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Suppression of switchable polarization in KDP by ionizing radiation

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Switching curves were obtained from KH_2PO_4 single crystals exposed to x-ray radiation for various time intervals, up to 8 h. The applied electric field was varied between 370 and 740 V/cm, as well. The temperature was held constant at 99 K. The switching curves were fit to a three-parameter nucleation and growth model based on the original works by Johnson and Mehl, and independently by Avrami. The two dynamic parameters, characteristic time t_c, and effective domain wall dimensionality n, produced values consistent with unirradiated studies, however, they did not show any clear dependancy on exposure time. The switchable polarization P decreased with increasing exposure time. A simple exponential decay is used to describe P as a function of exposure time. The rate coefficient k for the exponential, decreases with increasing electric field. [S0163-1829(98)00929-1]

I. INTRODUCTION

Potassium dihydrogen phosphate [KH_2PO_4 (KDP)], was identified as a ferroelectric by Bush and Scherrer[1] in 1935. Since then, many investigators have studied the ferroelectric properties of KDP. A review of the ferroelectric properties of KDP can be found in Ref. 2. Given the fact that KDP is one of the most widely known ferroelectrics, it is surprising that very few studies[3,4] have been performed using the electrical switching technique first developed by Merz.[5] This may be attributed to the experimental difficulties associated with KDP. One major difficulty relates to the fact that KDP crystals crack easily from stress due to applied electric fields or rapid temperature changes. Nevertheless, KDP is a very rich system to study. The first detailed measurements of the effects of ionizing radiation on KDP, using the electric technique, are reported here. Preliminary results were reported by the author in a previous[6] publication. In that study, switching curve responses were completely eliminated by 8 h exposures to x rays. In the present study, a range of exposure times was used for more quantitative results.

Numerous publications report the effects of radiation on other ferroelectric systems.[7–10] Most of the previous studies use dielectric type measurements or hystereses measurements which do not yield as much detailed information about domain wall dynamics as switching studies. Some of the more recent studies do use the switching method on ferroelectric systems.[11–14] Many of these systems are of interest from an applied perspective. Again, surprisingly few studies have been conducted on KDP and these utilized the dielectric measurements rather than the switching measurements.[15,16]

Understanding the effects of ionizing radiation on ferroelectric systems is important from both fundamental and applied standpoints. Some basic studies of ferroelectrics, in particular electron paramagnetic resonance[17] (EPR) studies, often use ionizing radiation to produce the necessary paramagnetic centers. Paramagnetic centers are produced by ionizing radiation through the reaction: $H_2PO_4^- \rightarrow H\mathring{P}O_4^- + \mathring{H}$. The dynamic epr studies on KDP, pioneered by the ferroelectric group at The University of South Carolina,[18] produced interesting results that seem inconsistent with those obtained from electrical measurements. The most recent EPR results from South Carolina report a value of $n \approx 0.5$ for the effective domain wall dimensionality, whereas the electrical measurements yields values from ~ 1.0 to ~ 2.25. This brings up the question as to whether these discrepancies are due to variations in the two measurement techniques or if the EPR technique is sensitive to something that the electronic method is not. A close comparison of the two techniques is needed. The present study is a first step in that direction.

Knowledge of radiation hardness in ferroelectrics is important in applications where they may be subject to high radiation environments. One primary application of ferroelectrics is in electronic memories. Radiation-hard ferroelectric memories would be extremely useful in military applications, as well as in certain satellite applications. In addition, the results of this study indicate that the mechanisms that produce fatigue in ferroelectric memories are the same as those that suppress switchable polarization in irradiated ferroelectrics. A connection between switching polarization degradation due to radiation and degradation due to fatigue could be important from an applied standpoint. If radiation studies could be used to predict susceptibility to fatigue, they would be useful for fatigue testing and perhaps quality control.

