V. M. Varikash, E. V. Tarasevich, P. A. Pupkevich

Minsk Radiotechnical Institute, USSR

Dielectric, Piezoelectric, Elastic Properties and Internal Friction of TGSe Crystals with Large Unipolarity

In this work we have studied influence of temperature and external electric field on dielectric, elastic, piezoelectric properties and internal friction of D, L-α-alanine doped triglycine selenate crystals. Experimental result analysis allows to conclude that ferroelectric materials with stable physical properties may be created on doping crystals foundation.

В настоящей работе изучено влияние температуры и постоянного смещающего электрического поля на диэлектрические, упругие, пьезоэлектрические свойства и внутреннее трение кристаллов триглицинселената, легированных D, L-α-аланином. Анализ экспериментальных данных позволяет сделать заключение о возможности получения на основе легированных кристаллов сегнетоэлектрических материалов со стабильными физическими свойствами.

1. Introduction

TGSe crystals in paraelectric phase are known to belong to the prismatic class of monoclinic system and don't exhibit piezoelectric properties. After ferroelectric phase transformation without unipolar effects the crystal is devided into domains, so that its macroscopic properties symmetry returns to that in the original paraelectric phase. TGS group crystals with different additives and in particular α-alanine doped crystals (Bye and Keve; Bye, Whipps and Keve; Bye, Whipps, Keve and Josey; Hadni and Thomas; Kamisheva, Godovannaja, Milovidova and Konstantinova; Keve, Bye, Whipps and Annis; Lock; Varikash, Tarasevich, Lagutina) have attracted recently considerable attention. Strongly expressed unipolar state occurs in these crystals. Large enough samples and the crystal itself appear to be polarized, this state being stable and remaining after different external factors influence. The introduction of impurity with different concentration enables to obtain crystals with necessary dielectric permittivity values, elastic and piezoelectric modules and other parameters which create conditions for these crystals' practical application.

To deepen our knowledge of TGS group unipolar crystals physical properties and to give the possibility of their more wider practical application we have studied dielectric, piezoelectric, elastic properties and internal friction of triglycine sulphate, triglycine selenate, triglycine fluorberyllate doped with D, L-α-alanine and L-α-alanine. The results of these investigations for TGSe crystals doped with D, L-α-alanine are given in this paper.

2. Experimental

The crystals used for measurements were grown above T_c by slow cooling from 42 °C to 26 °C from a solution containing 20% D, L-α-alanine. The samples of the crystals in question have shown complex forms of dielectric hysteresis loops biased along E axis due to

its reverse bias field E_b availability. The Curie temperature determined according to the dielectric constant maximum value was 22.0 °C that is a little bit lower than the Curie temperature in non-doped crystals. The samples investigated were Y-cut square rods with 1.5 0.6 20.0 mm³ orientated by their length along Z-axis. Elastic compliance S_{33}^E and piezomodule d_{23} measurements have been performed by resonance technique using compression-extension longitudinal oscillations by means of a set (VARIKASH, ZAREMBOVSKAJA) with an electronic switch added (VARIKASH, LAGUTINA, TARASEVICH, ANDREEV). This switch enabled to determine not only the internal friction value by visual observations of piezoelectric resonator self mechanical oscillation damping but to avoid undesirable sample's warming in the process of measurements.

Elastic constant values S_{33}^E, electromechanical coupling k_{23}, piezomodule d_{23} (where l is the samples length, ϱ — the crystal density) were determined according to measured dielectric constant values ε_{22}, resonance f_r and antiresonance f_a frequencies in formula (1):

$$
\left.
\begin{aligned}
S_{33}^E &= \frac{1}{4l^2 \varrho f_r^2} ; \\[4mm]
k_{23} &= \sqrt{\frac{\dfrac{\pi}{2}\left[1 + \dfrac{f_a - f_r}{f_r}\right] \mathrm{tg}\,\dfrac{\pi(f_a - f_r)}{2f_r}}{1 + \dfrac{\pi}{2}\left[1 + \dfrac{f_a - f_r}{f_r}\right] \mathrm{tg}\,\dfrac{\pi(f_a - f_r)}{2f_r}}} ; \\[4mm]
d_{23} &= \frac{k_{23}}{2}\sqrt{\frac{\varepsilon_{22} \cdot S_{33}^E}{\pi}} .
\end{aligned}
\right\}
\qquad (1)
$$

All the calculations were performed on a computer Minsk-22. Before carrying out measurements the sample was maintained at the temperature of 30 °C for 30 minutes with subsequent slow cooling for 6 — 7 hours up to 14 °C.

3. Results

Figure 1 shows temperature dependence of dielectric constant of TGSe crystals doped with D, L-α-alanine measured with the constant biasing electric field of different values and directions. (Further we'll consider external fields coinciding in direction with the self biasing field to be positive). With the external field being absent, the curve $\varepsilon_{22} = f(T)$ has the flat maximum at $T = 22.0$ °C. The external electric field application to the sample doesn't change the dependence $\varepsilon_{22}(T)$ qualitatively but brings about the ε_{22} maximum value and its corresponding temperature change. Not only the value but the external field direction appear to play the decisive role in these measurements. The largest dielectric constant maximum value is observed with the $|-E_=| = E_b$ field (curve 4, Fig. 1a) when the net electric moment of the sample is zero. We consider E_b to be its maximum value determined by extrapolation the curve $E_b = f(\Delta T)$ to its maximum, this will be discussed in detail later.

