birefringence is measured with the aid of a Soleil-Babinet compensator as the variable birefringent plate.

The stress apparatus used for the application of uniaxial stress in these measurements and its function has already been described in reference [15]. The sample is sandwiched between the two blocks A and B. The proving ring with the strain gauge is fixed above the upper block A through a ball-and-socket arrangement. Another ball-and-socket arrangement connects the proving ring to a fine pitched screw, which is turned to apply

uniaxial stress to the specimens. The strain gauge, which is calibrated prior to the experiments, measures the stress applied to the specimens. In order to make sure that the applied stress is uniform over the crystal surface, two thin lead sheets have been kept between the sample and the two blocks A and B.

A 10 mW He–Ne laser is used as the light source. The chopper produces a 120 Hz square wave. The polarizer polarizes the light beam at  $45^\circ$  to the vertical direction. This light is then incident on one face of the crystal which is mounted in the stress apparatus as described above. The light transmitted through the crystal is then passed through a Soleil–Babinet compensator. An analyser is placed after the compensator and is crossed initially with respect to the polarizer. A silicon p–n junction diode, operated in the photovoltaic mode, serves as the detector and the signals are fed into the lock-in amplifier.

First an undoped KCl sample is used in the present set-up as the test specimen to measure the photoelastic constants. The compensator is calibrated and its constant  $s_\lambda$ , the distance through which the micrometer screw operating the quartz wedge is moved to introduce a path difference of  $\lambda$  of the light used, is determined [12]. The position of the micrometer screw is adjusted so that the intensity of the light received at the detector is exactly at the midpoint of the linear portion of the calibration curve of the compensator. This is called the  $(\lambda/4)$  optical biasing, the advantages of which have been discussed in detail in reference [12]. Now a maximum uniaxial stress of about  $1.5 \times 10^6 \text{ N m}^{-2}$  is applied to the specimen and the corresponding change in intensity of the light is noted. The path difference introduced by the crystal under the stressed condition is calculated as follows:

$$\Delta nl = (\lambda/s_\lambda)s \quad (12)$$

where  $s$  is the distance through which the upper quartz wedge is moved to restore the intensity back to its original value and  $l$  is the length of the sample (the dimension of the specimen along which light is transmitted). The corresponding stress-optic coefficient  $(q_{1111} - q_{1122})$  is then evaluated using the relation (7).

The experiment is repeated for the specimen cut with (110) plane and the expression (8) is then used to calculate the other stress-optic coefficient  $q_{1212}$  of the sample.

The stress-optic coefficients of all the doped systems are determined in the same fashion as that described for the evaluation of the coefficients of the undoped KCl samples.

### 2.3. Results

The values of the stress-optic coefficients  $(q_{1111} - q_{1122})$  and  $q_{1212}$  of undoped KCl as well as  $\text{KCl}_{0.8}\text{Br}_{0.2}$ ,  $\text{KCl}_{0.4}\text{Br}_{0.6}$ ,  $\text{KCl}:\text{Cd}^{2+}$  and  $\text{KCl}:\text{Mn}^{2+}$  crystals are given in table 1. For KCl,  $\text{KCl}_{0.8}\text{Br}_{0.2}$  and  $\text{KCl}_{0.4}\text{Br}_{0.6}$ , the values of  $n_0$  reported in [17] have been used in the calculations and for the other doped systems we have used the  $n_0$ -value of pure KCl. The values of the strain-optic coefficients, calculated using the relations (10) and (11), are also given in table 1. The  $q_{ijkl}$ -values of pure KCl crystal obtained by Bansigir and Iyengar [18] at  $\lambda = 589.3 \text{ nm}$  are also given in the table.

For pure KCl,  $\text{KCl}_{0.8}\text{Br}_{0.2}$  and  $\text{KCl}_{0.4}\text{Br}_{0.6}$  the elastic constants reported by Slagle and McKinstry [19] have been used for calculating the components of the  $\mathbf{p}$ -tensor. The elastic constants of the pure KCl crystal, reported by Slagle and McKinstry, have been used for calculating the components of the  $\mathbf{p}$ -tensor of  $\text{KCl}:\text{Cd}^{2+}$  and  $\text{KCl}:\text{Mn}^{2+}$  also and this is because, from the measurements of the ultrasonic velocity in  $\text{Cd}^{2+}$  ion-doped

**Table 1.** Values of the stress-optic ( $q_{ijkl}$ ) and strain-optic ( $p_{ijkl}$ ) coefficients of pure KCl,  $\text{KCl}_{0.8}\text{Br}_{0.2}$ ,  $\text{KCl}_{0.4}\text{Br}_{0.6}$ ,  $\text{KCl}:\text{Cd}^{2+}$  and  $\text{KCl}:\text{Mn}^{2+}$ ; units of  $q_{ijkl}$  are  $10^{-12} \text{ m}^2 \text{ N}^{-1}$ .

