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Brief Reports

Low-temperature ferroelectric polarization reversal monitored by electron spin resonance of AsO_4^{4-} in x-irradiated KD_2PO_4-KH_2AsO_4 mixed crystals

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Ferroelectric polarization reversal was monitored in the KD_2PO_4-KH_2AsO_4 system for electric fields up to 8 kV/cm by observing the time dependence of the line intensities of the electron spin resonance spectrum of the AsO_4^{4-} radical formed in x-irradiated crystals. The stronger the reversing electric field strength the more rapidly the polarization changes with time. For the largest reversing field strengths the measured values of the change in polarization showed a linear dependence on the time when plotted on a log-log scale.

Potassium dideuterium phosphate KD_2PO_4 (DKDP) and potassium dihydrogen arsenate KH_2AsO_4 are isomorphic members of the KDP class of uniaxial hydrogen-bonded ferroelectric crystals. At room temperature, DKDP crystallizes in the tetragonal $I\bar{4}2d(D_{2d}^{12})$ structure with each tetrahedral PO_4 group hydrogen-bonded to four neighboring PO_4 groups. The time-averaged position of the deuterium atom is located symmetrically between the upper oxygen of one PO_4 group and the lower oxygen of a neighboring PO_4 group, with the two PO_4 tetrahedra differing by approximately 32° in their angular orientation about the c axis of the crystal.[1-3] In the ferroelectric phase below 213 K, the symmetry becomes orthorhombic $Fdd2(C_{2v}^{19})$ with the orthorhombic X and Y axes rotated by approximately 45° from the tetragonal a and b axes.[4,5] In this state, two types of structural domains exist in which the deuteriums are ordered. In one type, the two deuterons associated with each PO_4 tetrahedron are closer to the upper side of the group (i.e., toward the $+c$ direction), while in the other type they are closer to the lower oxygens of the PO_4 group. These two $D_2PO_4^-$ configurations, with the accompanying ionic displacements in the complete (K^+-$D_2PO_4^-$) molecule, give rise to the microscopic electric dipoles along the $+c$ or $-c$ directions.[6] Macroscopic regions of similarly oriented (K^+-$D_2PO_4^-$) molecules thus form the domains of electric polarization that are characteristic of the ferroelectric phase.

The crystals used in this study were grown by slow evaporation from a 99.8% D_2O aqueous solution containing 5 mole% KH_2AsO_4 and 99 mole% isotopically pure KD_2PO_4. Graphite electrodes were placed on the crystal faces perpendicular to the ferroelectric c axis of rectangularly shaped specimens having cross-sectional dimensions of 2.5×2.5 mm^2 and a thickness d of 1.5 mm along the c direction. With this geometry the strength of the applied electric field varied somewhat across the sample, but nevertheless the expression $E=V/d$ was employed to calculate field strength E from applied voltage V. Samples were irradiated for several hours with 35-kV x rays at room temperature. The x-ray machine operated with a Cu target and a current of 15 mA. The ESR spectra were then obtained at 82 K in an x-band TE_{102} rectangular cavity with the c axis of the crystal perpendicular to the static magnetic field H_0 and the orthorhombic X or Y axis parallel to H_0.

The irradiated KD_2PO_4-KH_2AsO_4 mixed crystals give ESR signals from a number of centers as reported by other workers. In particular, the structure of the AsO_4^{4-} radical has been examined extensively.[7-13] The ESR spectrum is a superposition of the equal-intensity hyperfine quartets arising from the radicals in the two different domain types. The three highest field hyperfine components from the two domains are superimposed, while the lowest field ones have their maximum separation when the applied magnetic field is directed along the orthorhombic X or Y axis. The intensity of each low-field hyperfine component of the spectrum is then a measure of the volume of the crystal that is polarized in the direction of the corresponding domain type.

Figure 1(a) shows the equally intense low-field hyperfine components, I_1 and I_2, respectively, from the two domains in the absence of an applied electric field. The effects of applying electric fields of opposite polarity are indicated in Figs. 1(b) and 1(d). The changes in the line intensities I_1 and I_2 clearly show that the two lines arise from different domain types. These effects are analogous to those previously reported[14] for radicals in the two domain types of the system KH_2PO_4-KH_2AsO_4.

The fractional polarization state of the crystal at any time is represented by the function

$$p(t)=(I_1-I_2)/(I_1+I_2)\ . \tag{1}$$

The electric field dependence of the ESR monitored polarization has been studied previously in various KDP-type crystals and was found to exhibit hysteresis.[15-17] The present letter reports the changes in the polarization following the rapid reversal of the applied electric field. It is believed to be the first ESR measurement of polarization reversal in a ferroelectric crystal.

At the start of the experiment the crystal is polarized by an applied electric field to the initial value p_i. Then the electric field is changed to a new value and after a long time the system acquires a final value p_f. The rate at which the polarization $p(t)$ changes with time from p_i to p_f may be expressed in terms of the function $g(t)$.

