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# The Mechanism of the Reversal of the Spontaneous Polarization in $\text{LiH}_3(\text{SeO}_3)_2$ Single Crystals

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*Abstract.* The reversal of the spontaneous polarization in  $\text{LiH}_3(\text{SeO}_3)_2$  crystals has been studied as a function of applied electric field. Except for very low fields the switching time  $t_s$  follows a power law of the form:  $t_s = kE^{-5/2}$ . Thermal and electrical treatment of the sample showed that up to fields of 50 KV/cm the switching time is controlled primarily by the nucleation of new domains. It thus appears that the  $5/2$  power law is determined by the nucleation rather than by the domain wall motion. The interaction between domains and nuclei in  $\text{LiH}_3(\text{SeO}_3)_2$  was found to be very high. It is proposed that all ferroelectrics with a high spontaneous polarization like  $\text{BaTiO}_3$  and  $\text{LiH}_3(\text{SeO}_3)_2$  tend to show a strong domain-nucleus interaction.

## 1. Introduction

$\text{LiH}_3(\text{SeO}_3)_2$  is a new ferroelectric material described by PEPINSKY and VEDAM<sup>1)</sup>. They report a large spontaneous polarization at room temperature of  $15.0 \mu\text{coul}/\text{cm}^2$  and a 60 cycle coercive field of 1.4 KV/cm. No Curie point can be observed; the material decomposes at around  $100^\circ\text{C}$ . Due to the fact that this material is ferroelectric at room temperature and that the spontaneous polarization is very high it is interesting to study its switching properties.

In ferroelectrics the reversal of the spontaneous electrical polarization occurs through two mechanisms<sup>2)</sup>: first the nucleation of new domains and second the growth of these domains through the sample by domain wall motion. Based on these two mechanisms, a model has been developed by FATUZZO and MERZ<sup>3)</sup> which explains the experimental results in Tri-Glycine Sulfate and also in  $\text{BaTiO}_3$ . This model will now be applied to  $\text{LiH}_3(\text{SeO}_3)_2$ .

In  $\text{BaTiO}_3$  the nucleation was found to be the slower of the two mechanisms<sup>4)</sup> up to fields of 50 KV/cm. and thus it governs the switching time. In Tri-Glycine Sulfate<sup>3)</sup>, on the other hand, the switching was found to be determined by a nucleation process only in the low field region but by domain wall motion in the high field region.

We have investigated and reported about the domain-nucleus interaction in different materials<sup>3)</sup> and found that those materials which have

a high polarization tend to show a high interaction. We therefore expect  $\text{LiH}_3(\text{SeO}_3)_2$  (which has a high spontaneous polarization) to have a strong domain-nucleus interaction.

## 2. Preparation of the Samples

The crystals are grown from aqueous solution by the standard method and large crystals can be obtained. The material has a very pronounced cleavage plane parallel to the ferroelectric direction, so that the cutting and handling of the samples is rather delicate, as they can easily be broken along the cleavage direction. It is therefore very difficult to obtain samples thinner than about 0.1 mm. We have prepared all our samples by cutting the crystals by means of a wet thread, and then by carefully grinding them with abrasive powder and alcohol.

As electrodes we have used silver paste or evaporated gold; no noticeable difference between the two has been found. The electrode area must be kept relatively small, so as not to draw too much current from the pulse generator when high voltages are applied. On the other hand, if the electrodes are too small, a strong Barkhausen noise is observed, which does not permit measurements at very low fields. We have obtained the best result by using crystals with an electrode area of about 1 mm<sup>2</sup>.

## 3. Experimental Results

### 3.1. Switching time

The switching time  $t_s$  of  $\text{LiH}_3(\text{SeO}_3)_2$  depends considerably on the thickness of the sample. For thin samples ( $\sim 0.1$  mm)  $t_s$  is nearly as fast as in Tri-Glycine Sulfate, but for thicker samples it is slower than in that material. In Fig. 1 we have plotted the switching current  $i_s$  versus applied field  $E$ . Except for extremely low fields, where some deviation occurs, both the switching current and the switching time follow a law of the form:

$$i_s = kE^n \qquad t_s = KE^{-n}$$

where  $K = 2.6 \times 10^4$  and  $k = 3.9 \times 10^{-3}$  if  $i_s$  is measured in mA,  $t_s$  in  $\mu\text{sec}$  and  $E$  in KV/cm. Furthermore  $n \cong 5/2$ .

