Ammonium dihydrogen phosphate (ADP) impurity effects on phase transition and domain-wall freezing in potassium-ammonium dihydrogen phosphate $[(\mathrm{KDP})_{1-x}(\mathrm{ADP})_x]$ crystals

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Dielectric constants and polarization reversal currents are measured in $(\mathrm{KDP})_{1-x}(\mathrm{ADP})_x$ crystals for $x \lesssim 0.015$ to study the roles of ADP impurities. In this low-concentration limit it seems that the ADP impurities form hard defects responsible for lowering both the ferroelectric transition temperature (T_c) and the domain-wall freezing temperature (T_f). Qualitative discussion is given on the experimental observation of $|dT_f(x)/dx| > |dT_c(x)/dx|$, which causes the range of the plateau anomaly between T_c and T_f to widen rather than narrow in the presence of impurities.

A new interest is rapidly growing in the antiferroelectric ADP impurity effects in the crystals of the ferroelectric KDP ($\mathrm{KH_2PO_4}$) family.[1,2] In $\mathrm{Rb}_{1-x}(\mathrm{NH_4})_x\mathrm{H_2PO_4}$ crystals the ferroelectric transition temperature decreases rapidly with increasing x at the rate of $dT_c/dx \simeq -300$ K,[1] which is well over the value of $dT_c/dx \simeq 107$ K for the dueterated KDP crystals $\mathrm{K(H}_{1-x}\mathrm{D}_x)_2\mathrm{PO_4}$.[3]

It is well known that the transition temperature T_c of the mixed crystals between the isomorphic ferroelectric crystals lies in between the respective transition temperatures of the mixing crystals.[4] The $\mathrm{K(H}_{1-x}\mathrm{D}_x)_2\mathrm{PO_4}$ mixed crystals follow this general rule for a wide range of x, and the important roles of deuteron impurities could be well understood in terms of the tunneling effect. However, in $\mathrm{Rb}_{1-x}(\mathrm{NH_4})_x\mathrm{H_2PO_4}$ crystals the roles of $(\mathrm{NH_4})^+$ impurities are not well understood except that the mean-field behavior of hydrogen bonds in the mixed crystal is responsible for the spin-glass-like phase obtained for $x \gtrsim 0.22$.[1,2]

In this Brief Report we want to report on our experimental results of dielectric constants and polarization reversal currents in $(\mathrm{KDP})_{1-x}(\mathrm{ADP})_x$ crystals for $x \lesssim 0.015$, showing possibly that in this low-concentration limit of ADP impurities the c-axis ferroelectric interaction of ADP (Ref. 5) may be no less important than the a-axis antiferroelectric interaction in determining the dielectric properties of the $(\mathrm{KDP})_{1-x}(\mathrm{ADP})_x$ crystal.

The $(\mathrm{KDP})_{1-x}(\mathrm{ADP})_x$ single crystal was grown from a saturated solution with starting ADP concentrations of 1, 2, 5, and 10 wt.% and the grown crystals were analyzed to determine the molar concentration x of ADP impurities. Only $\sim 13\%$ of the starting ADP concentration was found to be doped into the grown crystals and optical quality (homogeneous) good crystals could not be obtained when the starting concentration exceeded 25 wt.%, probably because the lattice parameters of KDP did not match closely to those of ADP. c-cut samples were prepared, all with the thickness of 0.8 mm after final polishing, and silver-coated in the vacuum evaporator for making electrodes.

DIELECTRIC CONSTANTS

KDP ferroelectrics exhibit a plateau anomaly of the high dielectric constant from the ferroelectric transition point T_c to T_f, the domain freezing temperature below which the dielectric constant ϵ_c drops rapidly to normal values.[6] T_f depends on the probing field strength, and is defined usually as obtained in the weak field of the order of 1 V/cm.[7]

Fedosov and Sidorkin[8] proposed a quantitative explanation for this anomaly in terms of a two-dimensional (2D) ordering in the midlayer between the domains. The model is based on the classification of the domain-wall structures into type I (↑ · ↓) and type II (↑ ↓). The domain mobility barrier height determined by the difference of the surface free energy between the two types was proved to rise sharply at T_f, when the type-I to type-II transformation is realized by the 2D ordering in the midlayer.

In Fig. 1 we have displayed the dielectric constant ϵ_c measured at 10 kHz, where we can see a large shift of both T_c and T_f with increasing ADP concentration x.

