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Research Article

ANOMALOUS PHOTOVOLTAIC EFFECT IN DIELECTRICS

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ABSTRACT

In this work, a study of the anomalous photovoltaic effect (APhN - effect) in crystalline dielectrics was carried out. The nature of the effect is explained according to polarization processes. It is shown that in dielectrics, due to high thermal ionization photoionization energies, impurity complexes of the cluster type are mainly involved in the formation of the effect. Segregation of cluster complexes, apparently, under the action of polarized (coherent) light is activated and stimulates the formation of electrode domain walls. The electrons and holes separated by light will accumulate only in the domain walls, thus creating an elementary voltage (on the order of KT/q) on each domain wall. These elementary stresses are summed up at macro distances and lead to an abnormally high voltage.

Keywords

APhN - effect, polarization, photo, thermal ionization, cluster complexes, segregation, ferroelectrics, Curie point, dielectric constant, unit cell, perovskite, total polarization, dipole, dipole moment, electric domains, domain walls, domain stimulation and domain orientation.

Introduction

The development of technology in recent years is characterized by the widespread use of crystalline dielectrics. Thus, the successful development of quantum radio electronics, piezotechnics, electroacoustics, measuring technology, etc. is now unthinkable without the use of crystalline dielectrics. Only a complete knowledge of all the properties of crystalline dielectrics makes it possible to judge the prospects for its application in technology. The effects of anomalous photomagnetic voltage (APMV) in thin polycrystalline semiconductors have long been known [1-2]. There are a lot of works in this direction, the stages in the development of new physics in the technique and technology of the AFN - effect in thin semiconductor films were the works of E.I. Adirovich, R. Naimanbaev, S. Otazhonov and others [3]. Theories of the effect are developed and the areas of application of the AFN-effect are determined. However, studies of the AFN - effect in dielectrics are still at the initial stage of development. The effect of anomalously high photovoltages has been observed experimentally in a number of dielectrics (ferroelectrics). There are still few works in this area [4-6].

Ferroelectrics are called crystalline substances of the dielectric type, in which, in the absence of an external electric field, spontaneous polarization occurs in a certain range of temperatures and mechanical stresses, the direction of which can be changed by an electric field and, in some cases, mechanical stresses. Ferroelectric crystals are divided into separate regions (domains) that differ in the direction of spontaneous polarization.

Polarization is a multi-valued function of E. The value of P corresponding to saturation is denoted Ps and for a typical ferroelectric BaTiO3 it is 0.26 k/m2 at room temperature. The remanent polarization PR is the polarization that persists when, after saturation, the field E is reduced to zero. To reduce the polarization P to zero, it is necessary to apply a field of the opposite direction; this field is called the coercive force EC. PR and EC values depend not only on the nature of the material, but also on other factors such as impurities, crystallite size and heat treatment (Fig. 1)

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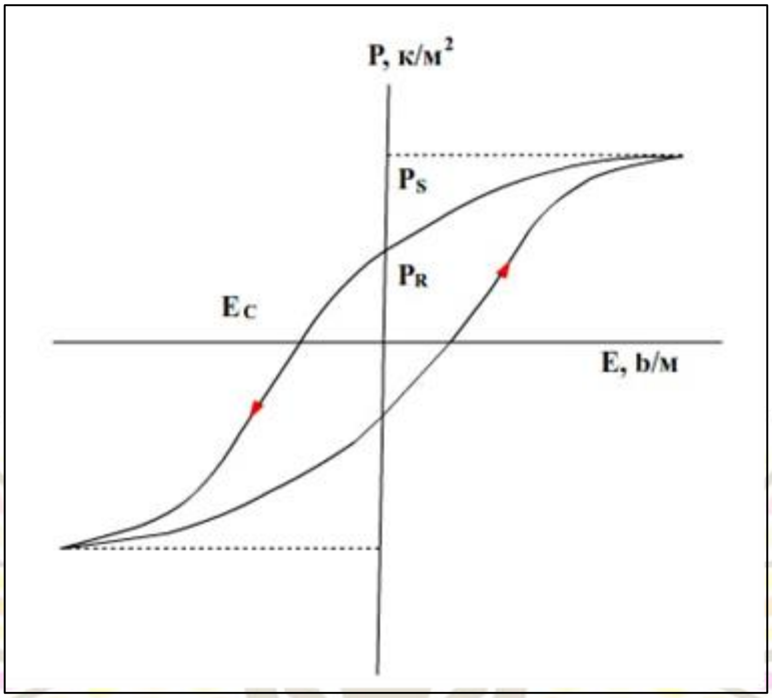

