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FAST POLARIZATION CHANGES IN FERROELECTRICS
AND THEIR APPLICATIONS IN ACCELERATORS

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Abstract

Several mechanisms are described which change the polarization in ferroelectric material. Provided the change is too rapid for the related surface charges to be screened or neutralized, the high charge density can lead to strong electric fields. The fields may possibly be used for emission and acceleration of electrons. First results of experiments are reported, in which fast spontaneous polarization changes by reversal or phase transition have been demonstrated. Electrons of 25 keV energy have been observed, emitted from triglycine sulfate (TGS) crystals during phase transition while being slowly heated across the Curie temperature. With fast polarization changes, electron beams of even higher energy and density are expected.

1. INTRODUCTION

Ferroelectric crystals become spontaneously polarized so that the charge density on their end-faces can reach 10^{14} charges per square centimetre. Normally, these charges are compensated or screened by equal and opposite, external or internal, surface charges. If a practical method could be found that would provoke a polarization change very quickly before charge compensation or screening could occur, thus leaving the surface charges exposed and in place, it would be possible to envisage the prospect of copious electron emission which might surpass that from present-day electron guns. The exposed surface charges are a potential source of accelerating fields.

In this paper, experimental results are reported which demonstrate that a sufficiently rapid change in spontaneous polarization is possible, and that electrons of high energy can be emitted from ferroelectric surfaces during phase transition. So far, it has not been shown clearly that the surface-charge densities of $10^{14}/cm^2$, linked to spontaneous polarization changes, would represent fields approaching the order of GV/m, but we permit ourselves to speculate on some ways of achieving this.

Since the ferroelectric properties of crystals are not generally well known to the accelerator community, we describe the phenomena and the methods of inducing polarization reversal or phase transition either in a slow or prompt fashion, and we discuss also the possibility of triggering electron emission by laser illumination.

2. BASIC FERROELECTRIC PHENOMENA

2.1 Spontaneous polarization and screening processes

Ferroelectric materials exist as single crystals or as ceramics which, when cooled below their Curie temperature T_C, become spontaneously polarized. The high spontaneous polarization $\vec{P}_s$ can be reversed by an external electric field. The process is characterized by a typical hysteresis loop. The spontaneous polarization is different from that induced in a normal dielectric by an applied field, since it is a permanent state of the crystal requiring no external field to sustain it. To polarize a normal dielectric to the same extent would require external fields of the order of GV/m.

At the Curie point a ferroelectric crystal undergoes a phase transition as a result of collective ion sublattice displacement (displacement phase transition) or permanent dipole moment orientation (order-disorder phase transition). At T_C, the spontaneous polarization appears instantly (first-order phase transition) or continuously (second-order phase transition). A typical example of the temperature dependence of $\vec{P}_s$ and ϵ_r (dielectric constant) for a $BaTiO_3$ crystal having first-order phase transition is shown in Fig. 1. Above T_C in the paraelectric phase (P phase), $\vec{P}_s$ is zero. At T_C, $\vec{P}_s$ jumps to $20\,\mu C/cm^2$ and ϵ_r has a maximum of 14,000.

The perfectly aligned electric dipoles in a ferroelectric terminate at the opposite surfaces with unpaired positive and negative bound charges. Provided compensation by opposite charges can be prevented, the associated electric field in such a fully polarized system is given by $\vec{E} = -\vec{P}_s/(\epsilon_r\epsilon_0)$. In the case of $PbTiO_3$, with $|\vec{P}_s| = 0.9\,C/m^2$, we expect an external field of the order of $100/\epsilon_r$ GV/m!

