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THE NEW ULTRASONIC METHOD OF INVESTIGATION OF NUCLEATION OF DOMAINS AND DOMAIN WALLS MOTION IN FERROELECTRICS AND SOME RESULTS FROM TRIGLYCINE SULPHATE

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A new method of investigation of nucleation of new domains and domain walls motion in ferroelectrics under an external influence (d.c electric field, pressure, irradiation, etc.) is suggested. The basic idea of the method is as follows: Via direct piezoelectic effect the ulrasonic wave generates an a.c. electric signal during its reflection from a surface of a ferroelectric sample. The amplitude of this signal depends on the structure of the domains in the vicinity of the surface. Any change of the domain structure and/or nucleation of new domains in the investigated region leads to a change of the amplitude of the a.c. signal.
The new method is very useful in the determination of the critical electric field strength at which the nucleation of new domains starts. It gives also information on domain walls motion. The main advantage of the method lies in the fact that the received information is given in real time and its application is non-destructive.
The temperature dependence of the critical electric field strength E_c for nucleation of the new domains in triglycine sulphate has been investigated using this method. The results show that $E_C = K(T_c - T)^{1/2}$, where $K = (24 \pm 2.5)$ V cm^{-1}K$^{-1/2}$, $T_C = 49,6°$C is Curie temperature and T is temperature.

1. Introduction

The problem of domains and domain walls motion has been attracting attention for many years.Many different methods have been developed for its study. One of the simplest is direct observation by means of a microscope in polarized light (1). However, this is not possible in some crystals, which have domains of the same linear optical properties. Then one can observe the domains at their intersection with the crystal surface, by etching, powder deposition or scanning electron micrography (2) (3). The observation of the domains is also possible with the second harmonic light, since all ferroelectrics have non-linear optical properties (4). These methods give information on static structure of the domains.

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Great attention has also been paid to dynamic properties like nucleation of new domains (5) the forward growth of the domains through the thickness of the crystal the sideways expansion of the domains (6 - 9) and the coalescence of the domains.

A large number of ferroelectric materials is used in the fabrication of acousto-optic and acousto-electric devices with an application of the surface acoustic waves. The elements of the devices where the surface acoustic wave is applied must be kept in a single domain state in order to achieve a regular function of the elements. A spontaneous creation of the new domains in the region where the surface wave propagates leads to disurbation of the normal performance of the used element. Therefore, the study of the critical conditions for nucleation of the domains and the investigation of the domain walls motion is very important also from the technical point of view.The investigation of a slow change of the domain structure is a complicated problem. It has been solved using the scanning electron micrography mainly (3). A great disa dvantage of the electron micrography lies in the fact that the investigated surface must be chemically etched. It is time consuming and destroys the used element.

One way of studying the domain walls motion utilizes ultrasonic waves. This one is based on the fact that ultrasonic wave propagating in the bulk of the ferroelectric material interacts with the moving domain walls. This is causes a change of its attenuation (10-12).

A new nondestructive and in real time operating method of the investigation of the nucleation of the new domains and the domain walls motion is presented in this paper. The method utilizes the fact that the ultrasonic wave generates a high frequency electric signal during its reflection from the investigated surface. This signal can be detected by electrodes placed in the vicinity of the surface and its amplitude depends on the structure of the domain walls at the surface. The suggested investigation can be performed with simultane ous application of the external influence evoking the change of the domain structure (d.c. electric field, pressure, irradiation, etc.) and it is very suitable for the determination of the critical conditions at which the nucleation of the new domains starts.

Some results obtained when polarization reversal process in triglycine sulphate (TGS) has been studied using this method are presented in this paper too.