In Fig. 2 the T_c and T_f dependence on ADP concentration x is shown, from which we obtain $dT_c/dx \simeq -250$ K and $dT_f/dx \simeq -850$ K. T_f was found to be more readily located as a maximum peak point in the dielectric loss tangent curve. This negative temperature shift may be consistent

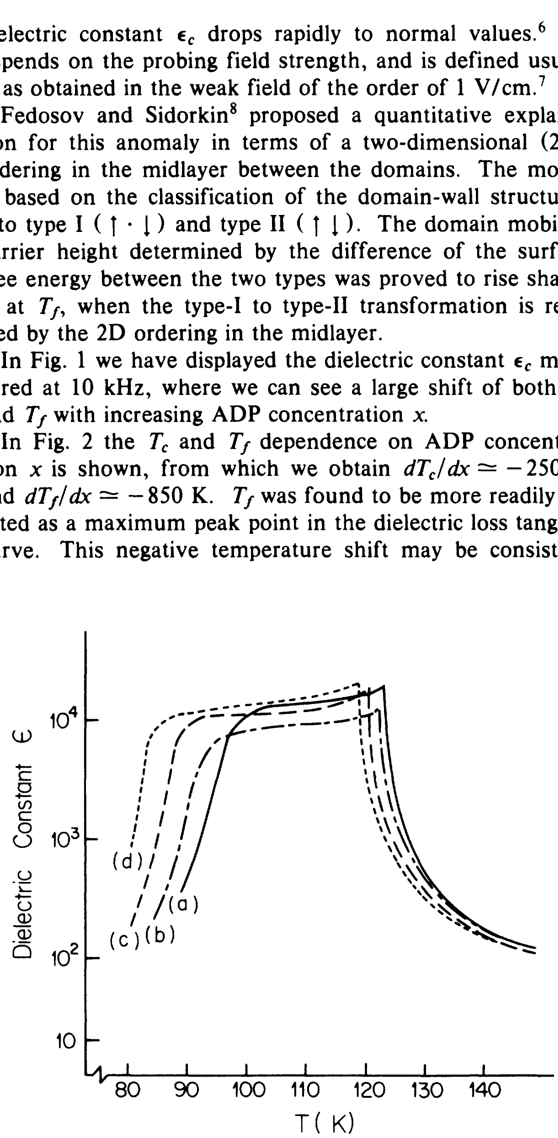

FIG. 1. Temperature dependence of dielectric constant ϵ_c of $(\mathrm{KDP})_{1-x}(\mathrm{ADP})_x$ crystals for (a) $x=0$, (b) $x=0.0032$, (c) $x=0.0069$, and (d) $x=0.0141$.

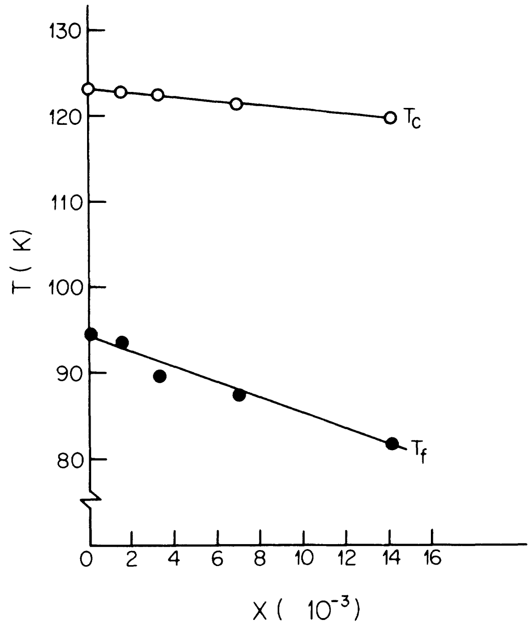

FIG. 2. ADP concentration (x) dependence of ferroelectric transition temperature (T_c) and domain freezing temperature (T_f) in $(\mathrm{KDP})_{1-x}(\mathrm{ADP})_x$ crystals.

with the empirical rule on T_c of mixed crystals if we consider ADP as a c-axis ferroelectrics of T_c equal to -17 K (Ref. 5) rather than the a-axis antiferroelectrics of T_c equal to 148 K.

This hard defect character[9] of ADP impurities may be better understood from the more pronounced effects on the domain-wall freezing temperature T_f.