Fig.1. Hysteresis loop of a ferroelectric

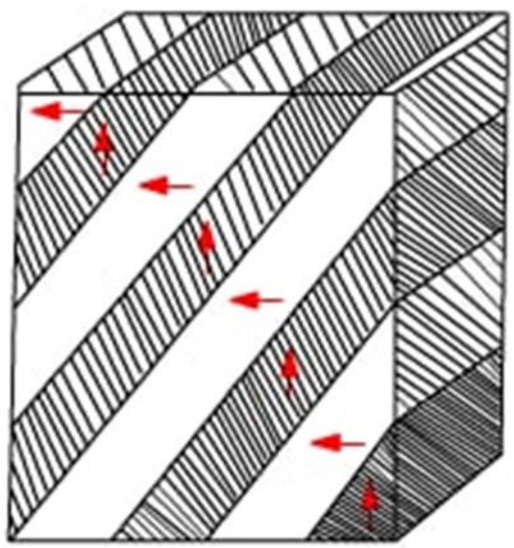
Fig.2. Ferroelectric domains

The general similarity of the hysteresis loops of ferroelectrics with the hysteresis loops of ferromagnets naturally led to the search for ferroelectric domains and they were found in BaTiO3 (Fig. 2). Inside an individual domain, the polarization coincides with the crystallographic

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direction. The total polarization of a massive piece of material is the vector sum of the polarizations of all domains, and the contribution of each domain is proportional to its volume. If an electric field is applied to such a crystal, the following phenomena can be observed:

1) Polarization can vary in magnitude in each domain;
2) Domain polarization can change its direction;
3) The most favorably oriented domains, i.e., those domains whose polarization makes a small angle with the vector E, can grow due to the displacement of the boundaries between the domains. Each of these three processes changes the overall polarization of the entire solid.

The nature of spontaneous polarization has been studied only partially. In reality, the details of the phenomenon may be somewhat different for each of the ferroelectrics. In addition, understanding the nature of the phenomenon is complicated by the fact that various ferroelectric materials have complex crystal structures. However, in one of the substances, BaTiO3, the structure is simple enough to reveal the atomic configuration that leads to spontaneous polarization.

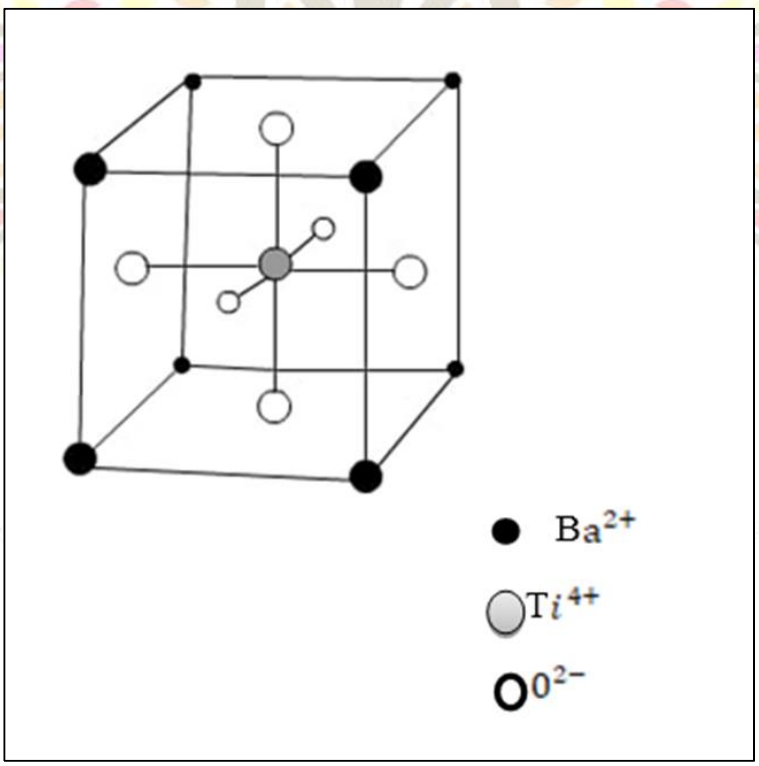

Fig.3. Unit cell of barium titanate

The elementary cubic cell of this material is shown schematically in Fig.3. In this cell (a perovskite-type structure), the Ba ions are located at the corners of the cube, the Ti ion is in the center of the cube, and the O ions are in the centers of the cube faces. The elementary cell of such a structure does not have a dipole moment, since all charges are arranged symmetrically. If, however, the Ti and O ions are displaced relative to the Ba ions, dipoles with a certain configuration are formed. Let us assume that the Ti ion is displaced in the direction of the O ion located on one of the faces of the cube; in this case, the elementary cube acquires a dipole moment in the indicated direction. If such a displacement of Ti ions occurs in all unit cells of the crystal, then the total polarization of the entire solid occurs. From the value of Ps measured for BaTiO3, it can be calculated that a shift of the Ti ion by only 0.1 A would be quite sufficient to obtain the observed effect. Therefore, the considered model is very plausible. The latest research has shown that in BaTiO3 there is, apparently, a displacement of both Ti and O ions, but in each pair of ions these displacements occur in opposite directions.