2. The Ultrasonic Method of Investigation of the Nucleation of the New Domains and the Domain Walls Motion in Ferroelectrics

Some ultrasonic waves (UW) propagating in piezoelectric materials are accompanied with an electric field. These ones are called "piezoelectrically active modes". The electric strength vector of the field accompanying the piezoelectrically active mode is parallel to the wave vector of the UW. This field cannot be detected by electrodes placed outside of the sample. A different situation is observed when the UW is reflected from an intersection between the piezoelectric and non-piezoelectric materials. The piezoelectrically active and also some piezoelectrically inactive modes generate a high frequency electric field in this case. The electric field strength vector of this field has generally two components:a normal and a tangential with respect to the surface and its

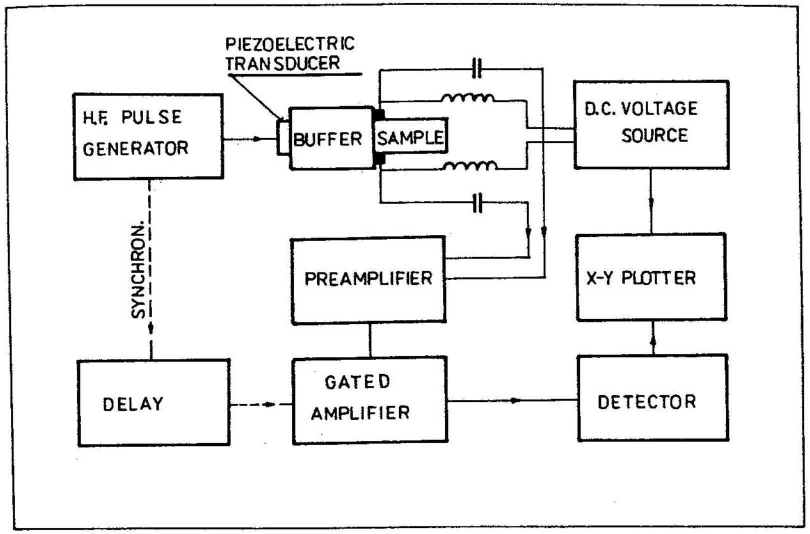

Fig. 1. The block diagram of experimental setup for investigation of the polarization reversal process in TGS by ultrasonic waves.

frequency is the same as the frequency of the UW. This field can be detected by the electrodes placed at the vicinity of the investigated surface.

The direction of the electric field strength vector of the signal generated by the UW at the surface depends on the crystal class of the sample and orientation of the surface (13). Assuming that the electrodes are parallel, their distance is L and the surface is S, the amplitude of the voltage between electrods U_0 is given as

$$U_0 = \{\text{maximum over one periode}\} \int_{(S)} \frac{L}{S} \vec{E} d\vec{S}$$

where $\vec{E}$ is the electric field strength at the surface $d\vec{S}$. If the interface as a homogeneous plane and the incident UW has its wave vector perpendicular to the surface, the electric field strength vectors at different elements $d\vec{S}$ will have the same amplitude and phase, the $U_0 = E_0 L$. When due to any disturbance a change of the amplitude and/or phase of the electric field is evoked even in a small part of the investigated surface a change of the amplitude U_0 is observed.

A change of the amplitude U_0 is always observed when due to any disturbance a change of the amplitude and/or phase of the electric field is evoked even in small part of the surface between the electrodes. This fact is used to investigate the nucleation of new domains and the domain walls motion as follows: A pulse modulated UW is sent towards the investigated surface of the ferroelectric sample. The UW can be either longitudinal or transversal and can be sent to the surface either from the bulk of the sample or from the outside space. Using discussion presented in (13), one can select