The behaviour of the elastic constant S_{33}^E (Fig. 2) of D, L-α-alanine doped crystals was also due to the availability of self biasing field of a considerable value. If the external constant field applied to the sample coincides in its direction with E_b (Fig. 2b) then gradual maxima smoothing on curves $S_{33}(T)_E$ and their displacement to higher temperature range occur. If the external field is reversed in its direction to the E_b self field and is smaller than its absolute value then $S_{33\ max}^E$ rising occurs and its corresponding temperature value is displaced to more lower value range (Fig. 2a). Just as in the case of dielectric constants S_{33}^E rising, $T_{S\ max}$ temperature shift and elastic constant growth velocity increasing are of nonmonotone character.

The behaviour of temperature dependence of piezomodule and logarithmic decrement is of special interest. The external electric field being absent, sharply expressed maximum on the curve $d_{23} = f(T)_E$ was observed and it is interesting to note

that the sample continues to resonate even at the temperatures exceeding by 10 °C the Curie temperature T_c. The external electric field $+E_=$ being applied to the sample, the curvature lowering of both ascending and descending branches of the $d_{23}(T)_E$ curve, the decreasing of d_{23} maximum values and their shift to larger temperatures were observed (Fig. 3b). If the external field is reverse to E_b, then the $d_{23}(T)_E$ curve curvature is increasing and $d_{23\,max}$ rising was observed only at comparatively poor fields (curve 2, Fig. 3a). With the further increase of $|-E_=|$, the maximum piezomodule values sharply decrease. Piezomodule has negative sign if $|-E_=| > E_{b\,max}$ (curves 7, 8, Fig. 3a). The d_{23} piezomodule temperature run when the constant field $E_= = -3.9$ kV · cm^{-1} is applied to the sample (curve 5, Fig. 3a) is of special interest. The behaviour of the $d_{23} = f(T)_E$ curve in the above mentioned field predicted theoretically on the base of the self bias field temperature dependence was proved experimentally. To explain the above mentioned facts it was preliminarly necessary to concretize how the $E_b = f(\varDelta T)$ curve dependence was obtained (Fig. 3b, curve 3). The self bias field values were determined from the expression $E_b = |E_{cr\,1} + E_{cr\,2}|/2$, where $E_{cr\,1'}$ and $E_{cr\,2}$ are external field values at which the sample is in the state of macroscopical polarization equal to zero during the process of observing piezoelectric hysteresis loops when the external field changes according to the scheme $+E_{=max} \to 0 \to$ $\to |-E_=|_{max}$, $|-E_=|_{max} \to 0 \to +E_{=max}$, respectively. For TGSe crystals having the above mentioned percentage of D, L-α-alanine impurity rather poor dependence of E_b was observed, if the temperature differs by more than $3°$ from the phase transformation temperature. By applying the field $|-E_=| \leqq E_b$ to the sample at corresponding temperatures the piezomodule has the positive sign. But at temperature rising the state is achieved when $|-E_=| = E_b$. Under such conditions the sample macroscopical polarization is equal to zero. At further temperature rise the piezoelectric module should change its sign. Having analysed curve 3 (Fig. 3b) we expected that the piezomodule sign change should occur at $|-E_=| = 3.9$ kV · cm^{-1} if $\varDelta T \leqq |-0.4|$ °. Under the above mentioned external field we have got the piezomodule sign change at $\varDelta T = -0.2°$ experimentally. This coincidence in the limit of error is quite satisfactory.

TGSe crystal internal friction near the Curie temperature was exclusively high. So, for pure TGSe crystals the value $\lambda_{33\,max}$ was 5 and 16 times larger than for TGS and TGFBe respectively. The D, L-α-alanine impurity insertion leads to $\lambda_{33\,max}$ decreasing. This impurity insertion brings about the increase of logarithmic decrement in a rather wide temperature range near T_c and the smoother curve $\lambda_{33} = f(T)$. When the external electric field direction coincides with the E_b direction (Fig. 4b), the $\lambda_{33\,max}$ value decrease and the shift of corresponding $\lambda_{33\,max}$ temperatures to larger values was observed. If the external field $|-E_=|$ is reverse to the E_b direction then the run of the $\lambda_{33} = f(T)_E$ curves is considerably complicated depending on the $|-E_=|$ value (Fig. 4a). It should be noted that logarithmic decrement maximum values on curves 3, 4, 5 Fig. 4a were observed at which unflatness of corresponding $d_{23}(T)_E$ curves occurred (Fig. 3a, curves 3, 4, 5).