### 3.2. Shape of the Switching Pulse

The switching pulse was studied as a function of applied field. We found no change in the shape of the pulse from low to high applied fields; the pulse is for all fields almost symmetrical. The 'symmetry'<sup>3)</sup> which is defined as the ratio of 'rise time' to 'decay time' of the switching pulse is very close to 1 over the whole range of applied fields. Even for very low fields, where a rather strong Barkhausen noise is observed, the shape of the switching pulse remains the same.

There seems to be some indication of a slight dependence of the symmetry of the pulse on crystal thickness; thin samples give switching pulses with a slight asymmetry.

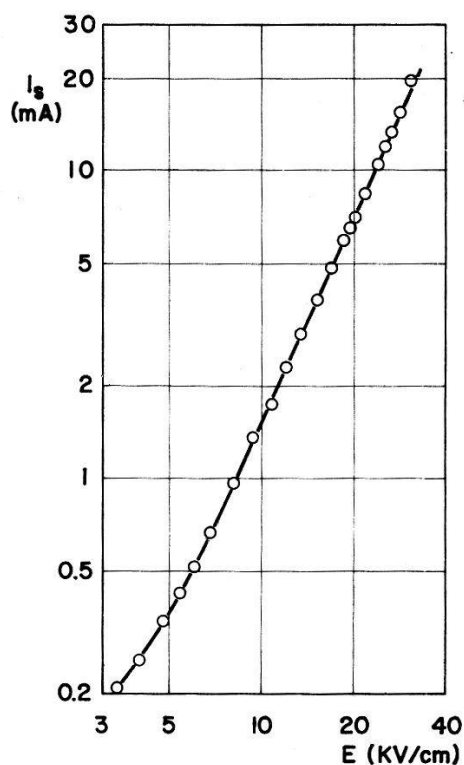


Fig. 1. Switching current versus applied field.  
The electrode area is  $6 \times 10^{-3} \text{ cm}^2$ .

### 3.3. Thermal and Electrical Treatment

We tried to determine whether the switching pulse is controlled by domain wall motion or by nucleation. This was done by using the techniques of surface-heating and switching in parts as described for Tri-Glycine Sulfate in a previous publication<sup>3</sup>). The three following facts indicate that *the nucleation* is the slower process in  $\text{LiH}_3(\text{SeO}_3)_2$  and thus determines primarily the switching time and the shape of the switching pulse.

(a) A small heater is placed in front of one electrode and then removed after a very short time. During the heating period, the switching time  $t_s$  decreases by a factor of 5 to 6 in just a few seconds. Upon removal of the heater,  $t_s$  returns to almost the original value in a few seconds. During the warming and cooling of the surface the pulse keeps its symmetry unchanged.

(b) By applying to the sample 4 or 5 pulses which are shorter than the switching time  $t_s$ , we are able to reverse the polarization in steps whereby the shape of the small individual current pulses fit together and add up

to the complete switching pulse which is obtained when only one long voltage pulse is applied.

(c) By applying pulses having a duration shorter than a certain critical time  $t^*$ , the polarization does not reverse, even if very many of them with the same polarity are applied. In  $\text{LiH}_3(\text{SeO}_3)_2$  the critical time  $t^*$  is much shorter than the switching time  $t_s$ .

#### 4. Discussion

The  $5/2$  power law for the switching time in  $\text{LiH}_3(\text{SeO}_3)_2$  up to very high fields is a very interesting result, as it might be related to the  $3/2$  power law found by G. J. GOLDSMITH<sup>5)</sup> in Thiourea and by H. L. STADLER<sup>6)</sup> in  $\text{BaTiO}_3$  at extremely high fields. In Tri Glycine Sulfate we found<sup>3)</sup> that at low fields  $t_s$  follows an exponential law and at high fields a linear law. It is difficult to see how a  $5/2$  (or  $3/2$ ) power law can fit into the model developed for Tri Glycine Sulfate. However, we first have to know whether nucleation or domain wall motion is the dominating factor.

Since the shape of the switching pulse does not depend on applied field it follows<sup>3)</sup> that only one of the two mechanisms controls the switching time. Furthermore, the three experimental facts described in section 3.3 indicate that the dominating mechanism should be nucleation for the following reasons:

(a) The response of the switching pulse to the heating of the surface is very prompt. In this short time the heating can affect only the surface of the sample hence only the rate of nucleation<sup>3)</sup> and not the wall motion in the interior. This result is different from that obtained on GASH<sup>7)</sup>. There, 5 min are necessary to change the switching time by only 20% by heating of the surface. The switching time is in that case primarily determined by the wall velocity inside the sample.

