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## Exoelectron Emission and Defects in Ferroelectric Crystals

The attention paid to the exoelectron emission has been traditionally attributed to its sensitivity to structural imperfections in the thin surface layer of the solid. The exoelectron emission kinetic parameters carry information on the energetic stability of defects, whereas exoelectron emission topography makes it possible to obtain their spatial distribution (KORTOV et al.).

The appearance of various types of defects (point, linear, two-dimensional) in solids of whatever nature changes their properties drastically. In exoemission one may distinguish direct and indirect influence of defects. The direct influence of defects on the emission current is observed in linear dielectrics wherein they act as traps for electrons and consequently serve as active centres from which the exoemission takes place (KORTOV et al.; MINTS et al.).

In ferroelectrics the direct influence of defects was revealed during the investigation of the exoemission in TGS. The high-temperature maximum occurring in para-phase in crystals of TGS doped by L- $\alpha$  alanine was due to self-drift of electrons during the decay of electret polarization of space-charge type formed under the action of pyrofield (ROSENMAN et al. 1980). The indirect influence of defects is displayed in the formation of electret charge and field when the defects themselves are not active emission centres. For example, in doped lithium molybdate relaxation polarization takes place wherein the main parts are played by reoriented dipole groups (impurity ion-vacancy). Such defect complexes change the total charge and the field at the surface and can suppress or enhance the field exoemission effect (ROSENMAN et al. 1982).

Structural defects in ferroelectrics, besides influencing the main parameters, common to linear dielectrics, can make a specific contribution, namely: change the spontaneous polarization of a crystal. This additional contribution  $\Delta P$  and the internal bias field  $E_b = \Delta P/\epsilon_0$  connected with it according to LAINS and GLASS are made up of two components, the first of which is due to the change of dipole moment at the site of the defect, whereas the second one is caused by the displacement of the charge in the surrounding lattice as a result of the presence of the defect. The magnitude of field  $E_b$  depends linearly on the defect concentration  $N$ , since  $\Delta P = N\Delta\mu$  ( $\Delta\mu$  is the defect dipole moment) (LAINS, GLASS). The concentration of defects and their spatial distribution depend on the crystal growth conditions, quantity of interstitial and substitutional impurities introduced at the growth stage (TSEDRIK).

The defects and the internal bias field  $E_b$  due to them have a considerable effect on the development of ferroelectric phase transitions and switching processes, change the dielectric constant, conductivity and the pyroelectric coefficient. The phase transition is smeared, the Curie temperature is shifted, the domain structure is fixed, the unipolarity exhibits a growth connected with the fixation of polar moments (LAINS, GLASS).

The transformation of the macroscopical properties of a defective ferroelectric should show up in the change of its exoemission activity. This follows from ROSENMAN et al. 1983, 1984; ROSENMAN, where it is shown that the emission current density, electron energy, determined by the depolarizing field, depend on the domain dynamic properties, pyroelectric activity, conductivity, etc. The dependence of the main emission parameters on these ferroelectric physical properties and their changes upon the introduction of defects are indirect, since the primary parameter is the depolarizing field. It is this indirect link makes it possible, when investigating the kinetic regularities of the exoemission effect, to obtain information of the main physical processes taking place in the crystal and on the influence of structural imperfections.

The present work is devoted to the investigation of the effect of defects in ferroelectric crystals on their exoemission, dielectric and other properties.

The influence of defects of growth and impurity origin has been investigated. Crystals ADTGSP grown in a solution containing deuterium, 10 mol% L- $\alpha$  alanine and orthophosphoric acid have been studied. The following parameters have been varied: 1) the content of  $H_3PO_4$  in the solution has been in three concentrations — 10, 30 and 50 mol%; 2) the growth temperature has been equal to 20, 35 and 55 °C; 3) supersaturation of the solution at two levels:  $(1.3 \pm 0.2) \cdot 10^{-3}$  and  $(0.4 \pm 0.1) \cdot 10^{-3}$  (see Table).

The following have been taken as the main emission parameters:  $I_{em}$  — maximum density of emission current,  $T_1$  — the upper temperature limit of the existence of emission current, as well as additional parameters: the half-width of the maximum  $\Delta T_{1/2}$  characterizing the integral emission effect, the relaxation time  $\tau_r$  determined from the exoemission decay curves at constant temperature.

