Recent trends in the study of switching processes in ferroelectrics

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Abstract. Several ferroelectrics and materials showing ferroelectric-like switching behaviour have been widely investigated and both an exponential or power law of \( t \) on \( E \) have been reported. However, the mechanism of polarization reversal and domain dynamics show a complexity that makes it difficult to generalize and draw a common rule for all types of ferroelectrics. Radiation damage, internal biasing fields and defects alter the switching characteristics and in this review including some of the work of the authors on TGS, sodium nitrite CRP etc, the present trends in the study of switching and the electroluminescence during switching have been discussed.

Keywords. Polarization reversal; radiation damage; ferroelectrics; switching processes.

1. Introduction

The characteristic property which distinguishes a ferroelectric is its macroscopic polarization which can be switched or reoriented by the application of an appropriate external electric field. This property makes ferroelectrics very attractive candidates for memory device applications where one of the prerequisites is a bistable material property which can be switched between two well-defined states. In addition to this, the recent discovery of the large coupling between optical and electrical properties in some of the ferroelectrics has revived interest in the use of these ferroelectrics in optical device applications. In these materials, an optical property such as refractive index, birefringence or the sense of optical rotation can be controlled by the application of an external electric field. In spite of such potential applications existing for ferroelectric materials, several inherent disadvantages have precluded their widespread use. Most ferroelectrics do not possess a well-defined coercive field in contrast to ferromagnets. This was due to the fact that in ferroelectrics the polarization could be switched by even very small electric fields applied over a sufficiently long time. Also devices based on such ferroelectric materials would not be immune to noise signals. Further subjecting the ferroelectric material to repeated switching by an external field tends to fatigue the material and causes the coercive field to rise. The response to applied field also slows down.

A more detailed study of the switching process in ferroelectrics is therefore desirable to understand the mechanism of the processes and also to produce ferroelectrics with improved properties. The experimental methods for studying the switching process are based on a method originally developed by Merz (1954). In this method, a train of square pulses is applied to the sample in the form of a capacitor. Information about the switching process can be obtained from the switching current transient flowing in the sample during the switching process. An important development has been the use of computers for the acquisition and analysis of data obtained from switching process studies (Montoto and Jacque 1978).

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The presence of defects originating during the material preparation, radiation damage or due to doping can alter the switching processes in ferroelectrics. The presence of defects stabilizes a well-defined coercive field. In analogy to ferromagnetic materials, the switching in ferroelectrics proceeds through the motion of domain walls enlarging the size of favourably oriented domains in the material. The domain wall motion is clamped by the defects present in the material. Thus in order to elucidate the role of the defects on the switching process, switching studies on typical ferroelectrics such as roto have been carried out. In addition to investigating the switching processes in materials such as gadolinium molybdate and lead germanate, switching processes in liquid crystals and polymers which show ferroelectric-like behaviour have also been studied. The electroluminescence observed during switching has also been investigated (Montoto and Jacque 1978). This has been verified to occur from the recombination of uncompensated charge in the surface layers.

2. Theory

The macroscopic polarization of ferroelectric can be switched or reoriented by an external field. During the switching process, a transient current flows in the sample. The transient has a sharp initial spike (duration ~ 0-1 μsec) followed by a hump whose peak appears after a time interval called switching time \( t_s \) ranging from microseconds to minutes from the initial point of the transient. The spike occurs due to stray capacitance inherent in the apparatus used to excite and detect switching. The

![Graph](image)

**Figure 1.** Variation of switched charge density \( Q \), Maximum current density \( J_{\text{max}} \), and switching time \( t_{\text{max}} \) with electric field in PVDF (from Buscman 1973)
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switching time $t_s$ depends on various parameters such as the magnitude of the applied electric field, the ferroelectric material, the temperature, the pressure and so on. The relationship between $t_s$ and applied electric field $E$ is described by

$$\frac{1}{t_s} = \gamma E \exp\left( -\frac{\alpha}{E} \right),$$

$$\frac{1}{t_s} = \frac{1}{t_m} \exp\left( -\frac{\delta}{E} \right).$$

Relation (1) has been used by Pulvari and Kuebler (1958) while the second has been derived from Miller and Weinreich (1960). Equation (2) is applicable in the low electric field region when $t_s$ exhibits a non-linear relationship. Relation (2) can be used both in the low and high $E$ regime. In the high $E$ regime an additional relation (Merz 1954).

$$\frac{1}{t_s} = BE^*$$

can also be used. The quantities $\alpha$, $\delta$, are called activation fields which can be related to the internal biasing fields and the coercive field of the crystal. The activation fields increase with decrease in temperature, increase in pressure and also whenever defects are present in the ferroelectric. This increase presages a slowing down (rise in $t_s$) of the switching process. Further

$$\gamma = \mu/d,$$

where $\mu$ is the mobility and $d$ is the sample thickness. $\mu$ can be identified with the spread of the switching process over the volume of the ferroelectric.