(b) In  $\text{LiH}_3(\text{SeO}_3)_2$  it is possible to reverse the polarization in steps by applying many short pulses, which is a further confirmation<sup>3)</sup> that in the whole range of fields used the nucleation time is larger than the domain wall motion time, otherwise the growing domains would collapse back every time the field is removed and no switching would be possible.

(c) The fact that the critical time  $t^*$  is much shorter than  $t_s$  is another argument that in  $\text{LiH}_3(\text{SeO}_3)_2$  the switching is governed primarily by the nucleation, because in this case the critical time  $t^*$  is given by the domain wall motion time<sup>3)</sup>.

#### 5. Conclusions

We have shown that in  $\text{LiH}_3(\text{SeO}_3)_2$  over the whole range of fields the nucleation seems to be slower than the domain wall motion and thus controls the switching time. From this follows that the nucleation, and not the domain wall motion is responsible for the  $5/2$  power law of the

switching time. It is a rather remarkable result that the nucleation time does not depend exponentially on the applied field but follows a power law. On the other hand, it appears that the  $3/2$  power law observed by GOLDSMITH<sup>5)</sup> in Thiourea and by STADLER<sup>6)</sup> in  $\text{BaTiO}_3$  might be due to the same mechanism. In Tri Glycine Sulfate too, the nucleation time does not follow the exponential law up to very high fields<sup>3)</sup>.

The interaction between domains and nuclei can be determined from the 'symmetry' of the switching pulse<sup>3)</sup> which in  $\text{LiH}_3(\text{SeO}_3)_2$  is almost 1. Thus the interaction is very strong, almost as strong as in  $\text{BaTiO}_3$ . There seems to be some indication, however, of a slight decrease of the interaction with decreasing thickness of the sample.

Based on the experimental facts, we propose that in every ferroelectric material the field dependence of the switching current and switching time can be described in the following way. There is a low field region I in which the switching time is controlled by the nucleation time and a high field region II in which the switching time is controlled by the domain wall motion time. Furthermore, the 'nucleation region I' itself can consist of two parts, a very low field region IA in which the nucleation time follows the usual exponential law  $t_n = t_0 e^{+\alpha/E}$  and a medium field region IB in which it follows a power law  $t_n = kE^{-n}$ .

Following this proposal, we conclude that in  $\text{BaTiO}_3$  it has not been possible to reach region II in which one would expect to find a linear dependence of  $1/t_d$  on  $E$ . In this material only region IA and IB are observed that is to say an exponential and a power law behavior both of which are controlled by the nucleation of domains; in  $\text{BaTiO}_3$  one never reaches the 'domain wall motion region II'. On the other hand, Tri Glycine Sulfate only shows region IA and II, that is an exponential nucleation region and a linear domain wall motion region; region IB is very small and cannot be detected.  $\text{LiH}_3(\text{SeO}_3)_2$  seems to follow the same pattern like  $\text{BaTiO}_3$  that is it shows an exponential low field region and a power law high field region both of which are governed by nucleation. However, the transition from the exponential to the power law occurs at much lower fields than in  $\text{BaTiO}_3$ .

It is interesting to note that  $\text{LiH}_3(\text{SeO}_3)_2$  is in many respects very similar to  $\text{BaTiO}_3$ ; it shows a high electrical spontaneous polarization, shows a strong domain-nucleus interaction which manifests itself in a symmetrical switching pulse whose shape does not depend on electrical field<sup>3)</sup>, and the switching time versus field curve consists only of regions IA and IB (the linear domain wall motion region cannot be reached).

This then raises the question whether all ferroelectrics with a high spontaneous polarization must show a strong domain-nucleus interaction and a switching behavior which is primarily determined by nucleation up



to very high applied fields. The other extreme, a ferroelectric with a very small spontaneous polarization is represented by Guanidine Aluminum Sulfate Hexahydrate (GASH). This material, as a matter of fact, does show a very weak domain-nucleus interaction and a linear behavior in switching time, which already at rather low fields is governed by the domain wall motion time<sup>7)</sup>. We will report about the results in GASH in a separate paper.

### 6. Acknowledgement

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