When a d.c. electric field E_{dc} is applied, an uncompensated polydomain structure can be generated, and even single-domain structures are formed. However, the enormous electric field strength due to $\vec{P}_s$ will not build up to the theoretical limit, and it cannot exist permanently. Neighbouring domains can align themselves in opposite directions (180° structure), or can become distributed at 90° or 60° to each other, depending on the symmetry of the ferroelectric crystal structure. Various effects screen the spontaneous polarization and prevent the formation of a macroscopic field, even though they do not cancel the spontaneous polarization of the crystal. Their principal causes are as follows:

i) Electric discharges may occur between the surface areas of neighbouring domains of opposite polarization, and between such a domain and the electrodes. In single-domain structures, flashover between different surfaces can take place.

ii) Ion defects and electrons from the bulk of the crystal will screen $\vec{P}_s$ in a time proportional to the resistivity. These free carriers build up an additional space-charge polarization $\vec{P}_{sp.ch.}$, which plays a very important role in the dynamical behaviour of ferroelectrics. Whilst the free-charge carriers can be mutually neutralized, the bound surface charges due to $\vec{P}_s$ can only be screened.

As a result of these screening effects, a dense distribution of $\vec{P}_{sp.ch.}$ builds up on the faces of the crystal, and at the same time the domains may be realigned. The surface charges screen the outside world from the spontaneous dipole moment of the crystal, and the electric field associated with $\vec{P}_s$ can appear only for a short time and generally with a lower amplitude than the theoretical amplitude.

In spite of the screening effects, the main features of ferroelectrics, i.e. surface-charge densities of as much as $10^{14}/cm^2$ and strong transient electric fast changes of $\vec{P}_s$ or $\vec{P}_{sp.ch.}$, make these substances potentially interesting for the field of particle accelerators. However, these properties can only be made to become visible in a real crystal by choosing well-defined conditions, and by suppressing, as much as possible, the phenomena which work against their appearance. The purpose of this work is to point out possible ways of doing this. The most promising conditions are expected during fast polarization reversal or fast phase transitions across the phase boundary, triggered externally by a fast electric field pulse and/or a fast pressure pulse.

2.2 Phase transitions by an electric field and mechanical pressure

The following phase transitions exist in ferroelectrics having not only paraelectric (P) and ferroelectric (F) phases (as in Fig. 1) but also an antiferroelectric (A) structure: A $\rightleftarrows$ F $\rightleftarrows$ P (Type I) and F $\rightleftarrows$ A $\rightleftarrows$ P (Type II). The phase boundaries are affected by temperature, pressure, and electric field (Fig. 2). In antiferroelectrics, each neighbouring dipole chain is antiparallel-oriented, resulting in a zero macroscopic polarization. Nevertheless the crystal is in a microscopically polarized state.
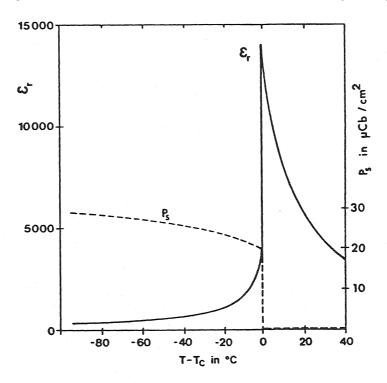

Fig. 1 Temperature dependence of spontaneous polarization $\vec{P}_s$ and dielectric constant ϵ_r near the Curie point T_C, in the case of a first-order phase transition (example: BaTiO$_3$ single crystal).
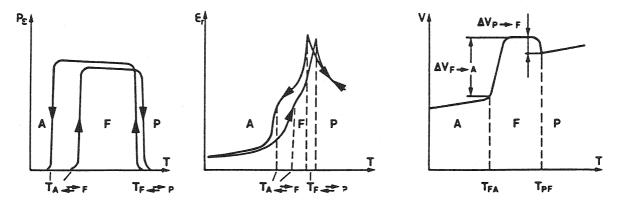
Fig. 2   The temperature dependence of a) spontaneous polarization $\vec{P}_s$, b) electric permittivity ϵ_r, and c) unit cell volume V, for PbZrO₃ and Pb(Zr,Ti)O₃ with A–F–P phase-transition sequences [4, 5].

The PbZrO₃ crystals and solid solutions with Ti content up to 5% (PZT) are of the first type [1] (Fig. 2). The intermediate F phase appears in a narrow temperature region below the Curie temperature ($T_C \equiv T_{FP}$).