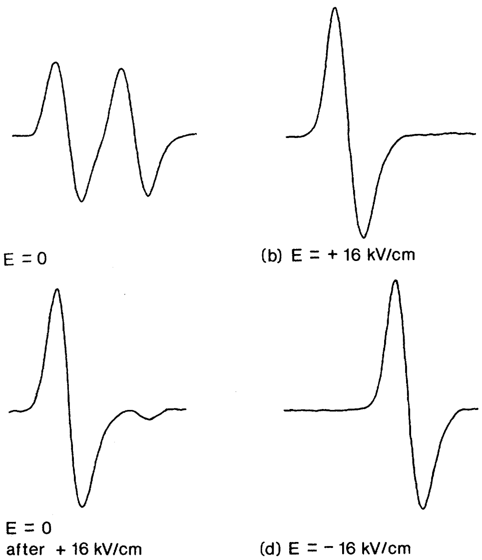
$$g(t)=[p(t)-p_f]/(p_i-p_f)\ . \tag{2}$$

In the present investigation the sample was initially almost completely polarized corresponding to $I_2 \sim 0$ and $p_i \sim 1$, and after a long time the final limiting polarization satisfied the condition $I_1 \sim 0$ and $p_f \sim -1$. As a result Eq. (2) assumes the approximate form

$$g(t)=I_1/(I_1+I_2) \tag{3}$$

that was employed in this work. Here $g(t)$ is the fraction of the crystal which has not yet switched from the initial to the final polarization direction.

In this experiment the crystal was first polarized with an electric field of 16 kV/cm in a direction such that I_2 became zero as in Fig. 1(b). The electric field was then removed to allow spontaneous backswitching to occur as revealed by the small increase in I_2 in Fig. 1(c). Then the electric field was reversed in polarity and the time dependence of the line intensities were monitored by making repeated rapid scales scans through the spectrum at ~40-sec intervals. The reversing electric field had a risetime of 1 μsec and remained on as long as the


(a) E = 0

(b) E = + 16 kV/cm

E = 0
(c) after + 16 kV/cm

(d) E = − 16 kV/cm

FIG. 1. the effect of an applied field on the ESR spectrum of AsO_4^{4-} in KD_2PO_4 at 82 K with $H_0 \perp c$ and H_0 parallel to the orthorhombic X axis.

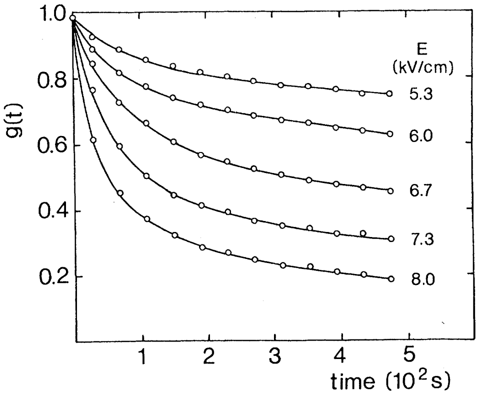


FIG. 2. Time dependence of $g(t)=I_1/(I_1+I_2)$ for various reversing electric field strengths at 82 K.

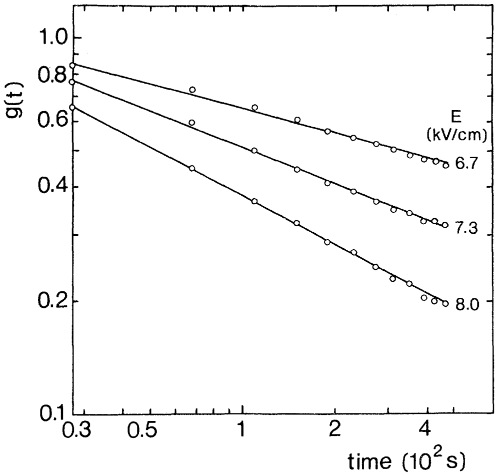


FIG. 3. Plot of $g(t)$ vs time on a log-log scale for the three highest electric field strength curves of Fig. 2.

spectrum was being monitored.

Figure 2 shows how $g(t)$ varies with time for various values of the reversing electric field strength between 5.3 and 8.0 kV/cm. We see from the figure that the larger values of E produce more rapid changes in $g(t)$. Data obtained at four smaller electric field strengths in the range from 2.7 to 4.7 kV/cm exhibited the same trends shown in Fig. 2. At the largest electric field strengths the measured values of $g(t)$ produced linear graphs illustrated in Fig. 3 when they were plotted on a log-log scale corresponding to a time dependence of the form

$$g(t)=g_0 t^{-a} \tag{4}$$

over the range where the data were obtained. Both g_0 and the slope a were functions of the electric field strength with the values $a=0.23$ for $E=6.7$ kV/cm, $a=0.32$ for $E=7.3$ kV/cm, and $a=0.43$ for $E=8.0$ kV/cm. Equation (4) will not, of course, remain valid for extremely short times.

Work is continuing to determine more precisely the polarization reversal behavior of this system. Measurements made on a second sample provided a set of curves that had the same appearance as those presented in Fig. 2, but differed quantitatively from those in this figure. This is to be expected in view of the sample dependence of the coercive field in this system. A more complete report will be made later on these experiments and on the relation of these results to other studies[18-20] of the polarization reversal process in pure KDP-type ferroelectric crystals.

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