4. Discussion

So, D, L-α-alanine doped TGSe crystals have rather particular behaviour of dielectric, piezoelectric, elastic and absorption properties. This particular behaviour is associated with the presence of self bias field of considerable value up to 4.2 kv cm. The reasons of self bias field appearence in TGSe crystals with α-alanine impurity insertion have not been investigated up to now but similar question has been considered in some works devoted to α-alanine doped TGS crystals. So, according to the structural model of (KEVE, BYE, WHIPPS and ANNIS) the E_b field formation in doped
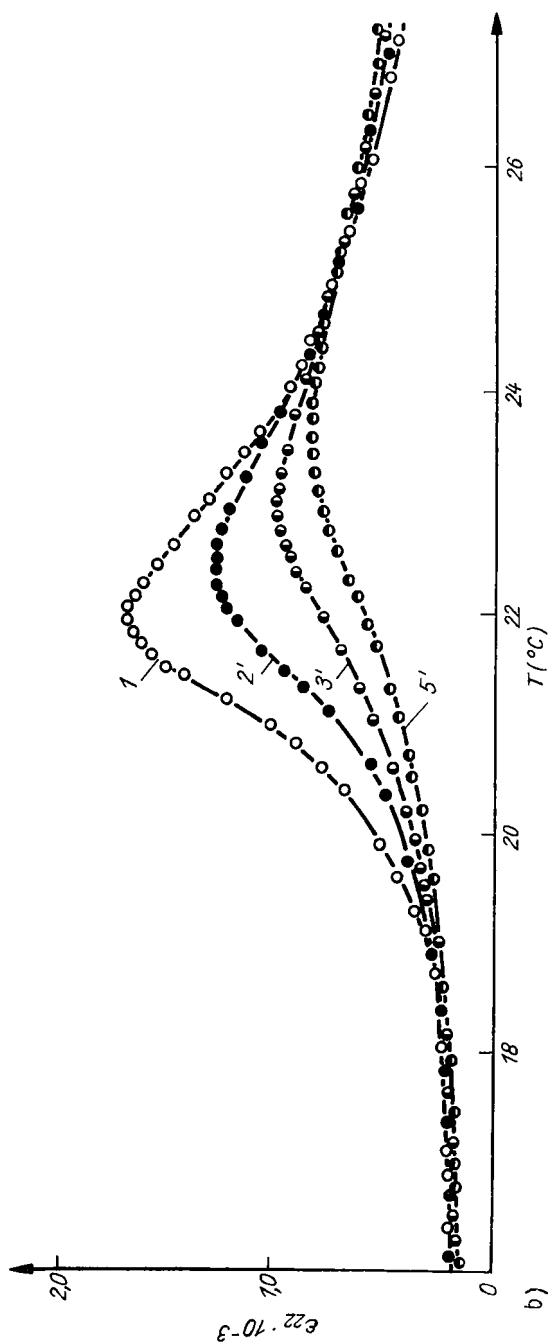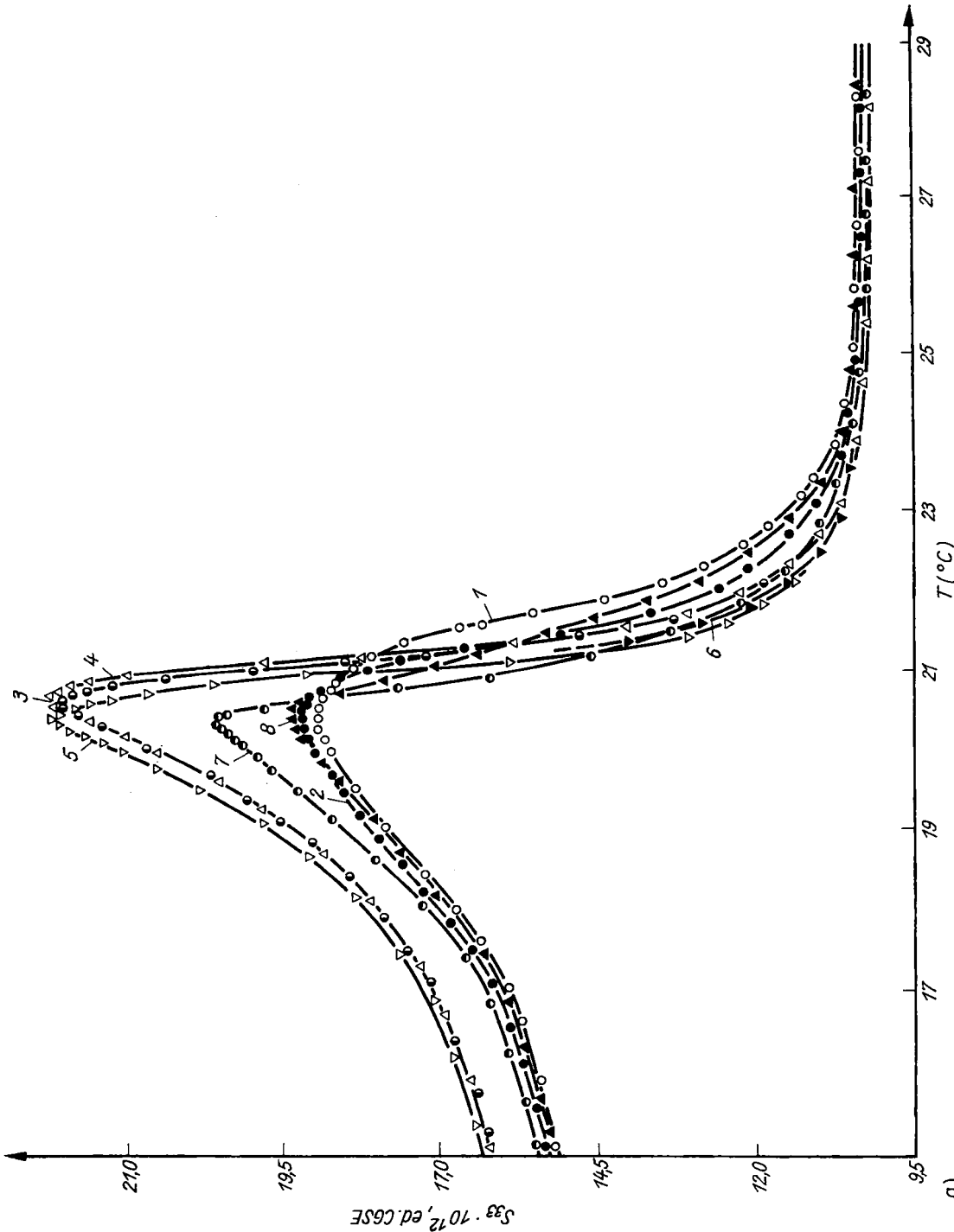
a)
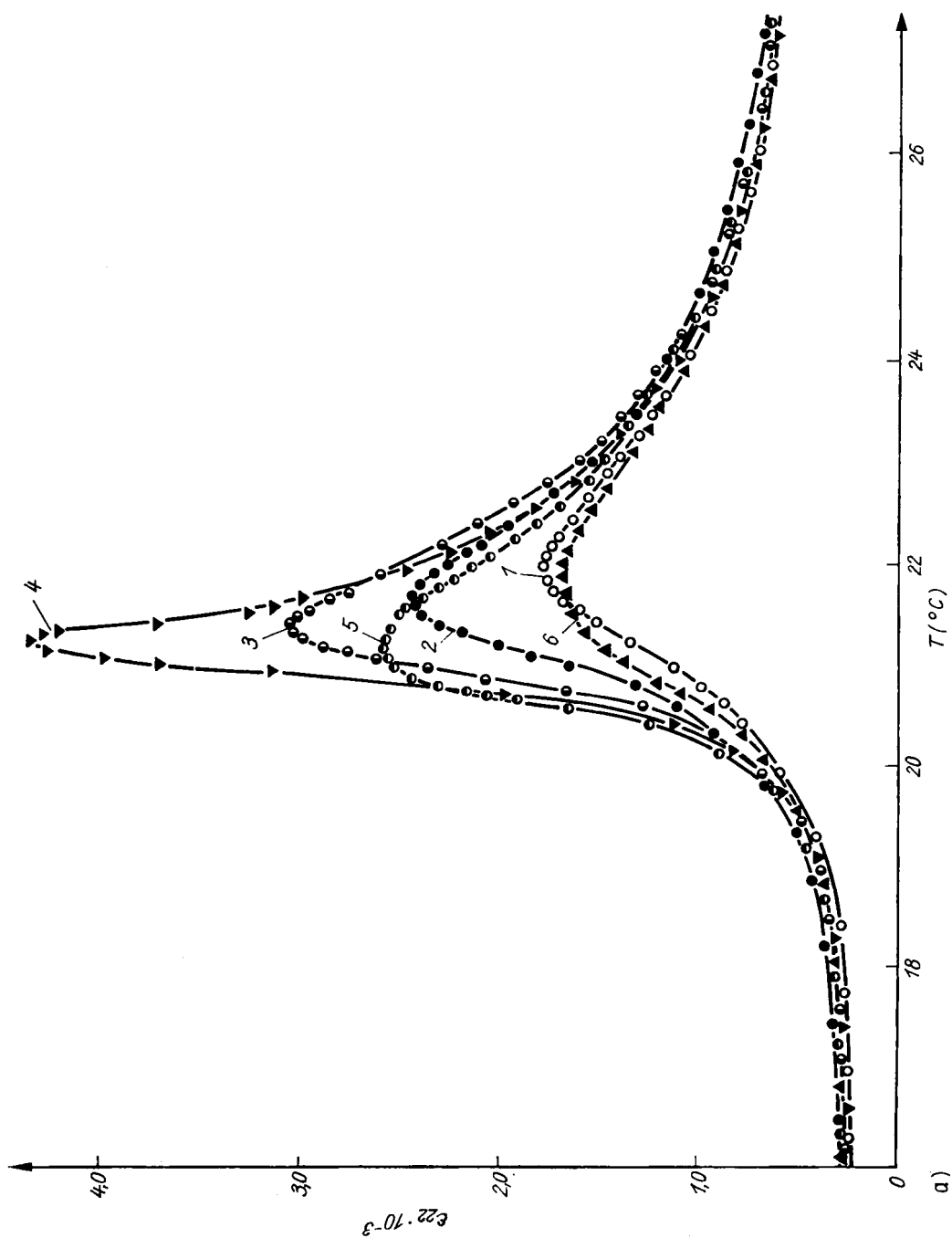
Fig. 1. Dielectric constant ε_{22} temperature dependence under constant electric field of different value and direction. (1) $E_= = 0$; (2), (2') $E_= = 1$ kv/cm; (3), (3') $E_= = 3.4$ kv/cm; (4) $E_= = 4.2$ kv/cm; (5), (5') $E_= = 5.5$ kv/cm; (6) $E_= = 6.9$ kv/cm. a) The external field $E_=$ is reverse to the self bias field E_b (curves 2–6), b) $E_=$ coincides in direction with E_b (curves 2', 3', 5')
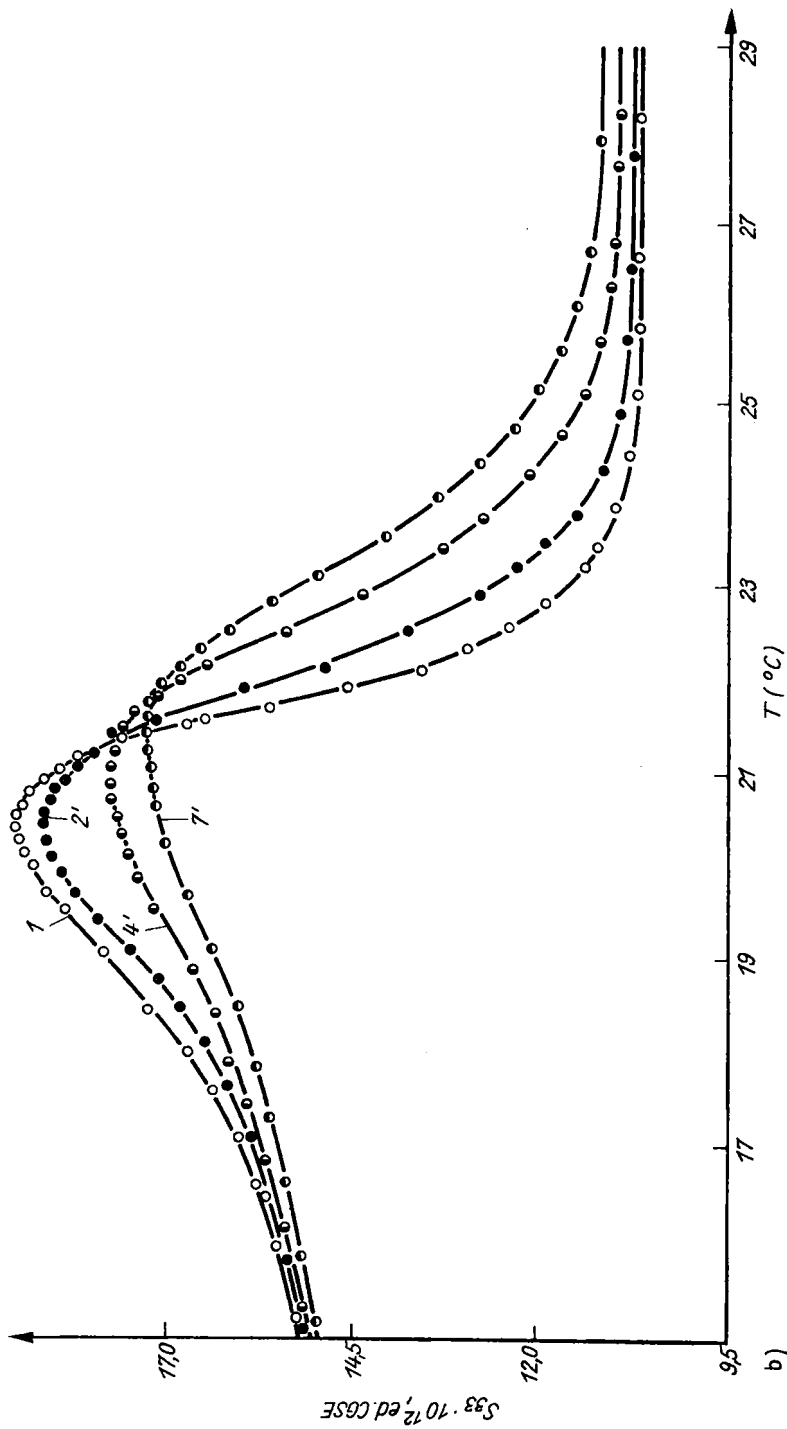
a)