An applied electric field increases the temperature for the ferroelectric phase transition F ⇄ P, whereas the temperature for the F ⇄ A phase transition is decreased in the case of the phase sequence A–F–P (Fig. 3a). Electric fields thus increase the phase width of the F state [2, 3].

When mechanical pressure is applied, the result is the opposite, giving rise to a narrower F state (Fig. 3b). We should mention that the F phase in those materials having a A–F–P phase sequence vanishes when the applied pressure exceeds a critical value (p > p$_c$) [1, 3].
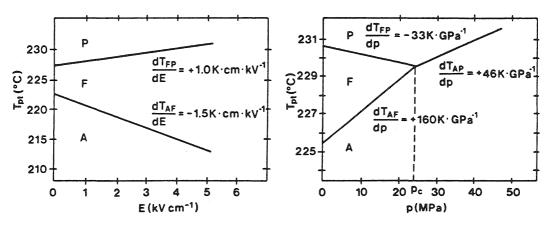

Fig. 3   The dependence of phase-transition temperatures T_{pt} on a) the applied electric field strength [2] and b) hydrostatic pressure for PbZrO₃ [2, 3].

Similar processes take place also in grains of polycrystalline (ceramic) materials. The macroscopic $\vec{P}_s$ appears in such materials when an electric field is applied. Under the influence of the aligning field the resultant polarization of individual domains and grains is oriented according to the crystallographic conditions.

The $\vec{P}_{sp.ch.}$ can be formed by an electric field as well by ion defects and free-electron displacement over macroscopic distances. Most of these defects are concentrated in a thin layer on the grain boundaries. Because of their increased mobility in these places, macroscopic $\vec{P}_{sp.ch.}$ is formed on the surface layers of the ceramic samples. In the case of electroded samples, injected charges also play an important role. The $\vec{P}_{sp.ch.}$ formed under a d.c. electric field at higher temperatures can be frozen by cooling while still under the influence of the field, thus forming a metastable poled state.
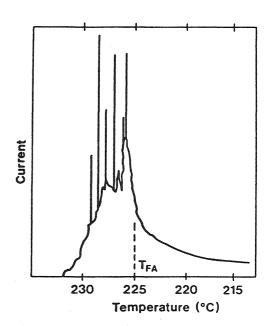
2.3 Diffuse phase transitions

The phase transitions in some macroscopic homogeneous materials are characterized by the fact that the phase-transition temperatures are not sharply defined as in classical ferroelectrics. These so-called diffuse phase transitions (DPTs) are spread over a certain temperature interval, resulting in a gradual change of physical properties in that region.

Local inhomogeneity in material composition and differences in internal electric field and mechanical strain cause the local phase-transition temperatures to differ in individual domains and grains. These internal factors have an influence on phase-transition temperatures which is similar to the influences of the external electric field and the mechanical pressure described above. In individual domains the conditions for these transitions depend on the conditions prevailing in the vicinity of the domains. For the majority of domains, these phase transitions occur near the average phase-transition temperatures, whereas for a remarkable number of microdomains they take place at temperatures that are higher or lower. The macroscopically observed phase transitions are DPTs. Here, the difference in the electrical and chemical properties of the surface layers plays an important role.

As an example, for the $PbZrO_3$ and $Pb(Zr,Ti)O_3$ materials considered by us, the diffuse character of $F \rightleftarrows P$ and $F \rightleftarrows A$ phase transitions has been confirmed, based on X-ray and pyroelectric measurements [4, 5]. An example of temperature change in the pyrocurrent during cooling through $T_{F \rightarrow A}$ is shown in Fig. 4 [5]. A large number of very sharp Barkhausen pulses are visible on the background of the proper pyrocurrent.

Fig. 4

Temperature dependence of pyroelectric current in $PbZrO_3$ during cooling. Strong Barkhausen pulses are observed on top of the normal pyroelectric current [5].