Spontaneous polarization of ferroelectrics is preserved, not up to their melting points. For every material, it exists at low temperatures up to a certain maximum temperature, called the ferroelectric Curie point. Apparently, the strong motion of atoms at temperatures exceeding the Curie temperature Tc is sufficient to destroy the effect of directed displacement of ions in neighboring unit cells. The relative permittivity of ferroelectrics is of less interest than r of normal dielectrics, since this value changes with the electric field (E). However, if it is defined in this case as well, then using expression (1) it is possible to compare ferroelectrics with normal dielectrics,

$P = \varepsilon_V \cdot x_e \cdot E 1)$, где $\varepsilon_V = \frac{\varepsilon}{\varepsilon_r}$, $P = \varepsilon_V \cdot (\varepsilon_r - 1)E$, $\varepsilon_r - 1 = x_e$ (1)

dielectric susceptibility. In isotropic dielectrics, the D, P, and E vectors have the same directions.

$D = \varepsilon \cdot E, D = \varepsilon_V \cdot E + P, D = \varepsilon_V \cdot \frac{\varepsilon}{\varepsilon_V}, E = \varepsilon_v \cdot \varepsilon_r \cdot E$, $\varepsilon = \varepsilon_v \cdot \varepsilon_r$ (2)

The value of ferroelectrics is usually much greater than that of other solid dielectrics at the same electric field strength. For example, an ordinary dielectric mica has a relative permittivity (independent of E) of the order of 7.

The relative permittivity of the BaTiO3 ferroelectric at room temperature in a field of 106 V/M is on the order of several thousand (from $3 \cdot 10^3$ to $5 \cdot 10^3$).

The polarization of individual atoms and molecules in an electric field can be due to three reasons:

1. An electric field can cause a relative displacement of the positive and negative charge in an atom, inducing a dipole moment on the atom.

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2. Positively and negatively charged ions can also experience a shift under the action of the field, causing ionic polarization.
3. Permanent dipoles (ie, dipoles that exist in the absence of an external field) can be rotated by the field from random directions in the direction of the field, causing polarization to occur due to the orientation of the permanent dipoles.

Sets of spontaneously polarized unit cells form regions called domains. In ferroelectrics within each domain, all unit cells are oriented in the same way, the domains in this case have a macroscopic spontaneous polarization, in neighboring domains of ferroelectrics they make certain angles with each other. When considering possible boundaries between domains in ferroelectrics, one should take into account not only geometric considerations, but also the condition of electrical neutrality of the boundary, which corresponds to the minimum energy of the crystal. This necessitates such an orientation of the dipole in neighboring domains, in which the projection of the polarization vector onto the boundary from the sides of one domain is equal in magnitude and opposite in sign to the projection of the polarization vector of the other (neighboring) domain (the orientation of domains according to the “head” of the dipole of some domains sticks to “ tail” of the dipole of neighboring domains).

It is known that the degree of polarization and the absorption process are interrelated. In the process of polarization of dielectrics, energy is accumulated in the crystal by means of internal and external fields. Exactly this situation occurs during absorption (reflection, transmission of light by a dielectric). In ferroelectrics, the main role in the process of polarization is played by the domain walls of crystals of polycrystalline and single-crystal dielectrics. In this work, we study the APV effect in a metastable, orthorhombic titanite (BaTiO3) single crystal. The single crystal was grown by the Czochralski method [5]. Samples of BaTiO3 single crystals were rectangular parallelepipeds 2x2x1mm3 in size. The faces of the samples were perpendicular to the [001] polar axis, along which the spontaneous polarization was directed. The potential difference between the faces was measured. Measurements were made using an electrometer (Cactus). The resistance of the samples is not less than 10^12 m. Subsequent experiments showed that the generation and recombination of carriers in a titanite sample is primarily affected by shallow energy levels, and that domain walls do not play an important role in the formation of an anomalous photovoltaic effect in a single crystal of the ferroelectric dielectric BaTiO3.

At present, interest in the study of ferroelectrics and hybrid dielectric materials is growing. Using these materials, it is possible to produce highly efficient solar cells, which are widely used in various fields of science and technology [7-10].

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