



# Switching Current Measurements in $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ Relaxor Ferroelectric Single Crystals

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**Abstract.** Switching current measurements have been carried out on relaxor ferroelectric single crystal-PZN, and the solid solution 0.86PZN-0.04PT and 0.91PZN-0.09PT for crystallographic directions [001] and [111]. The experiments showed the presence of two maximum points in the switching current for 0.86PZN-0.04PT and 0.91PZN-0.09PT that can be attributed to the co-existence of two phases. The switching time inverse shows a two-fold linear dependence on applied field for both [001] and [111]. This suggests that the polarization reversal in the relaxor systems is related to the mobility of the domains. The switching time in relaxor ferroelectric is long (milliseconds) compared to the reported data on normal ferroelectric Barium titanate (microseconds). The switching time is dependent on the composition of the crystal along both [001] and [111]. Along [111], the switching time decreases as the PT component increases in the crystal while along [001], the switching time increases as the PT increases.

**Keywords:** relaxor materials, single crystals, polarization reversal, switching time, switching current

## I. Introduction

Single crystals of  $0.91 \text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 - 0.09 \text{PbTiO}_3$  are known to show very high values of electromechanical coupling factor  $k_{33}$  of 92–95% and piezoelectric constant  $d_{33}$  of 1500 pC/N [1, 2]. In this system, PZN having rhombohedral symmetry is a relaxor ferroelectric material that undergoes a diffuse phase transition around 140°C. Also significant frequency dependence of permittivity implying dielectric relaxation suggests slow domain motion in these materials. On the other hand, lead titanate PT having a tetragonal symmetry is a normal ferroelectric with a sharp phase transition at 490°C. These two compositions form a solid solution with a morphotropic phase boundary (MPB) around 0.91PZN-0.09PT. This MPB composition changes symmetry from rhombohedral at room temperature to tetragonal and finally to cubic with increasing temperature. It has to be mentioned that the very high values of  $k_{33}$  and  $d_{33}$  are obtained when crystals with spontaneous polarization direction  $P_s$  along [111] axis of perovskite are electrically poled along [001] i.e., a totally different direction from  $P_s$ .

The spontaneous polarization direction for tetragonal crystals is [001].

We have carried out transient current studies on these relaxor ferroelectric single crystals in order to clarify the domain reversal mechanism. In this paper, the experimental results of switching current measurements for PZN, PZN-PT single crystals and their dependence on crystal orientation are reported. Their switching behavior is examined in terms of the presently accepted model of domain nucleation and growth.

Measurement of switching current to study the polarization reversal phenomena is well known [3]. In this method, a series of symmetric bipolar voltage pulses, which produce polarization reversal is applied to the crystal, and the transient current is measured across a resistor connected in series with the sample. Information on the polarization reversal process was obtained by the switching current measurements for  $\text{BaTiO}_3$  (BT) [4, 5]. These measurements showed that the total polarization reversal time depends on the applied field. This dependence was explained in terms of nucleation of antiparallel domains, forward and sidewise motion

of the  $180^\circ$  domains under the influence of the electric field [4, 5].

## II. Experimental

All the single crystals PZN and  $(1-x)\text{PZN} - x\text{PT}$  used for the measurements were grown by flux method. The crystal direction [001] and [111] were determined by the Laue back reflection method. The crystals were then cut, polished to form rectangular plates with the desired orientation perpendicular to major faces. The thickness of all the samples varied from 0.25 mm–0.30 mm and the area was  $4 \text{ mm} \times 1.3 \text{ mm}$ . Gold was sputtered as electrodes. The compositions with  $x = 0, 0.04, 0.09$  (all having rhombohedral compositions) were studied in the present experiment.

A function synthesizer (NF Electronics DF-194) in conjunction with an amplifier (KEPCO BOP1000M) was used to apply rectangular pulses of one-second duration to the sample. A resistor was used in series with the sample and voltage across was measured using an oscilloscope (Tektronix-340 A) for determining the switching current. The rise time of the amplifier was 0.2 millisecond. We tried a much quicker rise time using a different amplifier, but this was found to cause crack initiation in many cases. Thus the 0.2 msec rise time was inevitably used. Thus care must be taken while calculating the real switch times.

Representative values corresponding to applied voltage and switching voltage taken across the resistor when a positive pulse is applied to the sample are shown in Fig. 1. The normal displacement voltage transient obtained when the second positive pulse is applied is also shown in the same figure. This displacement current is subtracted to obtain the actual switching current. This figure also shows that the switching current reaches its maximum point after the applied voltage has attained the maximum value.