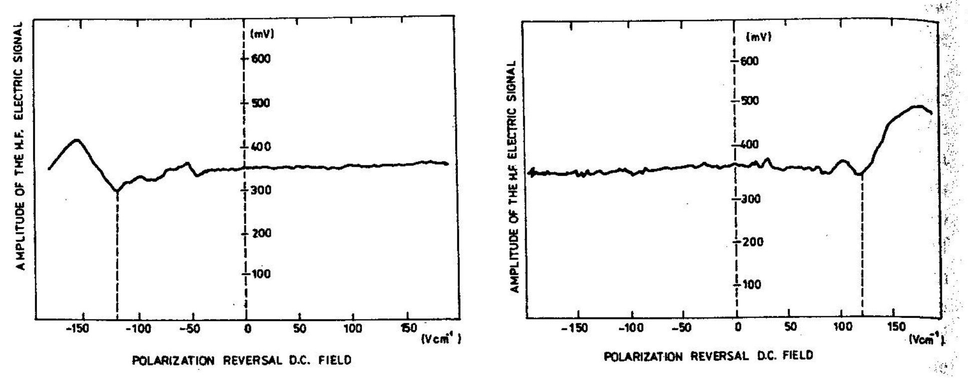

Fig. 2. The amplitude of the high frequency electrical signal generated by the ultrasonic wave at Z - surface of TGS versus d.c. electric field strength at room temperature. (a) d.c. fields runs from +1 to -1 kV/cm (b) d.c. field runs from -1 to -1 kV/cm

such a direction and such a mode of the UW in the investigated crystal that during the excitation of the crystal surface generates the electric field, which strength vector has only a tangentional component with respect to the surface. Then electrodes can be conveniently placed on the surface as two parallel metal strips, which are perpendicular to the electric field strength vector. Any change of piezoelectrical properties evoking a change of the amplitude and/or phase of the electric field at the surface results in a change of the amplitude of the voltage between the electrodes.

If one observe the amplitude of voltage U_0 during the polarization reversal process or during the time when the sample is exposed to an external influence evoking the nucleation of the new domains and the domain walls motion a change of U_0 is registered. This change is the consequence of the fact that the nucleation of the new domains and domain walls motion leads to the change of the crystallographic orientation of the surface and also to the creation of the space charge at the surface and thus to the change of the amplitude and or phase of the electric field.

Thus the suggested method gives the possibility to observe the changes of the domain structure at the investigated surface in real time. Another advatage of the method consists in the fact the it is non-destructive one. Combining this method with ,e.g., optical ones a better understanding of dynamical properties of ferroelectric domains can be achieved.

In the further we present an example of the utilization of the suggested method when polarization reversal process in triglycine sulphate (TGS) was studied.

3. The Study of the Polarization Reversal Process in TGS.

The single crystal of TGS belongs to the monoclinic class 2, with ferroelectric axis oriented along the crystallographic direction Y. The quasi- longitudinal wave propagated

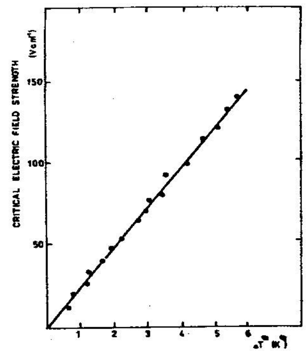

Fig. 3. The temperature dependence of the critical electric field strength in TGS

along the Z direction generates during perpendicular reflection from the Z surface the electric field which strength vector is parallel to the Y axis. A d.c. electric field evoking polarization reversal process is also parallel to Y. It gives the possibility to use the same electrodes for application of the d.c. field and also for the reception of the field generated by the UW.

The block diagram of the experimental set up for the investigation of the polarization reversal process using the UW in TGS is in Fig. 1. The apparatuses work as follows:

The UW pulses are generated by X- cut quartz transducer which is excited by h.f. pulse generator. The UW pulses are propagated through the fused silica buffer towards the Z surface of the TGS sample which is acoustically bonded to the buffer. The electrodes for a simultaneous application of the d.c. field and reception of h.f. electric voltage are placed perpendicularly at the buffer - sample intersection. The h.f. voltage signal has the same frequency as the UW. The signal is amplified and then led to the gated amplifier. The gate of the amplifier is open just during the time when the first UW pulse is reflected from the Z surface of the sample. The output signal is detected and then led to X input of the X - Y plotter, which X input is driven by the d.c. voltage. Thus we can plot the amplitude of the h.f. voltage versus the d.c. voltage during the polarization reversal process directly.