The quantities $\alpha$, $\delta$, $\mu$ are uniquely defined for a single temperature, pressure, sample material etc. The activation fields are defined with respect to the applied field.

The temperature-independent activation energies $E_a$ are defined by relations of the type,

$$\frac{1}{t_s} = A \exp\left( -\frac{E_a}{kT} \right).$$

$E_a$ can be evaluated as the slope of a plot of $\ln(1/t_s)$ vs $(1/T)$.

The activation field is a measure of the constraints encountered by the individual domain polarizations in switching in response to the applied field. As the temperature moves away from the transition temperature into the ferroelectric region, some of the domain polarizations get clamped. The presence of defects also produces similar effects. Further, in the transition from the para- to ferroelectric state, there can be drastic changes in the molecular environment as first order transitions are always accompanied by latent heat changes and molecular rearrangement. Thus for first order ferroelectrics an internal biasing field can be present. This denotes the difficulty encountered by the individual domain polarizations in switching. Sometimes the internal biasing fields can be so high that switching occurs only in very high electric fields with very low values of macroscopic polarization. In such cases switching can be observed only in a region close to the transition temperature, and only with the application of very high fields at lower temperature.

3. Switching studies in individual ferroelectrics

3.1 Polyvinylidene-difluoride (PVDF)

PVDF exists in various polymeric phases. The most common polymorph $\alpha$ is nonpolar. Uniaxial drawing transforms $\alpha$ phase into $\beta$-phase which is polar and the molecules
adopt a planar zig-zag conformation. The molecular dipoles inherent to the monomer unit (\(-\text{CF}_2\text{-CF}_2\)-) are all aligned in the same direction perpendicular to the chain axes. Polarization reversal in PVDF was originally considered to be a slow process on account of the poling conditions employed by Kawai (1969), who used long time (\(\sim 30\) min) and high temperature (\(> 100^\circ\text{C}\)).

Using these poling conditions, Buchman (1973) made the first switching studies on PVDF using the Merz method. He observed slow switching processes (several minutes) at temperatures above \(100^\circ\text{C}\) and in low fields below \(15 \text{ MV/cm}\). He inferred that the slow switching process arose from the long-chain nature of the molecules. The results of Buchman (1973) are presented in figures 1 and 2.

Later investigations by Furukawa and Johnson (1983) and Takase and Odajima (1983) have shown that switching can occur at lower temperatures (\(20^\circ\text{C}\) to \(-100^\circ\text{C}\)) at much higher fields (\(\sim 200 \text{ MV/cm}\)) and can be a much faster process (several microseconds).

Dvey-Aharon \textit{et al} (1981) have theoretically investigated the switching process in PVDF in terms of the propagation of a kink of rotation or a solitary wave along the molecular chain. They have shown that a model involving \(60^\circ\) rotation of the chains yields results in conformity with experiment. According to this model the individual domain polarizations are out of alignment by \(60^\circ\) from those of adjacent domain polarizations. Poling and switching in the presence of an applied field proceed through the nucleation of domains with favourably oriented domains by propagation of \(60^\circ\) rotations of chains in unfavourably oriented domains.

Takase and Odajima (1982) evaluated the activation field as \(1.3 \text{ GV/m}\) (at \(20^\circ\text{C}\)) and the activation energy as \(0.63 \text{ eV}\). These results are in agreement with those of Furukawa and Johnson (1983), which are presented in figure 3. The activation field in this case varies from \(1.1 \text{ GV/m}\) (\(20^\circ\text{C}\)) to \(1.9 \text{ GV/m}\) (\(-60^\circ\text{C}\)).

In PVDF the large value of the activation field suggests that the switching process occurs mainly in the field range where \(1/t\), has an exponential dependence on \(E\). The low

![Figure 2](image-url)

\textbf{Figure 2.} Variation of switching time, \(t_{\text{max}}\text{-and current density with temperature in PVDF}\) (from Buchman 1973)
field range has been identified (Merz 1954) as the region in which nucleation of favourably oriented domains occupies most of the switching time. In PVDF, switching cannot be observed below a threshold field at lower temperatures (120 MV/cm at 20°C). At very low fields, switching can be observed only at temperatures above 100°C. This threshold effect and large activation fields arise from the energy of formation of the domains by 60° rotation of the long chain molecules.