## III. Estimation of the Switching Time

The sample and the resistor (the larger resistance among the output impedance of the power supply and the externally connected resistance) in series is equivalent to an RC circuit with the basic equation [6] as

$$R \frac{dq}{dt} + \frac{q}{C} = E \quad (1)$$

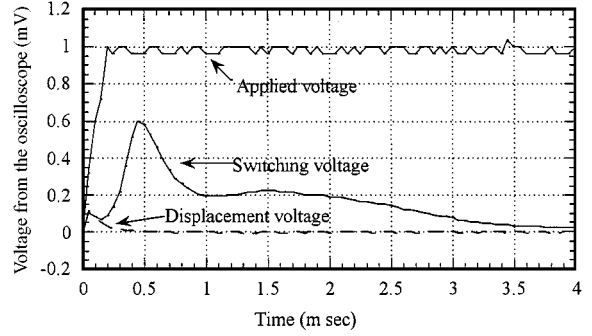


Fig. 1. A representative figure showing the switching voltage, displacement voltage due to capacitor nature of the sample. The applied voltage is also shown in the figure.

where  $q$  is the charge on the capacitor,  $C$  is the capacitance,  $R$  is the resistor, and  $E$  is the applied field. For a pseudo-step applied field

$$E = \frac{E_0}{\tau} t \quad \text{for } 0 < t \leq \tau, \quad (2)$$

$$E = E_0 \quad \text{for } t < T$$

where  $\tau$  is the rise time. We obtain the current

$$I = \frac{CE}{\tau} - \frac{CE}{\tau} e^{-\frac{t}{RC}} \quad \text{for } 0 < t \leq \tau \quad (3)$$

$$I = -\frac{E_0 C}{\tau} (e^{-\frac{t}{RC}} - 1) e^{-\frac{(t-\tau)}{RC}} \quad \text{for } \tau < t \leq T \quad (4)$$

The experimental  $I$  vs  $t$  curve is fitted with the model curve from Eqs. (3) and (4) by varying the parameters.  $R$  and  $C$ . This is shown in Fig. 2. Once the parameters  $R$  and  $C$  are obtained the ideal switching current for the ideal case where the  $E_0$  is instantaneously applied

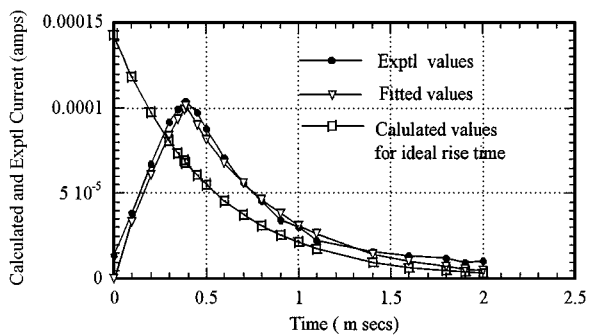


Fig. 2. A representative showing the method of calculation of switching time to take into account the rise time of the amplifier used in the experiment.

is calculated using the Eq. (1). The switching times are then obtained as the time where  $I$  reaches 10% of its initial maximum value. Note that the non-negligible resistance was intentionally introduced in the experiment to avoid breakage of the single crystal of the sample during the measurement.

Ideally, a double RC circuit should be used to calculate the switching time for the double peaks observed. For simplification, a single RC circuit using the first peak has been used to calculate the switching time in the present experiment. Modeling of this double peak behavior using a double RC circuit is a topic that needs to be studied further.

#### IV. Results

The switching time data thus obtained are discussed below.

##### 1. Presence of Double Maximum Current Points in the Switching Current

The crystals used in the experiment are PZN having rhombohedral phase and 0.96PZN-0.04PT and 0.91PZN-0.09PT having mixed rhombohedral and

tetragonal phases. The spontaneous polarization direction for rhombohedral phase is [111] and that for tetragonal phase is [001]. The mixed phase was observed under optical microscope as shown in Fig. 3.

The highlight of the experiment was the observation of the double peak in the crystals having mixed phase—0.96PZN-0.04PT and 0.91PZN-0.09PT. This is shown in Fig. 4. With the field = 6–9 kV/cm along [001], such peaks were observed for 0.91PZN-0.09PT. Initially, the first peak is higher in intensity and reduces, while the second peak increases in intensity. No such double peaks were observed for both PZN and 0.86PZN-0.04PT.