3. FAST POLARIZATION CHANGES

3.1 Electrical procedure

The switching time of the $\vec{P}_s$ vector depends very much on the temperature, on the applied d.c. electric field strength and on a number of other factors [6]. We now consider a prepoled sample having two phase transitions (A $\rightleftarrows$ F $\rightleftarrows$ P). The existence of space-charge layers at the surface of the crystal gives rise to a strong electric field directed perpendicularly to the surface. When we apply an electric field to the crystal in the direction opposite to its polarization, each existing antiparallel domain starts growing immediately by way of the forward and sideways domain-wall motion [7]. A fast change of $\vec{P}_s$ due to HV pulses will result in large surface charges (e.g. 0.1–1 C/m^2) and can be the source of short HV spikes as well as a source of electron emission.

In order to achieve a phase transition electrically, we must work at a temperature very near to the regions of the phase transition A $\rightleftarrows$ F or F $\rightleftarrows$ P, as we are inside the A or P state (Fig. 3a). For a given HV strength, the sample will undergo a phase transition into or out of the F-state, giving rise to the simultaneous appearance or disappearance of $\vec{P}_s$. The crossing of the phase boundaries can be as fast as nanoseconds. However, using a grid or semitransparent electrode, we also expect strongly enhanced electron emission during quick phase transitions, in particular during A $\rightleftarrows$ F. It was previously shown [5] that in the narrow temperature region close to T_{AF}, there also exist compensated F domains in the A matrix. These permit a very rapid macroscopic $\vec{P}_s$ forming and reversing speed, even in the subnanosecond range, because of the very fast sideways motion of existing domain walls without a need for nucleation of new domains. On the contrary, inside the F state the $\vec{P}_s$ change and reversal speed is controlled by the much slower process of the formation of new domains with opposite polarization vectors.

3.2 Pressure procedure

Here we may have two cases: p $\geq$ p$_c$ and p $<$ p$_c$ (Fig. 3b). We again consider the prepoled sample at a temperature inside the F phase. An applied mechanical pulse will give rise to the disappearance of the F state. In such a case a HV spike is expected, as well as electron emission due to the fast P$_s$ disappearance. The well-known electrical-mechanical transformation of a piezoelectric sample can be utilized to form fast and short mechanical pulses. The investigated sample, together with a piezoelectric elongator, forms a type of electrical-mechanical-electrical converter. Such converters allow the pressure to be changed very rapidly [8]. Here we should mention that the piezoelectric response has been reported to exist in at least a submicrosecond time scale [9], which makes this method very promising for fast polarization changes.

3.3 Optical-electrical procedure

The highest surface-charge densities are expected to be produced by the combined fast change of the $\vec{P}_s$ vector and the liberation of space charges by pulsed laser illumination. This photoelectric effect will give rise to electron emission; hence ferroelectrics are potential candidates for replacing conventional photocathode materials. It is of particular interest to reverse the $\vec{P}_s$ vector in such a direction that electrons are generated on the illuminated surface. In addition, this will help to increase the electron emission. However, in order to achieve this, the use of semitransparent electrodes is preferable.

4. EXPERIMENTAL RESULTS

Electron emission by means of slow phase transitions (e.g. F $\rightleftarrows$ P) has been claimed by several authors [10-12]. A triglycine sulfate $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ (TGS) single crystal was slowly heated across the F-P phase boundary over a time of 10 s. In spite of only a second-order phase transition and of the low heating rate (0.2°/s), between β spectrometer, 10^5 and 10^6 electrons per cm^2, with 25 keV energy, have been measured with a β spectrometer (Fig. 5). The emission started in bursts, a few degrees below T_C and stopped completely above it. By taking into account the momentum resolution of the spectrometer, the total number of electrons (15-25) keV emitted from TGS during phase transition is $\sim 10^8-10^9$ per square centimetre. The TGS samples were never raised to the Curie temperature (T_C = 49 °C) after their production, prior to the measurement. They had no electrodes, and the electric field during the experiment was zero.
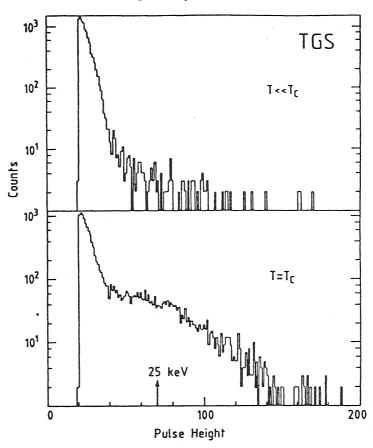