System	Impurity concentration (mol%)	$(q_{1111} - q_{1122})$	$q_{1212}$	$(p_{1111} - p_{1122})$	$p_{1212}$
KCl	—	1.678	-4.212	0.056	-0.030
KCl <sup>†</sup>	—	1.47	-4.94	—	—
KCl:KBr	20.0	1.705	-4.285	0.055	-0.026
	60.0	1.723	-4.331	0.052	-0.024
KCl: Cd <sup>2+</sup>	0.13	4.958	-7.377	0.167	-0.053
KCl: Mn <sup>2+</sup>	0.083	4.100	-6.611	0.138	-0.047

<sup>†</sup> Values taken from reference [18], determined at  $\lambda = 589.3 \text{ nm}$ .

KCl crystals, made by Joharapurkar and co-workers [20] it has been found that the change is less than 1% of the values of the elastic constants of pure KCl crystal.

We have assumed the signs of the coefficients of the pure KCl crystal to be those of the reported values [18]. We have fixed the signs of the coefficients of the doped systems, noting the fact that the changes in intensity on the application of stress are in the same sense as for the pure KCl crystal.

It can be seen that there is a good agreement between the values for the coefficients obtained in the present case and those reported for pure KCl in the literature. There is no observable change in the values of the components of the **q**- and **p**-tensors on doping KCl with small amounts of  $\text{Br}^-$  and  $\text{Tl}^+$  ions. The  $q_{ijkl}$ -values of  $\text{KCl}_{0.8}\text{Br}_{0.2}$ ,  $\text{KCl}_{0.4}\text{Br}_{0.6}$ ,  $\text{KCl}:\text{Cd}^{2+}$  and  $\text{KCl}:\text{Mn}^{2+}$  have been enhanced over those of the pure KCl crystals. Since the values of the elastic coefficients of the KCl:KBr systems are smaller than those of the pure KCl, the  $p_{ijkl}$ -values computed here are small for these two systems.

#### 2.4. Discussion

The unequal changes in the refractive indices resulting from the deformation of the crystal may be attributed to (i) change in density of the crystal, and (ii) the change in the polarizability of the ions.

Let us look at the first reason—change in density of the crystal. If a unit volume of the crystal is stressed along, say, the  $x_3$  direction, a strain  $\eta$  along this direction and a corresponding strain  $\nu\eta$  along  $x_1$  and  $x_2$  directions occur, where  $\nu$  is the Poisson ratio. Hence the change in volume would bring about a change  $\delta N_i$  in the number of ions per unit volume and is given by  $\eta(1 - 2\nu)N_i$ , where  $N_i$  is the number of ions per unit volume.

Now let us look at the second reason—change in polarizability of the ions. A method of calculating this contribution has been outlined by Mueller [21]. A theory of piezo-optic birefringence in cubic crystals of NaCl structure was developed by Bansigir and Iyengar [22] and Ethiraj and Bansigir [23]. The above theory has been extended to the mixed crystals of NaCl structure of equimolar concentration with the same cation by Kumar and co-workers [24]. In the alkali halide crystals with rocksalt structure the inclusion of the strain polarizability effect as a parameter in the shell model by Srinivasan and Srinivasan [25] reduced the discrepancy between the calculated and measured values of the photoelastic constants.

From the response of a crystal containing impurities to an applied stress, definite information on local distortions can be obtained. In an attempt to define the inherent properties of a defect, the notion of a defect as an elastic dipole has been adopted. This concept of elastic dipole is also introduced in the phenomenological treatment of response of a collection of point defects in a crystal to an applied stress [26]. These defect dipoles can be aligned with an external stress field and the process of preferential alignment of a dilute concentration of such defects by an applied stress is known as stress-induced ordering. This realignment gives rise to a macroscopic anelastic strain  $\eta_{an}$ , which, at sufficiently small values of the stress  $\sigma$ , is proportional to the stress. The attainment of a final value of this response is only gradual and therefore the phenomenon is a relaxation process, specifically, the linear mechanical relaxation process is known as anelasticity.