II. EXPERIMENTAL PROCEDURES

Single, optical quality KDP crystals were donated by Lasermetric. They were cut using a wet wire saw and polished on wet silk. After polishing, gold electrodes were vapor deposited onto the two surfaces perpendicular to the ferroelectric c axis. Later, each sample was closely examined for flaws and measured using an optical microscope with a traveling stage. The electrode areas were approximately 0.20 cm^2, and the thickness of the crystals ranged from 0.15 to 0.20 cm. Each sample was placed in a cryostat. Electrical contact was made with each electrode. The cryostat was evacuated and the temperature was slowly (1 K/min) lowered to 99 K, well below the Curie point (123 K). A small (3 V) dc voltage was applied during cooling to reduce the chance of cracking as the sample was lowered through the Curie point. The assumption is that stresses are greater in multidomain crystals than in monodomain crystals. A small field, applied as the crystal passed through the Curie point, should favor one domain growth direction, producing a more monodomain crystal. Hysteresis curves were recorded to check the quality of the samples and electrical connections. It is believed that this also further eliminated some stress in the crystals. A cycle frequency of 20 Hz was used. In previous radiation studies by this author,[6] data were obtained with various preparation treatments such as the one described here, as well as on crystals that had not been treated at all. There was no qualitative difference in the results, except for a higher incidence of cracking and distorted switching curves in the untreated crystals.

Switching transients were recorded using the standard Merz technique. A simple pulse pattern of one negative pulse followed by a positive pulse was applied to the sample using a solid state pulse generator developed in our laboratory.[19] The negative and positive pulses were 245 ms in duration and separated by 50 ms. The applied electric field ranged from 370 to 740 V/cm. The switching current was recorded across a $10.00 \pm 0.03\,\Omega$ standard resistor. The pulse sequence was repeated and the scope trace was checked visually for repeatability. Afterwards, the voltage was increased and the pulse pattern was repeated at the increased voltage. The samples were then exposed to unfiltered x rays from the copper target of a Philips Norelco x-ray generator through a thin Mylar window in the cryostat. The samples were located 3.0 cm from the x-ray window with the *c* axis parallel to the direction of the beam. Switching currents were recorded every hour during radiation for 8 h. The same sequence of applied electric fields was used each time. The x rays were then turned off and the temperature was slowly raised. Some samples were annealed at room temperature for one day or longer. The entire measurement procedure was repeated on the annealed samples.

III. THEORY

Many models have been proposed to describe the switching curves obtained from the electric switching method. Most of the nucleation and growth models are based on the original works by Johnson and Mehl,[20] and independently by Avrami (JMA).[21] Ishibashi and Takagi[22] applied this theory to the subject of ferroelectric switching utilizing Kolmogorov's method. Furukawa[23] applied the nucleation and growth model to switching in certain copolymers. Dimmler *et al.*,[24] also applied this model to switching in thin films. More recently, Ishibashi[25] refined the theory to account for nonideal situations. The idealized model worked well for previous studies in KDP single crystals,[4] so it is used to analyze the present data. The following is a summary of that model.

By assuming that polarization reversal in an infinite crystal occurs by nucleation and subsequent growth of domains one may obtain the following expression for the fraction of charge switched during the polarization reversal:

$$Q(t) = 1 - e^{[-(t/t_c)^n]}, \tag{1}$$

where t is time and t_c is a characteristic time. The effective dimensionality n will be discussed later. Equation (1) differs from a simple exponential, expected in a rate-dependent process because, as nucleation sites nucleate and grow, they not only make themselves ineligible for reversal, they also render other potential nucleation sites ineligible. The displacement current is given by

$$i(t) = 2PA\,\frac{dQ(t)}{dt}, \tag{2}$$

where P is the polarization and A is the area of the electrode. Combining Eqs. (1) and (2), and defining the current density as $j \equiv I/A$, one obtains the following expression:

$$j(t) = \frac{2Pn}{t_c}\left(\frac{t}{t_c}\right)^{n-1} e^{[-(t/t_c)^n]}. \tag{3}$$

The effective dimensionality n is related to the actual dimensionality d of the domain wall motion. A value of one for d implies platelike domains with walls moving in one direction perpendicular to the ferroelectric axis. A value of 2 infers cylindrical domains with walls expanding in two directions. A value of 3 for d infers spherical domains with walls expanding in all three directions. The actual dimensionality d and the effective dimensionality n can be related depending upon which of the following assumptions is valid. Assumption 1: If domain wall motion proceeds with constant velocity and if no additional nuclei form during the growth of existing domains, then $n = d$. Assumption 2: If domain wall motion proceeds with constant velocity and if new nuclei are forming at a constant rate throughout the switching process, then $n = d + 1$.

Both assumptions can be valid to some extent with domain wall motion and nucleation occurring simultaneously. In other words, the situation is an intermediate case.