We now apply the most widely accepted KDP model—the Ising model with a transverse field[8,10]—to our problem:

$$\mathscr{H}=\sum_i \Omega_i S_i^x-\frac{1}{2}\sum_{\substack{i,j\\ i\neq j}} J_{ij}S_i^z S_j^z\ , \qquad (1)$$

where $J_{ij}=\mu_i I_{ij}\mu_j$ represents effective dipole-dipole interaction between different $\mathrm{H_2PO_4}^-$ groups, when T_c and T_f are given in the mean-field approximation as follows:

$$\mu^2\frac{I_0}{2\Omega}\tanh\left(\frac{\Omega}{2\kappa_B T_c}\right)=1\ , \qquad (2a)$$

$$\mu^2\frac{I_0'}{2\Omega}\tanh\left(\frac{\Omega}{2\kappa_B T_f}\right)=1\ , \qquad (2b)$$

where $I_0=\sum_{i,j}I_{ij}$ and for I_0' the pair ($i\neq j$) summation is restricted to the 2D layer.

We have $I_0>I_0'$ due to missing interaction in the 2D layer, and obtain $T_c>T_f$. The decrease of T_c in $(\mathrm{KDP})_{1-x}(\mathrm{ADP})_x$ can also be understood as due to the hard defect character of $\mathrm{NH_4}^+$ impurities, hindering the ferroelectric ordering of the host lattice, which can be expected from Eq. (2a) if $\Omega_2>\Omega_1$ or $\mu_2<\mu_1$ is the case, where 1 refers to host lattice sites and 2 to impurity sites.[9] The same can be extended to the calculation of the averaged susceptibility in the virtual crystal approximation, giving the transition temperature $T_c(x)$ of the mixed crystal[11] as from

$$(1-x)\mu_1^2\frac{I_0}{2\Omega_1}\tanh\left(\frac{\Omega_1}{2\kappa_B T_c(x)}\right)+x\mu_2^2\frac{I_0}{2\Omega_2}\tanh\left(\frac{\Omega_2}{2\kappa_B T_c(x)}\right)=1\ . \qquad (3)$$

We may assume that on the average the midlayer interactions with both sides of the antiparallel domains are canceled also in the impurity-perturbed crystal. Equation (3) can thus be applied to the case of a 2D midlayer simply by replacing I_0 with I_0' and $T_c(x)$ with $T_f(x)$. Within the lowest approximation, Ω_1 may also be put equal to Ω_2 since $\mathrm{NH_4}^+$ is not coupled directly to the tunneling H bonds. We can thus obtain from Eq. (3) $\Delta T_c(x)$ and $\Delta T_f(x)$, in the low-concentration limit, as follows:

$$\begin{aligned}\Delta T_c&=\left.\frac{\partial T_c(x)}{\partial x}\right|_{x=0}x\\&=\frac{2\kappa_B T_c^2}{\Omega}\sinh\left(\frac{\Omega}{2\kappa_B T_c}\right)\cosh\left(\frac{\Omega}{2\kappa_B T_c}\right)\left(\frac{\mu_2^2}{\mu_1^2}-1\right)x\\&=A\left(\frac{\mu_2^2}{\mu_1^2}-1\right)x\ ,\end{aligned} \qquad (4a)$$

$$\begin{aligned}\Delta T_f&=\left.\frac{\partial T_f(x)}{\partial x}\right|_{x=0}x\\&=\frac{2\kappa_B T_f^2}{\Omega}\sinh\left(\frac{\Omega}{2\kappa_B T_f}\right)\cosh\left(\frac{\Omega}{2\kappa_B T_f}\right)\left(\frac{\mu_2^2}{\mu_1^2}-1\right)x\\&=B\left(\frac{\mu_2^2}{\mu_1^2}-1\right)x\ ,\end{aligned} \qquad (4b)$$

where $\mu_2<\mu_1$ is assumed.

In Fig. 3 we plot the coefficients A and B as a function of tunneling integral Ω. If Ω is taken to be 300 K as estimat-

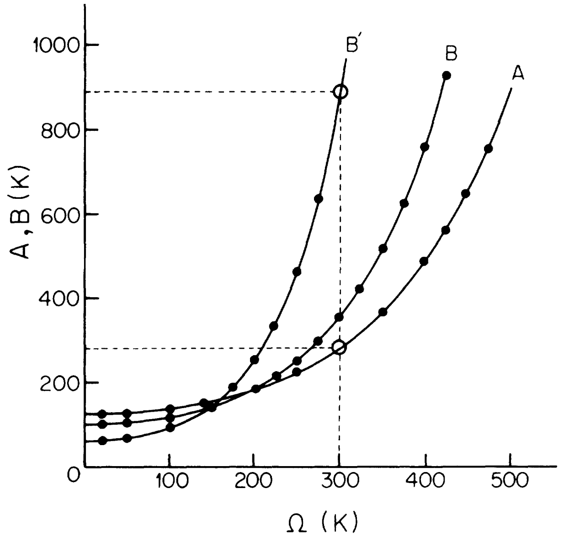

FIG. 3. Ω dependence of A, B coefficients (A with $T_c=123$ K, B with $T_f=95$ K, and B' with $T_f=60$ K). ○ refers to points where experimental values of dT_c/dx and dT_f/dx are obtained with $\Omega=300$ K.