Fig. 2. Elastic constant S_{33}^E temperature dependence under different $E=$. a) $E=$ is reverse to E_b, b) $E=$ coincides in direction with E_b.
(1) $E= = 0$; (2), (2') $E= = 1$ kv/cm; (3) $E= = 2,4$ kv/cm; (4), (4') $E= = 3,4$ kv/cm; (5) $E= = 3,9$ kv/cm; (6) $E= = 4,2$ kv/cm; (7), (7') $E= = 5,5$ kv/cm; (8) $E= = 6,9$ kv/cm
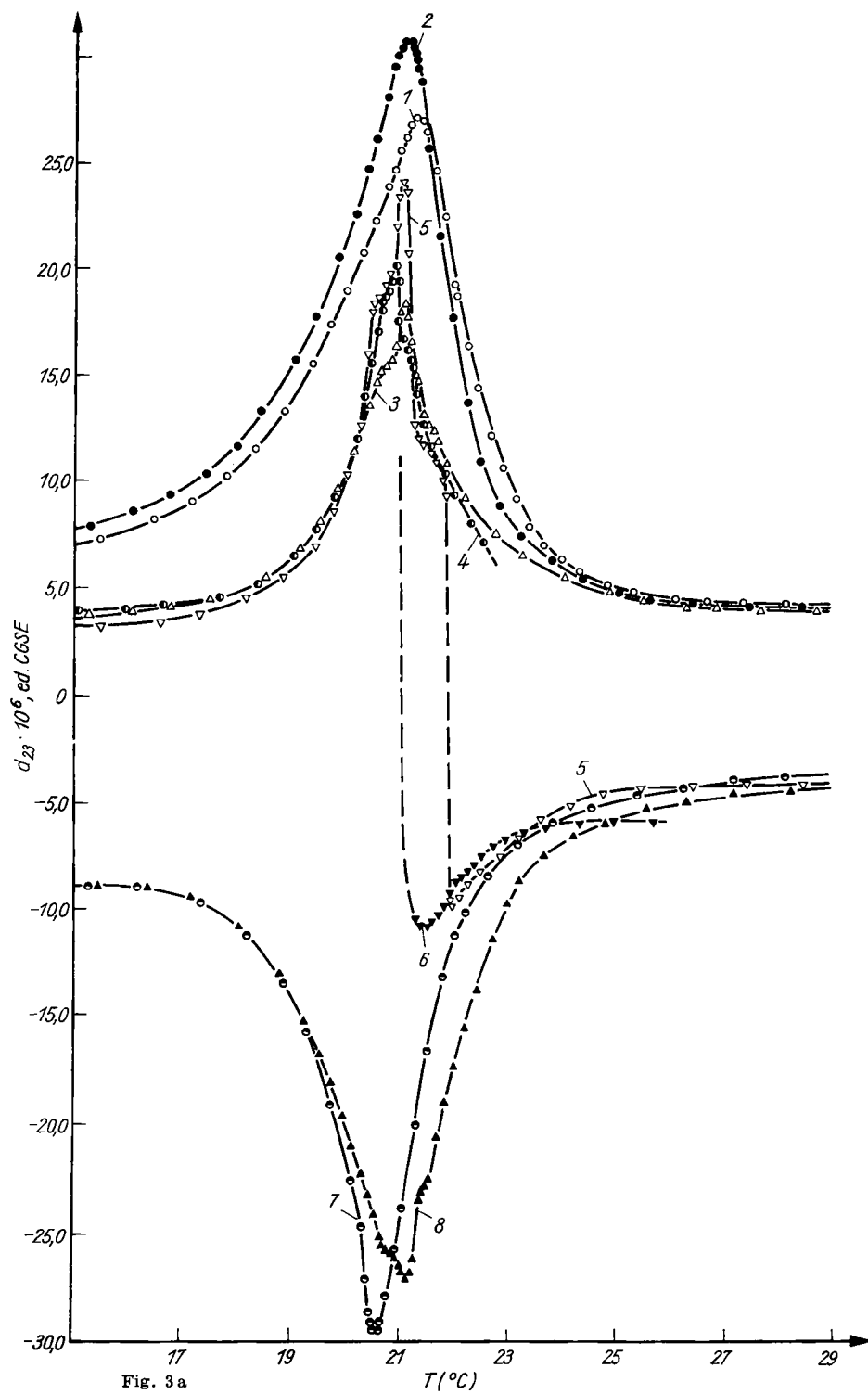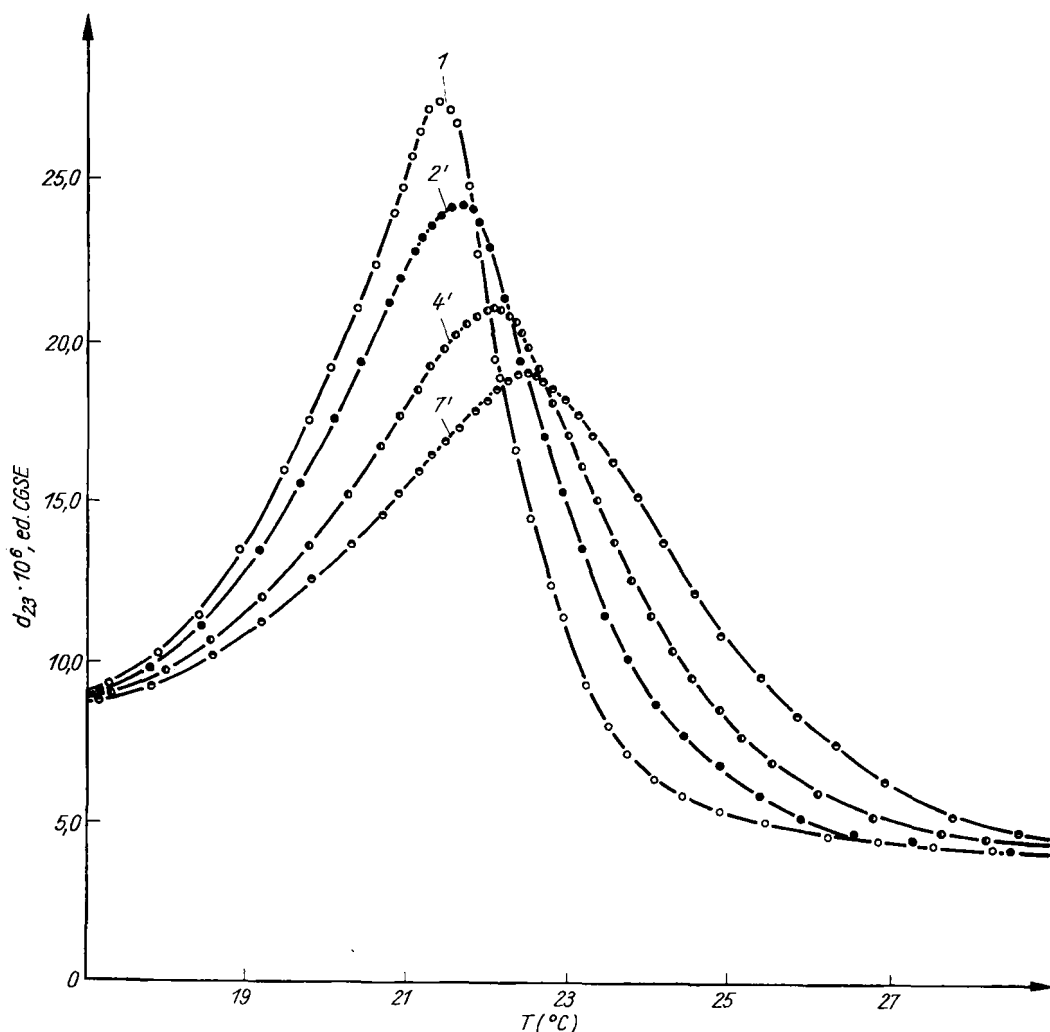
b)