Let us consider the effect of the growth temperature  $T_g$  on the emission properties of ADTGSP crystals under conditions of constant degree of supersaturation  $\delta$  and level of doping with  $(PO_4)^{-3}$ . In the Figure 1 are shown as an example experimental results of the exoemission of ADTGSP crystals (concentration of  $H_3PO_4$  — 10 mol%). Curves 1 and 2 correspond to growth temperatures 55 and 20 °C, respectively. The remaining data on exoemission and other parameters are listed in the Table. Generally the exoemission current curve  $I_e(T)$  has three sections: growth section, quasistationary section and drooping section. The maximum value  $I_{em}$  for all curves and whatever conditions lies in a narrow temperature range close to  $T_m \sim 313$  K. Measure-

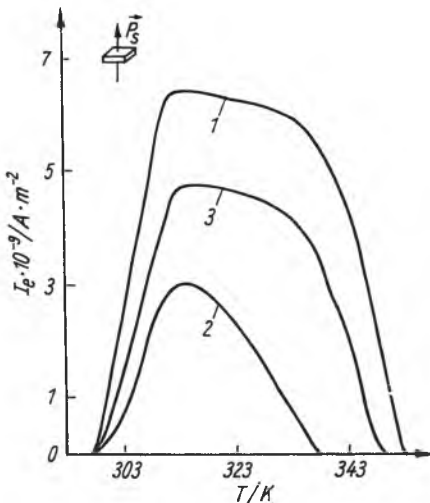


Fig. The effect of growth conditions of ADTGSP single crystals on the exoemission properties

Curve 1. Growth temperature  $T_g = 55$  °C, supersaturation  $\delta = (1.3 \pm 0.2) \cdot 10^{-3}$ ,  $H_3PO_4$  concentration 10 mol%;

Curve 2.  $T_g = 20$  °C,  $\delta = (1.3 \pm 0.2) \cdot 10^{-3}$ ,  $H_3PO_4$  concentration 10 mol%;

Curve 3.  $T_g = 55$  °C,  $\delta = (0.4 \pm 0.1) \cdot 10^{-3}$ ,  $H_3PO_4$  concentration 10 mol%

ments have shown that the Curie temperature, determined from the dependence  $\epsilon(T)$  is considerably higher and lies within 329–331 K. It has turned out that the value of  $T_m$  coincides with the temperature corresponding to the maximum value of the ratio  $\gamma/\epsilon$ .

It is readily seen (see Figure and Table) that the change in  $T_g$  has a considerable effect on the exoemission properties. The lowering of the growth temperature brings about a drop in  $I_{em}$  and  $T_l$ . The second section of the curve determined by  $\Delta T_{1/2}$  is reduced.  $\tau_r$  also decreases. All the investigated crystals have been grown in ferroelectric phase, but  $T_g = 55^\circ\text{C}$  practically coincides with  $T_c$ . By TSEDRIK plentiful data are given on the influence of the growth temperature on the electrophysical TGS parameters: pyroelectric coefficient and dielectric constant, as well as on the domain and defect structure. It is noted that crystals grown in the ferroelectric phase are characterized by an inhomogeneous distribution of defects. They emerge as a result of that in the process of growth there arise growth defects and domains interacting between themselves. According to DEMIDOVICH the mean density of dislocations is within  $10^5 - 10^6 \text{ cm}^{-2}$ . As  $T_g$  grows up to  $T_c$  the density of dislocations drops. In our case for all the crystals the concentration of L- $\alpha$ -alanine impurity, which fixes the domain structure most reliably, is the same. For this reason the crystals grow unipolar. As is known, the degree of fixation of the domain structure determined by the internal bias field depends on mechanical stresses in the crystal. The reduction of dislocation density with the growth of  $T_g$ , revealed by DEMIDOVICH, must diminish the level of internal stresses, thereby helping to form a less rigid domain structure. Indeed, the maximum dielectric constant  $\epsilon_m (T_g = 55^\circ\text{C}) = 2500$ , whereas  $\epsilon_m (T_g = 20^\circ\text{C}) = 720$  (see Table), this indicating a more mobile domain structure in

Table

The effect of growth conditions and the concentration of orthophosphoric acid in the solution on the exoemission, dielectric and pyroelectric properties of ADTGSP single crystals