3.2 Liquid crystals and related compounds

The first experimental study of ferroelectric-like switching behaviour in a material which exhibits liquid crystalline behaviour was by Williams and Heilemeir (1966). They studied the switching behaviour in azoxyphenetole and azoxyanisole, which exhibit nematic liquid crystalline phases. One interesting observation reported by them was that the ferroelectric switching behaviour was observed both in the liquid crystalline and in the isotropic liquid phase existing above the liquid crystal isotropic liquid phase transition.

Martinot Lagarde (1977) reported the observation of ferroelectric-like switching behaviour in the smectic (phase of HOBA CPC (P-hexyl-oxy benzylidene-P'-amino-2-chloro-propyl-cinnamate). Figure 4 shows the variation of polarization charge Q with temperature.

The smectic phase of a liquid crystal can be characterized by a director $\vec{n}$ which is at an angle to the normal to the layers making up the smectic phase. In a chiral smectic, $\vec{n}$ precesses about the layer normal and thereby determines the pitch which is 1–10 µm usually. Cladis et al (1983) have studied switching in a chiral smectic. The chiral smectic has a permanent polarization $\vec{P}$ perpendicular to both $\vec{n}$ and the layer normal (Meyer 1977). When an electric field $E$ is applied to the sample of chiral smectic, domains with polarizations $\vec{P}$ parallel to $E$ grow through wall motion in the form of solitary waves—called soliton motion. Walls separate regions with $\vec{P}$ oriented parallel and antiparallel to $E$. The regions with unfavourable $\vec{P}$ never vanish completely; there are small regions left over at the end of the switching process. The switching time between the original
state and the final state with most of the $\vec{P}$ parallel to $E$, has a $1/E$ dependence. In the case of switching in a chiral smectic, threshold field effect is not observed.

Brand and Cladis (1984) reported the observation of switching behaviour in the smectic $-X$ phase. They studied the switching behaviour in smectic $X$ phase of 8SI*-S-(+)-(4-2'-methylbutyl) phenyl 4'-A-octyl biphenyl-4-carboxylate. A linear relationship between $V$ and the sample temperature $T$ (figure 5) was observed. Here $V$ is the applied voltage and $t$ is the switching time between the non-oriented and oriented states.

**Azoxynbenzene** is the first member of the homologous series to which azoxyphenetole and azosyanisole belong. **Azoxynbenzene** is an isotropic liquid above 38°C. Ferroelectric-like switching behaviour was observed in the isotropic liquid phase (Ravi and Narayanan 1982). It was observed that the switching time depended linearly on the applied field (figures 6 and 7) and that the switching process was slower than in triglycerine sulphate for similar values of $E$.

**Figure 4.** Variation of polarization charge $Q$ with temperature in HOBACPC (from Martinot Lagare 1977)

**Figure 5.** Variation of $V \ln \epsilon$ with temperature in 8SI*-smectic X liquid crystal (from Brand and Cladis 1984).
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Figure 6. Variation of switching time with applied field at various temperatures in azoxybenzene (from Ravi and Narayanan 1982)

Figure 7. Variation of $\sigma$ and $\mu$ with temperature and thickness in azoxybenzene (from Ravi and Narayanan 1982)

3.3 Single crystals

3.3a Gadolinium molybdate: The ferroelectric switching behaviour of gadolinium molybdate was studied by Kumada (1969, 1972) and the data are given in figures 8 and 9.
3.3b Lead germanate: Iwasaki et al (1971, 1972) studied the switching behaviour of lead germanate. Lead germanate exhibits optical activity in the ferroelectric phase. The sense of the optical rotation can be reoriented by spontaneous polarization. The
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**Figure 10.** Variation of switching time in regions I, II and III in lead germanate (from Iwasaki et al 1972)

**Figure 11.** Switching time in regions II and III in lead germanate. (from Iwasaki et al 1972)
dependence of the switching time \( t_s \) on the applied electric field \( E \) exhibits 3 distinct regions:

(i) Region I (low field),

(ii) Region II (moderate applied field),

\[
1/t_s = 1/t_m \exp(-\alpha/E), \quad \alpha = 2.5 \times 10^4 \text{ V/cm}.
\]

(iii) Region III (high field)

\[
1/t_s = A \exp(-\beta), \quad \beta = 2.7; \quad A \text{ is a constant.}
\]

The data for variation of \( t_s \) on \( E \) is shown in figures 10 and 11.