Fig. 3 a

Fig. 3b

TGS crystals is associated with isomorphous substitution of some glycine I molecules by α-alanine molecules. As a result of this substitution a great many of irreversible dipoles occur in the crystal structure and under definite concentrations of these dipoles self bias field associated with local electric field and mechanical strains appears. This mechanism evidently occurs for TGSe crystals but, perhaps, it is not the only mechanism. Some Curie temperature displacement of α-alanine doped TGSe crystals to lower temperatures proves in favour of this assumption. This displacement was observed not only for the crystals described in this paper, but if the initial solution contains 5 and 10% alanine impurity, negligible monotone growth of the Curie temperature shift to lower temperature region being marked with impurity weight content increase.

As seen from the figures, the increase of dielectric constant ε_{22}, elastic constant S_{33}^E, piezomodule d_{23} and logarithmic decrement λ_{33} values occur near the Curie temperature. This curve behaviour for monodomainized samples is goodly explained in terms
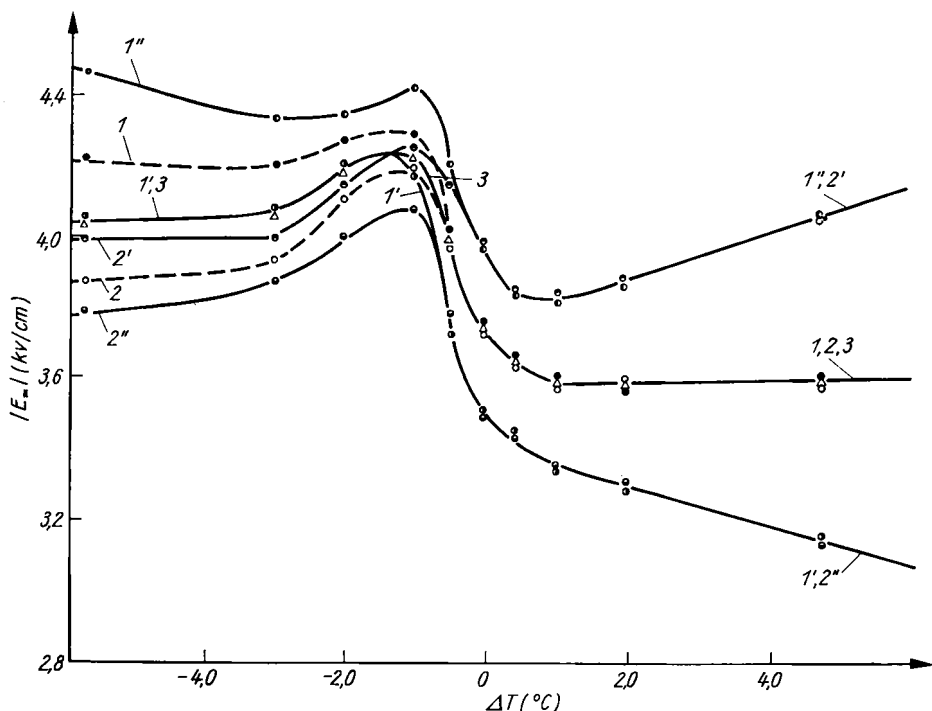
Fig. 3c

Fig. 3. a), b). $d_{23} = f(T)_E$ piezoelectric module dependence. Notation system is the same as in Figure 2. c) E_{cr1}, E_{cr2} and E_b as function of $\Delta T = T - T_c$ (curves 1, 2 and 3 respectively)

of phase transition thermodinamic theory taking into account polarization fluctuations. Moreover, one can expect that despite the availability of the self field of considerable value in the investigated crystals all the same there are domain boundaries and negligible part of domains is oriented in the direction reverse to the self field direction. Domain structure mobility increase with the approach