In the case of KCl doped with divalent cations  $Cd^{2+}$  and  $Mn^{2+}$ , the impurity–vacancy (I–V) complexes represent electric as well as elastic dipoles. Therefore, a mechanical stress can have a large influence on this system. In the unstressed crystal all the twelve  $\langle 110 \rangle$  equivalent orientations are equally populated. A mechanical stress applied to the crystal lifts the orientational degeneracy and thus induces anisotropy in the polarizability of the ions.

### 3. True electro-optic effect: evaluation and discussion

#### 3.1. Theoretical considerations

In the present investigation, since the strain-optic as well as the electrostriction coefficients have been determined separately, the contributions to the electro-optic coefficients ( $R_{1111} - R_{1122}$ ) and  $R_{1212}$  from the electrostriction have been computed as follows. In equation (3)  $\eta_{mn}$  is given by

$$\eta_{mn} = d_{mnl}^{\sigma} E_k E_l \tag{13}$$

where  $d_{mnl}^{\sigma}$  are the electrostrictive tensor coefficients. Therefore

$$\Delta \left( \frac{1}{n^2} \right)_{ij} = \sum_{k,l} \left( R_{ijkl}^{\eta} + \sum_{m,n} p_{ijmn}^E d_{mnl}^{\sigma} \right) E_k E_l \tag{14}$$

or

$$R_{ijkl}^{\sigma} = R_{ijkl}^{\eta} + \sum_{m,n} p_{ijmn}^E d_{mnl}^{\sigma} \tag{15}$$

Now we can write the following expressions:

$$R_{1111}^{\sigma} = R_{1111}^{\eta} + \sum_{m,n} p_{11mn}^E d_{mn11}^{\sigma} \tag{16}$$

$$R_{1122}^{\sigma} = R_{1122}^{\eta} + \sum_{m,n} p_{11mn}^E d_{mn22}^{\sigma} \tag{17}$$

The tensor product between the **p**- and **d**-tensors, leaving out the superscripts for the time being, is given by

$$\begin{aligned} \sum_{m,n} p_{11mn} d_{mn11} &= p_{1111} d_{1111} + 2p_{1122} d_{1122} \\ \sum_{m,n} p_{11mn} d_{mn22} &= p_{1111} d_{1122} + p_{1122} (d_{1111} + d_{1122}). \end{aligned}$$



**Table 2.** Values of the true electro-optic coefficients  $R_{ijk}^{\eta}$  (units  $10^{-17} \text{ m}^2 \text{ V}^{-2}$ ) and the percentage contribution of strain-optic effect of KCl containing different concentrations of  $\text{Br}^-$ ,  $\text{Tl}^+$ ,  $\text{Cd}^{2+}$  and  $\text{Mn}^{2+}$  ions.

System	Impurity concentration (mol%)	$(R_{111}^{\eta} - R_{122}^{\eta})$	$R_{1212}^{\eta}$	% contribution to $(R_{111}^{\eta} - R_{122}^{\eta})$	% contribution to $R_{1212}^{\eta}$
KCl:Br <sup>-</sup>	0.10	0.061	0.043	-0.15	0.06
	20.0	0.141	0.099	-0.19	0.05
	60.0	0.236	0.153	-0.13	0.04
KCl:Tl <sup>+</sup>	0.10	0.336	0.237	-0.04	0.01
KCl: Cd <sup>2+</sup>	0.13	6.423	4.198	-0.23	0.08
KCl: Mn <sup>2+</sup>	0.083	5.192	3.924	-0.14	0.05

Therefore,

$$R_{1111}^{\sigma} - R_{1122}^{\sigma} = R_{1111}^{\eta} - R_{1122}^{\eta} + (p_{1111}^E - p_{1122}^E)(d_{1111}^{\sigma} - d_{1122}^{\sigma}) \quad (18)$$

and

$$R_{1212}^{\sigma} = R_{1212}^{\eta} + p_{1212}^E d_{1212}^{\sigma}. \quad (19)$$

### 3.2. Results

Substituting the values of the electrostriction coefficients  $d_{1111}$ ,  $d_{1122}$  and  $d_{1212}$ , determined in reference [15], the strain-optic coefficients  $(p_{1111} - p_{1122})$  and  $p_{1212}$ , calculated in section 2 and the low-frequency Kerr constants determined in reference [12], in equations (18) and (19), the true or clamped quadratic electro-optic coefficients of doped KCl crystals have been evaluated and are listed in table 2. Also shown in the table are the percentage contributions of the strain-optic effect to the true electro-optic effect for all the doped KCl systems. Here we have assumed the signs of the unclamped or the low-frequency electro-optic coefficients of the doped systems to be the same as those of the pure KCl.

It is seen from the table that the contribution from the distortion of the lattice caused by the applied electric field is less than 1% of the true electro-optic effect in the various doped KCl systems studied here.