Fig. 5   Pulse-height spectrum of electrons measured with a β spectrometer for two temperatures of a TGS crystal (5 mm $\oslash$ and 3 mm thickness) during heating. Near T_C the measured electron energy was 25 keV(a). The PM background is shown in (b).

Fast phase transitions ($\ll$ 100 ns) have been performed with PZT samples, using polarization reversal and phase transitions initiated by the HV-pulse method. Figure 6 shows the response of a $Pb(Zr_{0.995},Ti_{0.005})O_3$ sample to many successive rectangular pulses of 50 kV/cm amplitude. The sample was cooled down from 256 °C (P phase) to the F phase boundary while being continuously pulsed with positive polarity. Breakdown of voltage (drop in U the lower trace in Fig. 6) across the sample occurred at 238°C as a demonstration of $\vec{P}_s$ formation under electric field (see Fig. 3). The Curie point (under zero field) is T_C = 233°C. When going back to the P phase (> 238°C for 50 kV/cm), the normal rectangular wave form reappeared.
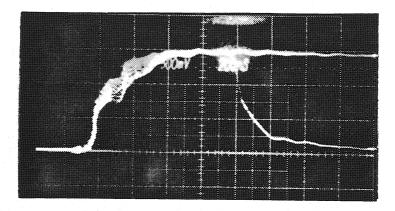
Fig. 6 Variation of the rise of the HV pulse wave-form shape across a PZT (0.5% Ti) sample at 50 kV/cm amplitude during cooling from the P state, 256 °C (upper traces), to the F phase boundary, 238 °C (lower trace with breakdown across the sample's surface). In the P phase the pulse rise-time decreases with rising temperature.

5. APPLICATIONS IN THE FIELD OF ACCELERATORS

At this stage in the infancy of our understanding, the most hopeful application of ferroelectricity seems to be that of an electron-emitting surface capable of releasing some sizeable fraction of the 10^{14} charges per square centimetre. High-density electron emission of 25 keV has been shown with a very slow phase transition without any external electric field. Much denser and more energetic beams can be expected by using the fast phase transition or polarization-reversal methods. Only 10^{10} electrons — provided they can be emitted in a short enough (< 30 ps) burst — would rival present photocathode surfaces for electron guns. Strong emission of electrons at the time of a phase transition is to be expected, and one might hope to control emission by illuminating the surface of a prepoled ferroelectric sample with pulsed laser light. Illumination with laser light ($\lambda < 1$ μm) can cause the liberation of electrons from the space-charge centres. Additional polarization reversal may amplify the electron emission. Our hope is not only to master this process but also to find an environment, parameters, and a geometry for the crystal, so that the large fields perpendicular to the surface layer can be used to give the electrons the initial acceleration they need in order to overcome their own space charge and produce a beam of small emittance.

One may also hope that ferroelectric photoemitting surfaces will not be as sensitive to contamination as the materials used for present-day photocathodes, since they are ceramics and they rely partly on the bulk properties of the materials. Another application which might stem from the laser-triggered or the polarization-reversal modes is to make use of a short burst of electrons to trigger high-power switches.

High electric fields can only be obtained in a ferroelectric when the spontaneous polarization is changed rapidly. In order for to be used in accelerator technology, the high fields must be precisely controlled in time. The electric pulse techniques and pressure methods are the most suitable since they offer fast and precise $\vec{P}_s$-reversal and transitions of the phase boundaries in both directions. In addition, the simultaneous illumination of certain ferroelectrics might well improve the density of surface charges. Devices based on these effects might be used as intense sources of electrons.

Acknowledgements

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