IV. RESULTS

Hundreds of switching curves were obtained at exposure times up to 8 h for various samples. Stress in the crystal distorts the switching curves or even produces cracks in the crystals. Attempts were made to reduce stress as described in the experimental section. Many samples did not withstand numerous pulse cycles. However, all the samples showed a reduction in switchable polarization after exposure. Three samples were particularly resilient, allowing a large amount of data to be obtained over a variety of electric fields ranging from 370 to 740 V/cm. The dimensions of the samples are given in Table I.

A matrix of data was obtained in which samples were exposed to the same electric fields over a range of exposure times, up to 6 h. Sample A was annealed twice. Samples B and C were not annealed. The temperature was held fixed at 99 K for all data. All three samples gave similar results.

Representative switching curves are shown in Fig. 1. The

TABLE I. Sample dimensions.

Sample	thickness (± 0.01 cm)	area (± 0.02 cm^2)
A	0.17	0.24
B	0.18	0.25
C	0.14	0.23

figure shows three switching curves from the same crystal (sample A) at exposure times of 1, 2, and 3 h. The electric field is 640 V/cm for all three curves. For each switching curve, the data are shown with the fit curve drawn through them.

The data were fit to the nucleation and growth model discussed in the theory section, which gave three parameters: the polarization P, the effective domain wall motion dimensionality n, and the characteristic time t_c. Each parameter was plotted separately as a function of exposure time. The effective domain wall dimensionality n varied between 1.0 and 2.0, consistent with previous results on nonirradiated KDP,[4] as is expected for platelike motion. Plots of n versus exposure time for constant electric field showed no clear dependence on exposure time. The characteristic times t_c, which varied between 2×10^{-6} and 2×10^{-4} s, also were independent of exposure time. These null results will be addressed in the discussion section.

The polarization did show a clear dependance on exposure time, with the polarization decreasing smoothly as a function of exposure time. Unfortunately, it is not possible to determine clearly if the decrease is exponential, stretched exponential, or power law. This will be discussed in more detail later. A representative family of curves obtained from sample A is shown in Fig. 2 for three different electric fields. The polarization at zero exposure time was omitted. Due to experimental complications, there was a time delay between the application of the first pulse and the initial exposure to x rays. This delay did not exist in subsequent pulse data. Although the zero exposure data did not show anything unusual, slight effects due to wait time could not be ruled out. In addition, thorough studies on switching in nonirradiated KDP have been performed.[4] Sample A gave similar results before and after annealing and the other samples also gave similar results. The polarization is plotted as a function of

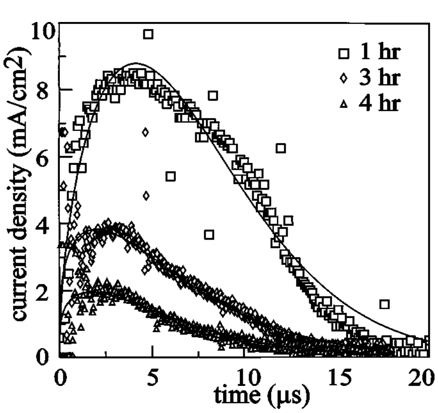

FIG. 1. Experimental and theoretical (smooth) switching curves for three different radiation exposure times. Sample A, $T=99$ K, $E=640$ V/cm.

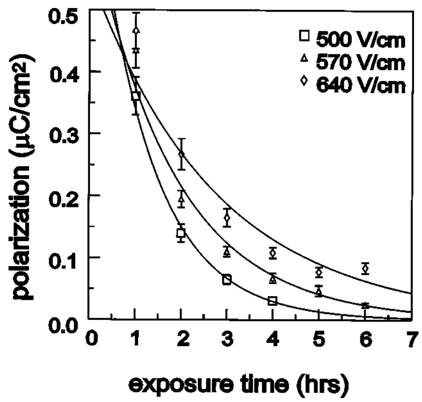

FIG. 2. Switchable polarization P as a function of radiation exposure time for three different electric fields. Sample A, $T=99$ K.

exposure time. The error bars were obtained from the statistical analysis. Note that the three data points for 640 V/cm and radiation times of 1, 3, and 5 h correspond to the three curves in Fig. 1.