In the case of pure alkali halides the electrostrictive elasto-optic contribution is of the same order of magnitude as that of the direct effect [14]. The theoretical work on the basis of the shell model [13], applied to NaI and NaF, has shown that the sign of the Kerr constant is governed by the contribution from electrostriction. The experimental and theoretical work on the Kerr effect in fluorite crystals, reported by Kaplyanskii and co-workers [27], also arrives at the same conclusion. In the case of oxygen-octahedra ferroelectrics in their paraelectric phase, a rough estimate yields approximately 25% clamping effect on the quadratic polarization optic (PO) coefficient  $g_{1111}$  and the sign of the low-frequency coefficient  $g_{1122}^{\sigma}$  is governed by the strain-optic contribution [1]. In  $\text{BaTiO}_3$ , the prototype oxygen-octahedra ferroelectric, the ratio of the strain-free to the

**Table 3.** Values of the ionicities of the bonds between the atoms of interest.

Bond	$f_i$	$f'_i$
K-Cl	0.70	0.95
K-Br	0.63	0.94
Tl-Cl	0.30	0.88
Cd-Cl	0.35	0.79
Mn-Cl	0.43	0.81

stress-free quadratic PO coefficients ( $g_{1111} - g_{1122}$ ) is 0.35, indicating that there is 65% contribution from the electrostrictive strain [28, 29].

### 3.3. Discussion

Thus it is seen that in KCl doped with various classes of impurities the contribution from electrostriction is very small compared to that from the anisotropy in the electronic polarizability of the ions. We can examine this situation from the viewpoint of bond type that exists between the cations and anions in the doped crystals.

The ionicity of a bond is defined as the fraction  $f_i$  of ionic character compared to the fraction  $f_c$  of the covalent character. Based on band theory [30, 31], there exists a critical ionicity  $F_i = 0.785 \pm 0.010$ . This means that for any value  $f_i > F_i$ , the structure is rocksalt (sixfold coordination) and the bond exhibits highly ionic character, whilst for  $f_i < F_i$ , the structure is a fourfold coordinated one.

The transition from ionic character to covalent is smooth and as far as the physical properties of the crystal are concerned, the diffuse transition region can be from about 90% to 85% ionicity [31]. In this region there is still appreciable electron sharing and covalency even though the crystal structures are all of the rocksalt type. Also, the reduction in ionic character of the bond implies that the ions become more polarizable. It may be noted that in the covalently bonded materials such as the *AB*-type semiconductors the electro-optic effect is due largely to the electronic polarizability [32].

In order to extend the above discussion to the present case we consider the following simple method of evaluating the ionicity of the bond between the elements of interest.

Pauling [33] introduced the concept of resonating bonds to define ionicity in crystals. The value of  $F_i$  obtained is about 0.80, in good agreement with the modern spectroscopic value of 0.785 [31] and hence this definition is valid for qualitative considerations. Table 3 shows the values of ionicity of the bonds between the elements of interest in the present case, calculated using the relation

$$f'_i = 1 - (N/M) + (N/M)f_i \quad (20)$$

where  $M$  is the coordination number and  $N$  the number of valence bonds of the atom. The  $f_i$ -values due to Pauling are also shown in table 3. In calculating the  $f'_i$ -values of the bonding of the  $\text{Tl}^+$ ,  $\text{Cd}^{2+}$  and  $\text{Mn}^{2+}$  ions with the  $\text{Cl}^-$  ions we have taken  $M$  to be six, since these dopants replace  $\text{K}^+$  ions and are thus in the same environment as that of the  $\text{K}^+$  ions in KCl.

Thus the substitution of  $\text{K}^+$  ion by a cation may bring down the ionic character of its bond with a  $\text{Cl}^-$  ion. This reduction in ionicity of the bond can be considered to be highly localized, i.e. the reduction of ionicity takes place only for those bonds that exist between

**Table 4.**  $E_\pi$ -values computed using the relation (22).

System	Impurity concentration (mol%)	$E_\pi$ (kV cm <sup>-1</sup> )
KCl <sup>†</sup>	—	2272.7
KTaO <sub>3</sub> <sup>‡</sup>	—	2.1
KCl:KBr	0.10	56.0
	20.0	36.3
	60.0	27.3
KCl:TI <sup>+</sup>	0.10	23.9
KCl: Cd <sup>2+</sup>	0.13	5.5
KCl: Mn <sup>2+</sup>	0.083	6.1

<sup>†</sup> ( $R_{111}^y - R_{122}^y$ )-value taken from reference [14], after correcting signs of  $d_{ijk}$ -values according to reference [34].