to the Curie point should also contribute to the growth of ε_{22}, S_{33}, d_{23}, λ_{33} values in the corresponding temperature interval. It should be noted that the temperature interval when considerable dependence of investigated values on external factors is observed noticably expands for unipolar crystals as compared with TGSe non-doped poorly unipolar crystals. The same behaviour is also inherent for TGS and TGFBe α-alanine doped crystals.

Under the external field application coinciding with the E_b direction all the curves $\varepsilon_{22}(T)_E$, $S_{33}(T)_E$, $d_{23}(T)_E$, $\lambda_{33}(T)_E$ are smoothed and their maxima are displaced to higher temperature region, the influence of reversely directed external field is of much more complex character. And in both cases the behaviour of investigated crystals has much in common with that of γ-radiated crystals of the same group (SILVESTROVA, YURIN).

When the external field is applied to the sample reversed to the self bias field direction then the increase of both ε_{22} and S_{33}^E maximum values was observed. This increase is quite readily explained if to take into consideration the fact that the sample's monodomainization degree is decreased, domain structure becomes more mobile and its contribution to the dielectric and elastic constant growth is increased at certain temperatures in the cause of internal field compensation. The behaviour of piezo-
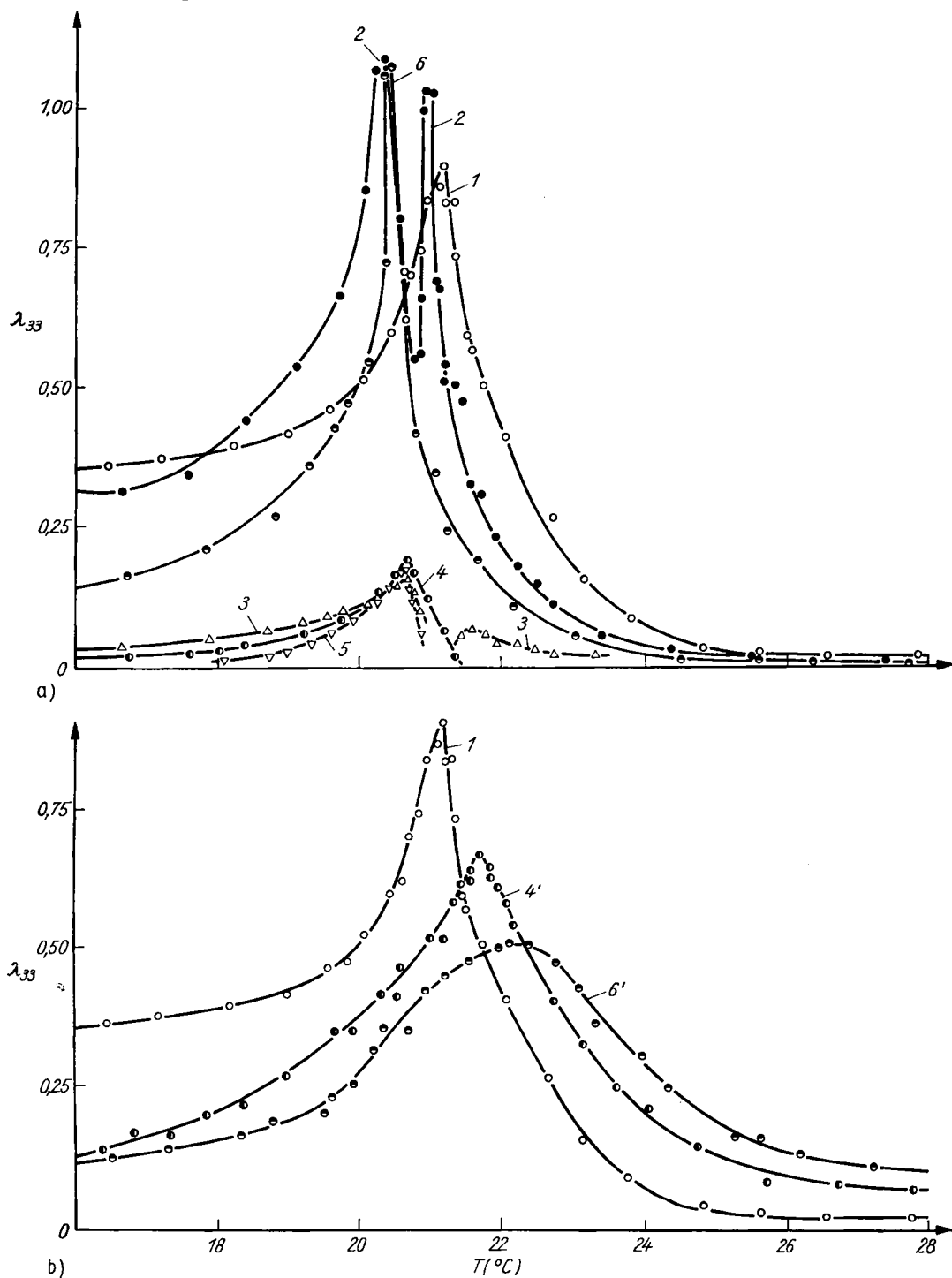
Fig. 4. Logarithmic decrement λ_{33} dependence on temperature. (1) $E_= = 0$; (2) $E_= =$ $= 1.0\,\mathrm{kv/cm}$; (3) $E_= = 2.4\,\mathrm{kv/cm}$; (4), (4') $E_= = 3.4\,\mathrm{kv/cm}$; (5) $E_= = 3.9\,\mathrm{kv/cm}$; (6), (6') $E_= =$ $= 5.5\,\mathrm{kv/cm}$. $E_=$ is reverse (a) and coincides (b) in direction with E_b