When the field is applied along [111], double maxima were observed for both compositions with 0.04PT and 0.09PT. Here again, the second peak increased in intensity with increasing field. No such peaks were observed for PZN. This implies that the double peaks seen in the switching curve can be attributed to co-existence of both rhombohedral and tetragonal phases. Such co-existence at room temperature, has been observed in these crystals by optical microscopy [7, 8]. It is not conclusive but possible to associate a particular peak with either rhombohedral or tetragonal component with the present data. Taking into account the difference of the coercive field between rhombohedral and tetragonal

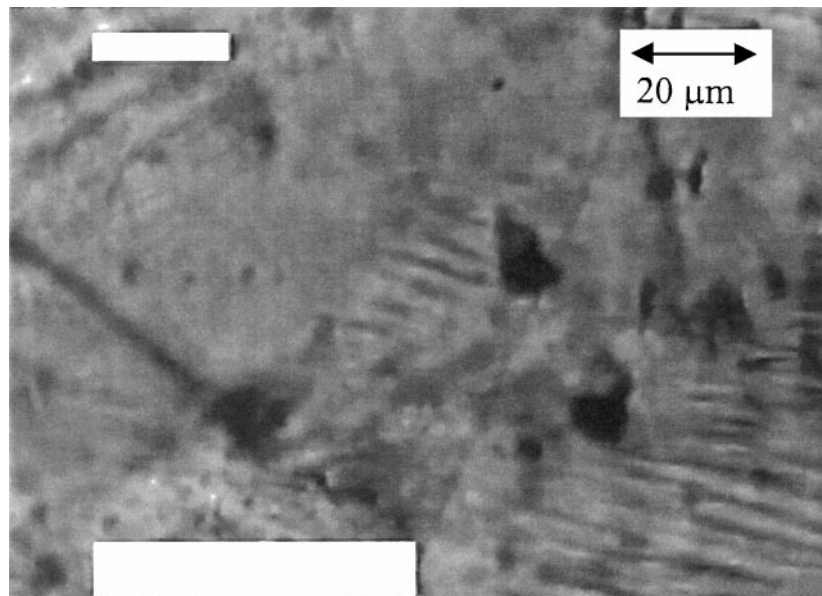


Fig. 3. Co-existence of rhombohedral (needle shaped) and tetragonal domains (stripe shaped) in the crystals near morphotropic phase boundary from optical, microscopy [7, 8].