<sup>‡</sup> ( $R_{111}^y - R_{122}^y$ )-value taken from Geusic and co-workers [2], determined at  $T = 4.2$  K.

the impurity ion and the six Cl<sup>-</sup> ions surrounding it. Consequently, this leads to relatively small displacements between the positive impurity ion and the Cl<sup>-</sup> ion in the presence of an applied electric field, when compared with the displacement between K<sup>+</sup> and Cl<sup>-</sup> ions. This, in turn, reduces the contribution to the electro-optic effect from the lattice distortion in doped KCl systems.

The dominance of the electronic contribution to the electro-optic effect in doped KCl crystals may be attributed to the reduction of ionicity (increase in covalency) of the bonds between the impurity ions and the Cl<sup>-</sup> ions locally.

It should be remembered that the change in ionicity of the bond due to the dopants is highly localized and this effect may not be felt in the measurements of bulk properties such as the dielectric constant of the crystal.

#### 4. Feasibility of the doped KCl systems for applications at high frequencies

First we calculate the field  $E_\pi$  (parallel to [100] direction) required to produce a  $\pi$  phase retardation between the two allowed polarizations for all the doped systems using the following relation:

$$\Delta nl = -\frac{1}{2}n_0^3(R_{111} - R_{122})E^2l \quad (21)$$

where we substitute  $\Delta nl = (\lambda/2)$ . Therefore,

$$E_\pi^2 = (\lambda/l)/n_0^3(R_{111} - R_{122}). \quad (22)$$

Taking  $l = 1$  cm and  $\lambda = 632.8$  nm, the calculated  $E_\pi$ -values of the doped systems studied here are listed in table 4. The values of the clamped or true electro-optic coefficients have been used for the calculations.

In order to evaluate the possible use of these doped KCl systems for microwave light modulation, one has to calculate the microwave power required to produce a  $\pi$  phase retardation. A further reduction in the required power can be obtained by applying a DC bias voltage such that the sample is biased to a phase retardation of  $n\pi$ , where  $n$  is a

**Table 5.** Microwave power  $P(\pi)$  in Watts calculated for KCl: Cd<sup>2+</sup>, KCl: Mn<sup>2+</sup> and KTaO<sub>3</sub> for  $n = 0$  and  $n = 1$ .

System	Impurity concentration (mol%)	$P(\pi)$ for $n = 0$ (W)	$P(\pi)$ for $n = 1$ (W)
KTaO <sub>3</sub>	—	3.540	0.607
KCl: Cd <sup>2+</sup>	0.13	0.114	0.020
KCl: Mn <sup>2+</sup>	0.083	0.141	0.024

positive integer. Therefore, the power required to change the phase retardation from  $n\pi$  to  $(n + 1)\pi$  is given by the following expression [2]:

$$P(\pi) \approx [\pi \epsilon_M \nu_M \lambda d^2 / (n_0^3 / 2) (R_{1111} - R_{1122}) Q] (\sqrt{n+1} - \sqrt{n})^2 \quad (23)$$

where  $\epsilon_M$  is the microwave dielectric constant,  $\nu_M$  the microwave frequency,  $Q$  the unloaded cavity quality factor and  $d^2$  the cross section of the sample normal to the direction of light propagation.

It is desirable to compare only KCl: Cd<sup>2+</sup> and KCl: Mn<sup>2+</sup> systems with KTaO<sub>3</sub>, since the DC bias voltage required to produce  $\pi$  retardations is within the limits of experimental feasibility. The microwave power  $P(\pi)$  has been calculated for the two cases  $n = 0$  and  $n = 1$ , for KCl: Cd<sup>2+</sup> and KCl: Mn<sup>2+</sup> and KTaO<sub>3</sub> and the results are listed in table 5. For KCl: Cd<sup>2+</sup> and KCl: Mn<sup>2+</sup> the respective static dielectric constants determined in reference [15], and for KTaO<sub>3</sub> the value given by Geusic and co-workers [2], have been used for the calculations. The other parameters involved in the expression (23) are the same as those used by Geusic and co-workers [2]:

$$\nu_M = 3 \text{ GHz} \quad d = 8 \times 10^{-4} \text{ m} \quad \lambda = 632.8 \text{ nm} \quad Q = 14000 \quad n = 0, 1.$$

It is interesting to note that the microwave power requirement for the two KCl systems doped with the divalent cations Cd<sup>2+</sup> and Mn<sup>2+</sup> is at least one order of magnitude less than that required for KTaO<sub>3</sub>.

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