Anisotropy of emission of exoelectrons in barium titanate in phase-transition regions

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Anisotropic radiation of exoelectrons emitted in the temperature intervals corresponding to the three known ferroelectric phase transitions of barium titanate have been observed in single crystals of this compound.

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In ferroelectric crystals, the vicinity of the Curie point is characterized by an anomalous development of the electronic processes that determine the singularities in the behavior of the photoelectric properties.[1,2] One can expect an abrupt change of the microscopic parameters in the region of the phase transition to exert a substantial influence also on the exoelectronic emission activity of the ferroelectric. The parameters of the emission current are sensitive to the physical surface state of the solid, including development of phase transitions[3–5] whose investigation in surface layers by other methods is difficult. In addition, a study of the electron emission in ferroelectrics is of interest because electrons emitted into a vacuum can conserve the velocity direction acquired by them as they move towards the surface in the spontaneous-induction field.

We investigated single-domain and multidomain single crystals of barium titanate grown by the Remeika method. The electrons were registered with a secondary-electron multiplier VÉU-1A in a vacuum of 10^{-6} Torr. The optical excitation was with a mercury-quartz lamp. The experiments were performed with the temperature varied nearly. The procedure used to measure the emission properties is described in[6].

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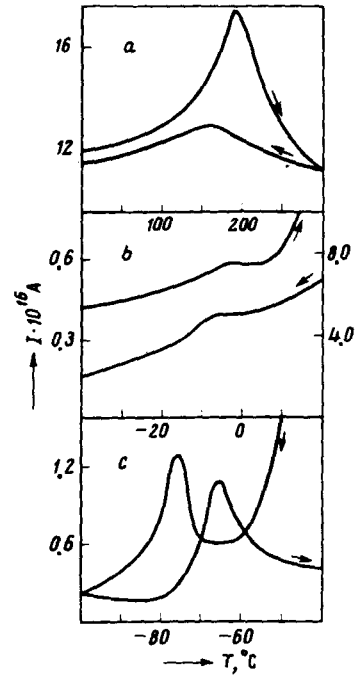

FIG. 1. Temperature dependence of the exoelectronic emission I of a single-domain barium-titanate single crystal (Fig. 1, b—the scale of I with decreasing temperature is shown on the right).

Figure 1 shows the dependence of the exoelectronic emission I of a single-domain crystal for the (001) plane, when the vector $\mathbf{P}_s$ is perpendicular to the sample surface and is directed towards the detector window. The results are presented in three temperature regions (a, b, c) that cover the phase-transition points known for $BaTiO_3$. It is seen that the emission current behaves anomalously in these intervals both with increasing and decreasing temperature. The maxima were registered at $T_1 = 118\,^\circ C$, $T_2 = -5\,^\circ C$, $T_3 = -65\,^\circ C$; when the temperature was increased and at $T'_1 = 112\,^\circ C$, $T'_2 = -8\,^\circ C$, $T'_3 = -75\,^\circ C$ with decreasing temperature, and correspond to the temperatures of the phase transitions in this crystal. The emission-current curves reveal the temperature hysteresis typical of the first-order phase transition that take place in $BaTiO_3$.[7] In the regions between the phase transitions, a smooth change in the exoelectronic emission is observed. However, between the two upper transitions (Fig. 1b) the rate of decrease of the emission current is much larger than in the other temperature intervals.

It is known that a jumplike change takes place in the width of the forbidden band of barium titanate in the course of the phase transitions.[8,9] However, the existence of a cascade of exoelectrons in the vicinity of the transitions, both when the temperature is lowered and when it is raised, excludes the possibility of electron emission for this reason. In semiconductors, electron emission under optical stimulation can proceed via direct and indirect interband transitions. Far from the phase-equilibrium point direct transitions with participation of a photon and an electron are more favored. In the course of the phase transition, the probability of indirect transitions with particip

tion of three particles increases sharply. The role of the third particle can be played by the quasiparticles produced in the phase transition.

When considering the migration of an optically excited electron towards the surface it can be assumed that an electron moving in an internal field of the ferroelectric will have a momentum that coincides in direction with the vector of spontaneous polarization and preserve its acquired velocity direction as it is emitted into vacuum. The detector will register most effectively those electrons which have a velocity direction normal to the surface, i.e., counting of electrons emitted from C domain is more favored. Then the transition of the single-domain ferroelectric into the nonpolar phase should be accompanied by a larger emission current than when a multidomain ferroelectric state is produced from the paraphase, i.e., $I(T_1) > I(T'_1)$, as was in fact observed in experiment (Fig. 1a).

It is known[10] that for $BaTiO_3$ in the region of the tetragonal-rhombic transition the vector $\mathbf{P}_s$ is first rotated through 90° in the (001) plane (a-domainization), after which the vector $\mathbf{P}_s$ changes its direction by 45°. In the second stage the vector rotates in the (001) plane in such a way that there is no positive projection of $\mathbf{P}_s$ nor is there a velocity component of the emitted electrons in the detector direction. It appears that it is precisely to these causes that one can attribute the appreciable decrease of the emission current during cooling in the region of the second transition, and the low value of the emission current at the maxima in this region of the phase transition.

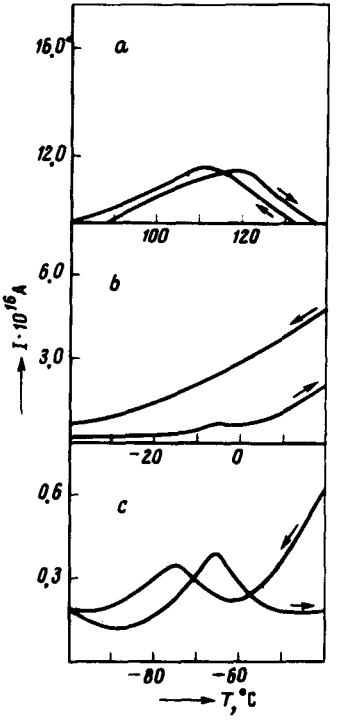

FIG. 2. Temperature dependence of the exoelectronic emission I of a multidomain single crystal of barium titanate.

The hypothesis that the emitted exoelectrons have angular anisotropy is confirmed also by comparison of the emission data for single-domain (Fig. 1) and multidomain (Fig. 2) samples. In the case of the multidomain state, the emission current for all the maxima is much lower; in the region of the high-temperature transition we have $I(T_1) \approx I(T')$; there is no maximum at $T = T'_2$. This is due to the decrease of the *C*-domain concentration for the multidomain crystal.

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