We studied the polarization reversal process using the following procedure: The sample was polarized by the d.c. field + 1 $kVcm^{-1}$ as long as the amplitude of the h.f. voltage signal was stable that means that the sample is in the single domain state.

Then the d.c. field was continuously changed to - 1 kV cm^{-1} during 20 s. The dependence of the amplitude of the h.f. voltage on d.c. voltage during this polarization reversal process at room temperature is in Fig. 2(a). The similar dependence was obtained when the d.c. field runs from - 1 to 1 $kVcm^{-1}$ (Fig 2(b)). Both dependecies show that a rapid domain reversal process in TGS at room temperature starts when the d.c. electric field strength reaches the value $E_c = 120$ Vcm^{-1}. The measured value of E_c remained unchanged also in the case when the speed of polarization reversal field (the change from +1 to -1 $kVcm^{-1}$ and vice versa) was increased from one reversal process during 20s to one reversal process during 2s. The smaller speed of the reversal process was used due to convenient work of X-Y plotter.

Since the value of E_C does not depend on the speed of polarization reversal process it can be considered as a notion that can be unambiguously defined as follows: The critical field strength E_C for nucleation of new domains is the value of E_C at which a rapid nucleation of the new domains stars in originally single domain sample during the polarization reversal process.

The notion of E_c differs from the term of the coercitive field which is not unambiguously defined in ferroelectrics and it is understood as the field at which the average polarization of the bulk ferroelectric sample during polarization reversal process reaches zero. The room temperature value of the coercitive field of TGS reported in (14) is 400 V cm^{-l}, while we measured the critical field $E_c = l20$ Vcm^{-l}. The higher value of coercitive field in comparison to critical field may be due to the fact that the domain walls kinetics at the vicinity of the surface differs from that in the bulk. This, however, according to (15) is less probable. The main reason for this difference is in different definitions. While in our case we measured critical field strength at which the rapid nucleation of new domains starts, the coercitive field value report on the state when due to the motion of the domain walls the average polarization of the sample reaches zero.

4. The Temperature Dependence of the Critical Field at Polarization Reversal Process in TGS.

The procedure discussed in the previous section has been used in the study of the temperature dependence of the critical field strength at which the rapid nucleation of the domains starts in TGS. The measured temperature dependence of E_C in TGS is in Fig. 3.

The temperature dependence of E_C can be, according to the experimental data, estimated by the following empirical formula:

$$E_C = K(T_C - T)^{1/2}$$

where $K = (24 \pm 2.5)$V cm$-$1K$^{-1/2}$, $T_C = 49,6°C$ is Curie temperature and T is the temperature.

It should be mentioned here that the spontaneous polarization of TGS P_S is also linearly proportional to $(T_C - T)^{1/2}$ [16-18]. The same temperature dependence of P_S and E_c lies in the fact that in order - disorder ferrolectrics like TGS a single particle potential has double well form which leads to the creation of an elementary ferroelectric dipole and consequently to a spontaneous polarization. The quantum mechanical tunneling of the elementary ferroelectric dipole through the potencial barrier between the two wells is negligible in order - disorder ferroelectric and therefore the rapid nucleation of the new domains starts when due to d.c. electric field evoking the polarization reversal process the ferrolectric dipole has the energy to jump over the barrier. Thus the temperature dependence of E_C as well as P_S yields implicit information on narrowing and lowering the barrier as a function of $T_C - T$.

5. Conclusions

The suggested method of the investigation of the changes of the domain structure in ferroelectrics using ultrasonic waves has been tested when polarization reversal process in TGS was studied. It has been proved that the method gives the possibility to observe change of the domain structure through the change of the high frequency electric signal generated by ultrasonic wave at the surface of the investigated crystal. We believe that the change of the domain structure will be observed also in the case when it is evoked by pressure, irradiation, or by some other external influence. From this point of view the method gives a new possibility of nondestructive investigation of ferroelectrics.

The method is especially useful in the determination of the critical conditions at which a rapid nucleation of the new domain starts.

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