Assuming a simple exponential for the relation between switchable polarization and exposure time, the rate coefficients of the exponential show a decrease with electric field as demonstrated by Fig. 3. The first three sets of points labeled A1, A2, and A3 are from the same sample with periods of annealing between each set of data. The sets of points labeled B and C correspond to different samples with no annealing. Due to the extensive analysis performed on the data to obtain the points in the figure, the error propagation is quite large, approximately 1.4 1/hr, consequently, the error bars would span most of the y axis and are omitted for clarity. The A3 points at 500, 570, and 640 V/cm correspond to Fig. 2.

V. DISCUSSION

Previous results by the author and coinvestigators[4] show clearly that the parameters t_c and n are sensitive to temperature and applied electric field which is to be expected because these factors effect domain wall mobility. In the present study, temperature and electric field were held fixed

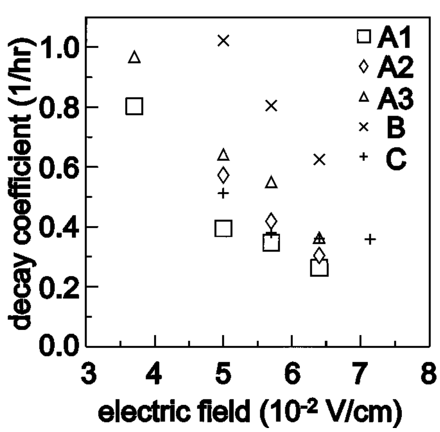

FIG. 3. Rate coefficient k as a function of applied electric field for three different samples. Sample A was annealed twice. $T=99$ K.

while varying exposure time to x rays in an attempt to determine the effect of ionizing radiation on domain wall dynamics. The null results indicate that t_c and n are insensitive to ionizing radiation.

Some researchers[26] have proposed that defect sites slow or even stop domain motion producing a viscous drag-type phenomenon. If this were the case, one would expect the parameters n and t_c to depend on exposure time. The results of the present study do not support this view, because n and t_c do not show the expected dependancy on exposure time. The same researchers further propose that the sites, presumably frozen, responsible for this viscous action are the same sites identified by EPR. This is in sharp contrast to the dynamic EPR switching studies[18] which specifically monitors the reversal of these sites.

A more consistent view focuses on the free charges produced by the radiation. In this model, charge centers produced by the ionizing radiation are trapped at defects, including the surfaces of the crystal. These charges screen the applied electric field, preventing the polarization reversal, effectively pinning these sites. It also is possible that these defects are nucleation sites for domains.

This screening effect or domain pinning has been proposed as a mechanism in the reduction of switchable polarization in fatigued ferroelectric films used as electronic memory elements.[27] Fatigue degrades the ability of the sample to respond to switching pulses after a large number of polarization reversals such as the ones that would occur in repeated read-write cycles of a ferroelectric memory. The model proposes that free charge is produced by the repeated read-write process and are trapped at defects. Thin film ferroelectrics are the primary candidates for modern ferroelectric memories. In these ferroelectrics, free charges can be trapped at grain boundaries.

The decrease in switchable polarization as a function of exposure time could be fit by more than a single function. Unfortunately, experimental conditions did not allow for the necessary range of data for clearly distinguishing between the possibilities. A stretched exponential would fit the data best, but at the expense of an additional parameter. Until the experimental problems can be addressed and a wider range of data obtained, a simple exponential decay will be used to describe the reduction of switchable polarization P with increasing exposure time r:

$$P = P_0 e^{-kr}, \tag{4}$$

with P_0 = the switchable polarization at exposure time $r=0$ and k = the rate coefficient. This implies that the rate of change of switchable polarization is proportional to the switchable polarization, indicating that the production of screening sites is a random process.

Figure 3 shows a decrease in the rate coefficient k with increasing applied electric field, ranging between 0.2 and 1.1 (1/hr). This figure shows the systematic error between samples. All of the data points would be expected to lie along the same line. Samples A and C are fairly consistent but sample B shows some variation. The dependence on electric field probably is due to the ability of large fields to overcome weakly pinned sites.

VI. CONCLUSION

Switchable polarization in ferroelectric KDP is reduced due to exposure to x rays. The characteristic time t_c and the effective domain wall dimensionality n are, within experimental uncertainty, independent of exposure time. This implies that the domain wall dynamics of the polarization is not effected, only the amount of reversible polarization is reduced. This reduction in switchable polarization is consistent with a view of trapped charges which are liberated during irradiation. These charges are probably trapped at defects, effectively reducing switchable polarization.

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