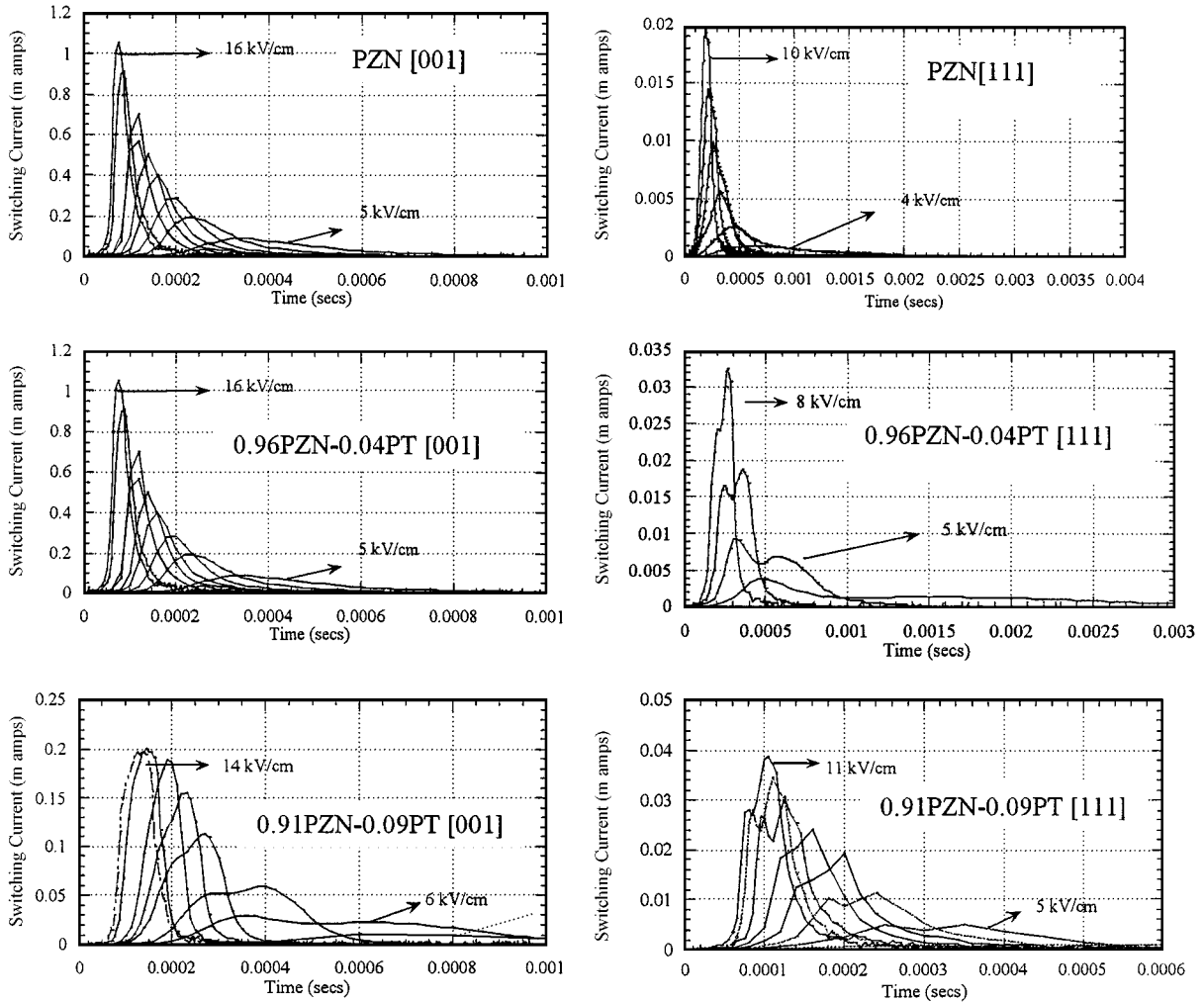


Fig. 4. Switching current showing the presence of double peaks in the crystals having a mixed phase and the absence in the single phase PZN.

phases, the first and second peaks are possibly due to rhombohedral and tetragonal domain changes respectively. The reason for the absence of double peak for 0.04PT along [001] is not clear at this stage but may be dependent on the fraction of PT in the crystal.

2. *Switching Time Dependence on Applied Field*

Figure 5 is a plot of the reciprocal switching time as a function of applied field. When the field is greater than the coercive field along [001], PZN, 0.96PZN-0.04PT and 0.91PZN-0.09PT showed a linear dependence above a certain electric field; 4, 4.5, 5.5 kV/cm

respectively, while for field along [111], a two-folding linear dependence on applied field with the slope changing near 9, 8 and 8 kV/cm for PZN, 0.96PZN-0.04PT and 0.91PZN-0.09PT respectively was obtained. Notice the presence of a plateau in the composition 0.09PT around 7–9 kV/cm that also indicates the mixture of two phases.

3. *Switching Time Dependence on Composition and Crystallographic Direction*

The switching time dependence on composition is shown in Fig. 6 for both [001] and [111] direction. With

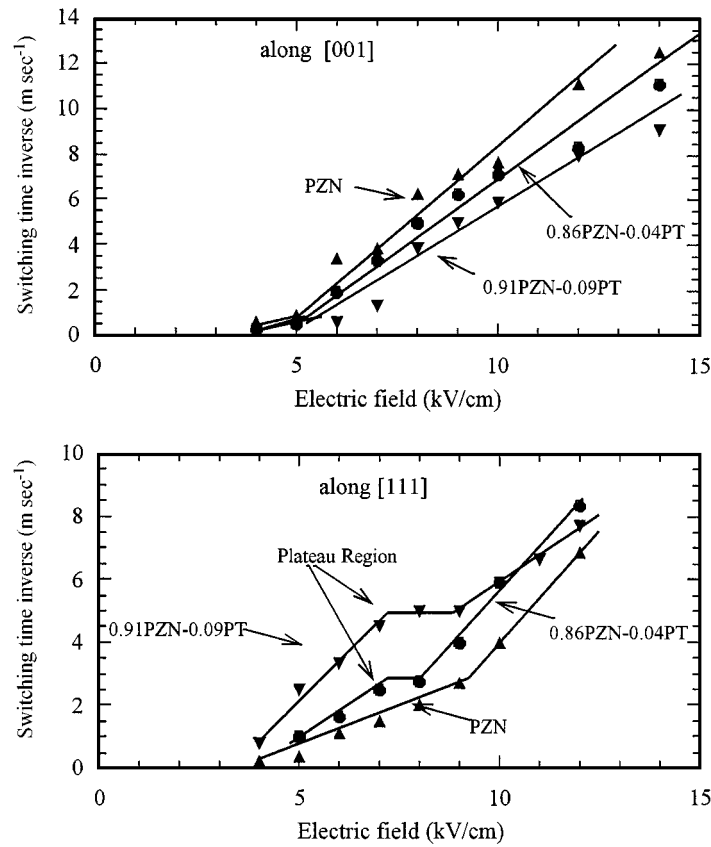


Fig. 5. Dependence of inverse switching time on electric field for both crystallographic directions [001] and [111].

the field along [001], the switching time increases as the PT fraction increases in the crystal. When the field along [111], the switching time tends to reduce as the PT fraction increases. Switching time along [001] is less in comparison to values along [111] for all compositions. This is probably due to large contribution from the tetragonal phase for high field region; the field along [001] reflects  $\sqrt{3}$  larger than along [111] for the tetragonal symmetry.