3.3c *Dicalcium strontium propionate (DSP)*: DSP is an improper ferroelectric below 8.5°C. Ferroelectric switching behaviour of DSP has been studied (Ramanath, Ravi and Narayan 1982). It was found (figures 12–13) that the switching time depends linearly on the applied electric field \( E \) and that the switching process is slower than in triglycine sulphate for comparable values of \( E \), in the temperature range in which the switching behaviour of DSP was studied.

3.4 *Irradiated single crystals*

3.4a *Triglycine sulphate*: The switching process in single crystals of triglycine sulphate radiation damaged by x-rays and gamma rays was investigated by Ravi and

![Figure 12](image-url)
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Figure 13. Temperature variation of mobility $\mu$ and activation field $\delta$, in dsp (from Ravi and Narayanan 1982)

Narayanan (1982). It was found that the switching time shows an exponential dependence on the applied field $E$ and that there is an increase in the activation field (figures 14–18).

Investigations (Fletcher et al 1976a, b) and the structure of irradiated TGS indicate that irradiation brings about changes in the hydrogen bond system of TGS. The nitrogen atom on glycine I in irradiated TGS has only two hydrogen atoms attached to it instead of the three hydrogen atoms in unirradiated TGS. The pseudo-mirror symmetry about

Figure 14. Variation of $1/\mu$ with $E$ in triglycine sulphate irradiated with 0.5 M rad of gamma rays.
the plane $Y = 1/4$ is destroyed and the switching of glycine I is made more difficult, and requires more energy. This is reflected as an increase in the activation fields for irradiated as compared to normal PEs.

3.4b Sodium nitrite: The switching process in gamma irradiated sodium nitrite has been studied (Ravi and Narayanan 1981a) and it has been observed that the switching time shows an exponential dependence on the applied field and that $x$ and $\delta$, increase (figures 19–21). In sodium nitrate, irradiation is found to produce neutral NO$_2$ radicals (Gesi and Takagi 1964). This alters the bonding between the dipole units responsible
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Figure 17. Variation of $\delta$ with temperature and radiation dose in triglycine sulphate.

Figure 18. Variation of $\mu$ with temperature and radiation dose in triglycine sulphate.

for switching and there is an increase in $\alpha$ and $\delta$. The switching process in irradiated crystals is slower and the temperature range for its occurrence is of lesser extent than in unirradiated crystals. The irradiation dose required to produce significant changes in
Figure 19. Variation of $1/t_m$ with $E$ according to (a) $1/t_m = \gamma E \exp(-\alpha/E)$ and (b) $1/t_m = 1/t_{m0} \exp(-\delta/E)$ in sodium nitrite.

Figure 20. Variation of (a) $\delta$, and (b) $\alpha$ with gamma radiation dose in sodium nitrite. $+$ = 7-2 Mrads, 0-70 Mrads, 0-100 Mrads, $-$ = 407 Mrads.

The switching characteristics of $\tau_{OS}$ is 0.1 Mrad while for sodium nitrite it is 100 Mrad. The hydrogen bonds of $\tau_{OS}$ are weaker and require lesser radiation dosage than the largely ionic bonds of sodium nitrite to produce changes in switching behaviour.

4. Electroluminescence during polarization switching

Light emission of electroluminescence has been observed during the polarization reversal process in $\tau_{OS}$ (Montoto and Jaque 1978), BaTiO$_3$ (Bhide and Shringi 1966;
Gonzalo et al (1980), KNbO₃ (Deshpande et al 1977), and Gd₂(MoO₄)₃ (Flerov and Taran 1979).

Simultaneous observation of the light emission and switching current in low fields showed that the light emission starts when the switching current passes through the peak, which shows that the switching current and light emission are out of phase. At higher applied fields, the current and emission are in phase. The light emission occurs when the electric field in the surface layer is a maximum, i.e. when the voltage drop in the surface layer is largest and when current transient is at its peak. The large electric fields in the surface layers could promote electron injection from the electrodes. Accumulation of uncompensated charge, carried by moving domain walls, in the surface layers can also promote charge injection from the electrodes. Thus it has been suggested that electroluminescence during switching arises from recombination phenomena in the surface layers. Experimental evidence for X-irradiated τro (Montoto and Jaque 1981) has been shown to fit in with theoretical calculations and this suggests that light emission originates in the surface layers.

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