Growth temperature ( $^\circ\text{C}$ ) $T_g$	super-saturation $\delta$	concentration of $\text{H}_3\text{PO}_4$ in the solution, mol%	$I_{em}$ $10^{-13}$ $\text{A} \cdot \text{cm}^{-2}$	limit temperature $T_l$ , K	relaxation time $\tau_r$ ( $T = 323\text{K}$ )	$(\gamma/\epsilon)_m$ $\text{C} \cdot \text{m}^{-2} \text{K}^{-1}$	$\epsilon_m$
55	$(1.3 \pm 0.2) \cdot 10^{-3}$	10	6.5	352	250	1.43	2500
		30	5.25	349	180	1.34	1900
		50	4.5	344	90	1.22	1650
55	$(0.4 \pm 0.1) \cdot 10^{-3}$	10	4.8	348	180	1.30	3400
		30	4.5	345	120	1.21	2100
		50	3.9	341	60	1.11	1800
35	$(1.3 \pm 0.2) \cdot 10^{-3}$	10	4.2	341	160	1.33	1100
		30	3.75	337	90	1.20	750
		50	3.3	333	40	1.11	570
35	$(0.4 \pm 0.1) \cdot 10^{-3}$	30	3.25	336	50	1.10	1620
20	$(1.3 \pm 0.2) \cdot 10^{-3}$	10	3.0	337	40	1.24	720

crystals with higher  $T_g$ . In accordance with TSEDRIK crystals with a high alanine content, grown at low  $T_g$ , have a lower pyroactivity and a lower value of parameter  $\gamma/\varepsilon$ . A similar regularity is observed also for exoemission. It is characteristic of all alloying levels and growth temperatures (see Table). It is notable that the sensitivity of the exoemission method is higher than that for the measurement of  $\gamma/\varepsilon$ . The relative change in emission current and  $\gamma/\varepsilon$  for supersaturation  $\delta = (1.3 \pm 0.2) \cdot 10^{-3}$  is  $I_{em}(T_g = 55^\circ\text{C})/I_{em}(T_g = 20^\circ\text{C}) = 2.16$ , whereas  $(\gamma/\varepsilon)_m(T_g = 55^\circ\text{C})/(\gamma/\varepsilon)_m(T_g = 20^\circ\text{C}) = 1.15$  (see Table).

The second main emission parameter is temperature  $T_1$ . The increase of  $T_g$ , all other conditions being equal, leads to a considerable displacement of  $T_1$  into the region of high temperatures (see Figure and Table). Analysis has shown that the drawing up of the emission current into the paraelectric region is due to the finite relaxation time of the uncompensated charge and the depolarizing field at the surface. The relaxation process of emission current decrease depends on the dielectric constant  $\varepsilon$  and conductivity  $\sigma$  of the crystal with characteristic time  $\tau_r$  (ROSENMAN et al. 1983, 1984; ROSENMAN), whereas the relaxation time of an uncompensated charge and field depend on the same quantities and is equal to  $\tau_M = \varepsilon\varepsilon_0/\sigma$ . As a result of the tunnel nature of exoemission  $\tau_r < \tau_M$  (ROSENMAN et al. 1983).

Hence, the dependences  $\varepsilon(T_g)$  and  $\sigma(T_g)$  determine the quantities  $\tau_r$  and  $\tau_M$  (see Table and Figure), and, consequently,  $T_1$ . It is shown by TSEDRIK that the raising of the growth temperature increases the domain dynamic properties, this having an effect on the corresponding growth of  $\varepsilon$  (see Table). Moreover, according to these data the conductivity of TGS crystals is also determined by the growth conditions, namely, the minimum value of  $\sigma$  has been registered for  $T_g \sim T_c$ . With a drop in  $T_g$  the conductivity exhibits a rise. Thus, a rise in  $T_g$  must bring about an increase of  $\tau_r$  and, consequently,  $T_1$ . Experimentally determined values of  $\tau_r$  have shown that the exoemission relaxation time increases with the growth of  $T_g$ . Correspondingly, with the growth of  $T_g$  we note a rise in  $T_1$  (see Figure and Table).