## V. Discussion

It was established by Merz [4] that in tetragonal phase  $\text{BaTiO}_3$  (BT), the switching time inverse depends linearly on the applied field and is related to mobility of the domains. Switching current measurement on BT in orthorhombic and rhombohedral phase along [001] made by Weider [9] showed a similar linear depen-

dence on the applied field and was again related to the mobility of the domains.

The present data follows a similar trend and it appears that the polarization reversal is related to the mobility of the domains. However, it is noteworthy that the switching time inverse shows a two folding linear curves for both [001] and [111] directions: the lines for lower field along [001] has a very low slope compared to the lines along [111]. The lines for the higher field that may be originating from the tetragonal phase, start at a lower critical field (5  $\text{kV/cm}$ ) along [001] than the field (8.5  $\text{kV/cm}$ ) along [111]. Application of the field along [001] leads to field induced phase transition from rhombohedral and tetragonal phase [8, 10]. Such transition may contribute to the switching current at higher fields. Also it is interesting to note that the ratio of critical field where the slope changes along [111] to that along [001] is  $8.5/5 \approx \sqrt{3}$ . It has to be mentioned that the ratio of polarization along [111] to that of

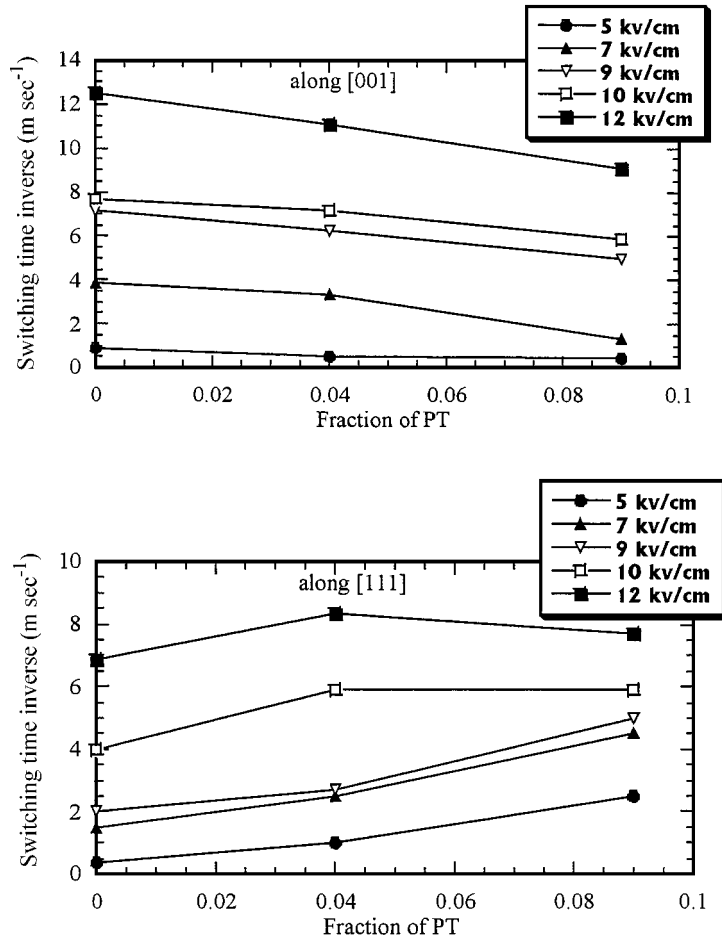


Fig. 6. Effect of fraction of PT on the switching time inverse for various applied fields.

along [001] is  $\sqrt{3}$  and seems to be consistent with the obtained results.

The switching time, however, is long (msecs) when compared to the reported BT data ( $\mu$ secs) [4, 9]. As explained in Section I, these crystals have frequency dependent permittivity suggesting slow motion of the domains. The frequency dependence of permittivity again can explain the long switching time observed as the amount of PZN is increased along [001].

#### Acknowledgment

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