ed from the dynamical tunneling cluster model,[12] the corresponding value of A, with $\mu_2=0.36\mu_1$, gives the observed value of $dT_c/dx \simeq -250$ K. However, B does not give the observed value of $dT_f/dx \simeq -850$ K when we take $T_f(0)=95$ K, $\Omega=300$ K, and $\mu_2=0.36\mu_1$. To obtain the observed value of $dT_f/dx \simeq -850$ K with $\mu_2=0.36\mu_1$ we have to put $T_f(0)=60$ K in Eq. (4b). This discrepancy may be understood if we note that Eq. (4b) is based upon the one-layer model while the $T_f(0)=95$ K observation in the pure KDP crystal represents the real domain freezing temperature, where the boundary layer has a finite thickness of roughness. On the same ground of the roughening transition of the solid-on-solid model system,[13] where the lower bound of the roughening transition temperature is the 2D Ising temperature, we may interpret $T_f(0)=60$ K as corresponding to the 2D single-layer model of Fedosov and Sidorkin,[8] a lower bound of the domain freezing temperature.

POLARIZATION REVERSAL CURRENTS

The c-cut crystals of varying ADP concentrations were employed in the resistance-capacitance differential circuit to measure the displacement current $J=dP/dt$ in the ferroelectric phase by applying a step-function field.[14]

The main component of the displacement current is derived from the polarization-reversal switching current when the applied field is antiparallel to the domain polarization.

At low fields of $E \lesssim 185$ V/cm as in the present work, the polarization reversal proceeds via the domain-wall motion due to the anomalously high mobility in the plateau region. And we may expect the polarization-reversal current dependence on temperature and ADP impurity concentration to be similar to that of the dielectric constant.

Indeed, this similarity, decreasing T_f with increasing ADP concentration x, is borne out in Fig. 4, where we depicted the switching current dependence on temperature at $E=185$ V/cm for $(\mathrm{KDP})_{1-x}(\mathrm{ADP})_x$ crystals. More details of this analysis including the field dependence will be published elsewhere.

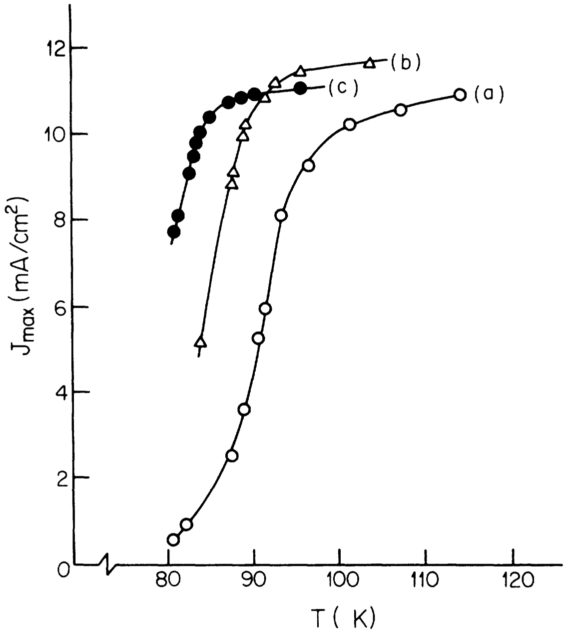

FIG. 4. Polarization-reversal current dependence on temperature at $E=185$ V/cm in $(\mathrm{KDP})_{1-x}(\mathrm{ADP})_x$ crystals for (a) $x=0$, (b) $x=0.0069$, and (c) $x=0.0141$.

In conclusion, it seems that ADP impurities in $(\mathrm{KDP})_{1-x}(\mathrm{ADP})_x$ crystals have a hard defect character, favoring the interfacial layer to remain in the $\uparrow \cdot \downarrow$ (type I, $\langle S_z\rangle=0$) state of the higher domain-wall mobility, in the low-concentration limit $x \lesssim 0.015$.

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