Let us examine the effect of the degree of supersaturation  $\delta$ . The quantity  $\delta$  determines in many ways the rate of crystallization presetting the crystal growth defects. A direct determination of the density of growth dislocations in TGS conducted by DEMIDOVICH has shown that an increase of relative supersaturation at all growth temperatures leads to a rise in linear defect concentration. For example, in a pure TGS at  $T_g = 32^\circ\text{C}$  a change in  $\delta$  from  $1.4 \cdot 10^{-3}$  to  $8.0 \cdot 10^{-3}$  caused an almost four-fold increase in the dislocation density from  $3.6 \cdot 10^5$  to  $1.3 \cdot 10^6 \text{ cm}^{-2}$ . The emergence of growth defects, as already has been mentioned, causes the appearance of an elastic stress field in the polar matrix and, because of its piezoelectric properties, induces the appearance of an internal bias field. The action of this field of defect origin is reduced to domain stabilization, suppression of  $\varepsilon$ ,  $\gamma$  and displacement of  $T_c$  into the high-temperature region (TSEDRIK).

These data (see Figure and Table) indicate that the increase in the degree of supersaturation changes the exoemission parameters too. At  $T_g = 55^\circ\text{C}$  a change in  $\delta$  from  $(1.3 \pm 0.2) \cdot 10^{-3}$  to  $(0.4 \pm 0.1) \cdot 10^{-3}$  (see Figure, curves 1 and 3) brings about a 1.33-fold drop in  $I_{em}$ , this corresponding to a decrease of  $\gamma/\varepsilon$ . The exoemission sensitivity noted above is conserved. For these samples  $(\gamma/\varepsilon)_m$  decrease 1.1-fold.

A decrease in the defect concentration reduces the domain structure rigidity. Thus, with  $\delta = (1.3 \pm 0.2) \cdot 10^{-3}$ ,  $T_g = 55^\circ\text{C}$ ,  $\varepsilon = 2500$ . A lowering of  $\delta$  down to  $(0.4 \pm 0.1) \cdot 10^{-3}$  yields  $\varepsilon = 3400$ . As a result, samples grown in a solution with a smaller degree of supersaturation have a lower limit temperature. It should be noted that the difference between the emission parameter  $T_1$  for crystals with equal  $T_g$  and levels of alloying, but different  $\delta$ , is insignificant and lies within 3–4 K.

Let us now consider the effect of doping with substitution impurities, namely the  $(\text{PO}_4)^{-3}$  group. It follows from BHALLA et al. that it replaces the  $(\text{SO}_4)^{-2}$  group. Such doping according to BHALLA et al. increases parameter  $\gamma/\epsilon$  to  $2.0 \cdot 10^{-5} \text{ C} \cdot \text{m}^{-2} \text{ K}^{-1}$ , the pyroelectric coefficient to  $6.5 \cdot 10^{-8} \text{ C} \cdot \text{cm}^{-2} \text{ K}^{-1}$ , lowering the dielectric constant. It should be noted that the ADTGSP crystals investigated in this work have not shown such results, namely: the quality parameter  $\gamma/\epsilon$  attained at best  $1.43 \cdot 10^{-5} \text{ C} \cdot \text{m}^{-2} \text{ K}^{-1}$  (Table). However, the introduction of a ligand into the initial solution for all the growth temperatures and degrees of supersaturation produces a sufficiently strong effect on the dielectric constant,  $\gamma/\epsilon$  and the emission activity. Changing the content of orthophosphoric acid from 10 to 50 mol% produces at  $T_g = 55^\circ \text{C}$  and  $\delta = (1.3 \pm 0.2) \cdot 10^{-3}$  a 1.17-fold drop in  $\gamma/\epsilon$  and a 1.44-fold decrease in exoemission current density. The action of this substitutional impurity is much similar to doping with alanine since the high concentration of  $\text{H}_3\text{PO}_4$  suppresses the dielectric constant, parameter  $\gamma/\epsilon$  and, correspondingly, reduces the exoemission current density. The data listed in the Table make it possible to draw a conclusion that the best properties have crystals grown at  $T_g = 55^\circ \text{C}$ ,  $\delta = (1.3 \pm 0.2) \cdot 10^{-3}$  and with a  $\text{H}_3\text{PO}_4$  concentration of 10 mol%. It is for these crystals one observes the highest values of parameter  $\gamma/\epsilon$  and exoemission activity.

Thus, pyroelectric materials may be arranged according to quality based on the results of measurement of exoemission activity.

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