electric module and logarithmic decrement at small enough $|-E_=|$ fields has the same character.

The ε_{22} and d_{23} temperature maxima for unipolar crystals don't coincide but this noncoincidence is not so expressed as for elastic constants. Sharp decrease of the d_{23} piezoelectric module maximum values at large enough compensating fields ($|-2.3|$ kV $\cdot$ cm$^{-1} \leqq |-E_=| \leqq E_b$) is due to significant spontaneous polarization decrease as dielectric and elastic maximum value reduction is negligible in the above mentioned fields. Under further external field $|-E_=|$ increase ε_{22}, S_{33}^E, $|d_{23}|$ maximum values were decreased, but their corresponding temperatures were increased. This behaviour of samples is quite natural as under these fields domain mechanism is switched off again step by step.

While investigating the internal friction in the kilocycle frequency range the λ_{33} behaviour pecularities are usually associated with the domain structure mobility change and also with contribution change of other relaxation losses (mechanical and dielectric). Such an explanation of the internal friction behaviour can be given in our case too but the complex character of some curves (curves 2, 3 Fig. 4a) requires more detailed discussion. One can suggest that investigated α-alanine doped TGSe crystals under certain conditions (some temperature interval and a restricted range of $-E_=$ fields) are characterized by complex domain structure, including domains with different activated energy.

Complex character of the λ_{33} and d_{23} temperature dependence at some $-E_=$ values, nonmonotone velocity of all the investigated parameters and the complex shift character of these values along the temperature scale in the cause of the $|-E_=|$ growth, are not the only proofs of this suggestion. As a proof of this suggestion we can also utilize the results obtained in the study of the constant external electric field influence on discussed crystal properties at fixed temperatures, in particular, the piezoelectric hysteresis triple unipolar loops characteristic for this crystal. Domain structure peculiarities of α-alanine doped TGS crystals and the nature of self bias field in these crystals will be discussed in further publications in more details.

References

Bye, K. L., Keve, E. F.: Ferroelectrics 4, 87 (1972)
Bye, K. L., Whipps, P. W., Keve, E. F.: Ferroelectrics 4, 253 (1972)
Bye, K. L., Whipps, P. W., Keve, E. F., Josey, M. R.: Ferroelectrics 7, 179 (1974)
Hadni, A., Thomas, R.: Appl. Physics 10, No 1, 1976
Kamisheva, L. N., Godovannaja, O. A., Milovidova, C. D., Konstantinova, V. P.: Izv. Akad. Nauk SSSR, Ser. fiz. 39, No 11 (1975)
Keve, E. F., Bye, K. L., Whipps, P. W., Annis, A. D.: Ferroelectrics 3, 39 (1971)
Lock, P. J.: Appl. Phys. Letters 19, No 10 (1971)
Silvestrova, I. M., Yurin, V. A.: Fiz. Tverd. Tela, 4, No 9 (1962)
Varikash, V. M., Lagutina, J. P., Tarasevich, E. V., Andreev, E. F.: Structure and Properties of Ferroelectrics, Minsk 1975, p. 43—56
Varikash, V. M., Tarasevich, E. V., Lagutina, J. P.: Structure and Properties of Ferroelectrics, Minsk 1976, p. 15—33
Varikash, V. M., Zarembovskaja, T. A.: Kristall und Technik 9, No 6 (1974)

Authors' address:
Dr. V. M. Varikash, E. V. Tarasevich, P. A. Pupkevich
Radiotechnikal Institute Minsk
Minsk — UdSSR 220069
Podlesnaja, 6