DEPENDENCE OF THE DOMAIN STRUCTURE OF TRIGLYCINE SULPHATE (TGS) CRYSTALS ON TEMPERATURE AND APPLIED ELECTRIC FIELD STRENGTH

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(Received January 30, 1971)

Results are presented on the effect of temperature and electric field strength on the domain structure of TGS crystals, pure and doped with Cu^{++} or Cr^{+++}. Frittering of the structure occurs already below the Curie temperature. The admixtures tend to stabilize the domain structure, as shown by the rise in polarizing field E_p' with increasing admixture concentration. Attention is drawn to differences between rejuvenation carried out thermally and in an AC electric field.

1. Introduction.

Domain structure in TGS crystals can be studied i. a. by the method of charged powders [1–3], etching [1, 4–9] and X-ray diffraction [10, 11]. Petroff [10], and Meleshina [12], studied the effect of an electric field on the nucleation and mobility of domain walls in TGS crystals.

This paper gives results on the effect of temperature and an external electric field on the domain structure of TGS crystals, both pure and containing admixtures of copper Cu^{++} and chromium Cr^{+++}, grown above and below the Curie point.

2. Experimental

1. Temperature dependence of domain structure

A TGS crystal plate 5 mm thick, obtained by cleavage perpendicularly to the ferroelectric b-axis, was maintained consecutively at temperatures 20, 35, 40, 45 and 48°C. After 5 hrs at each of these temperatures, the plate was etched in a 10% aqueous solution of NH_4OH. Observation in all cases concerned the same micro-region of the same plate.

Fig. 1 shows the domain structure of an aged TGS specimen (one that had never been at a temperature exceeding the Curie point) in function of the temperature. At 20°C, the

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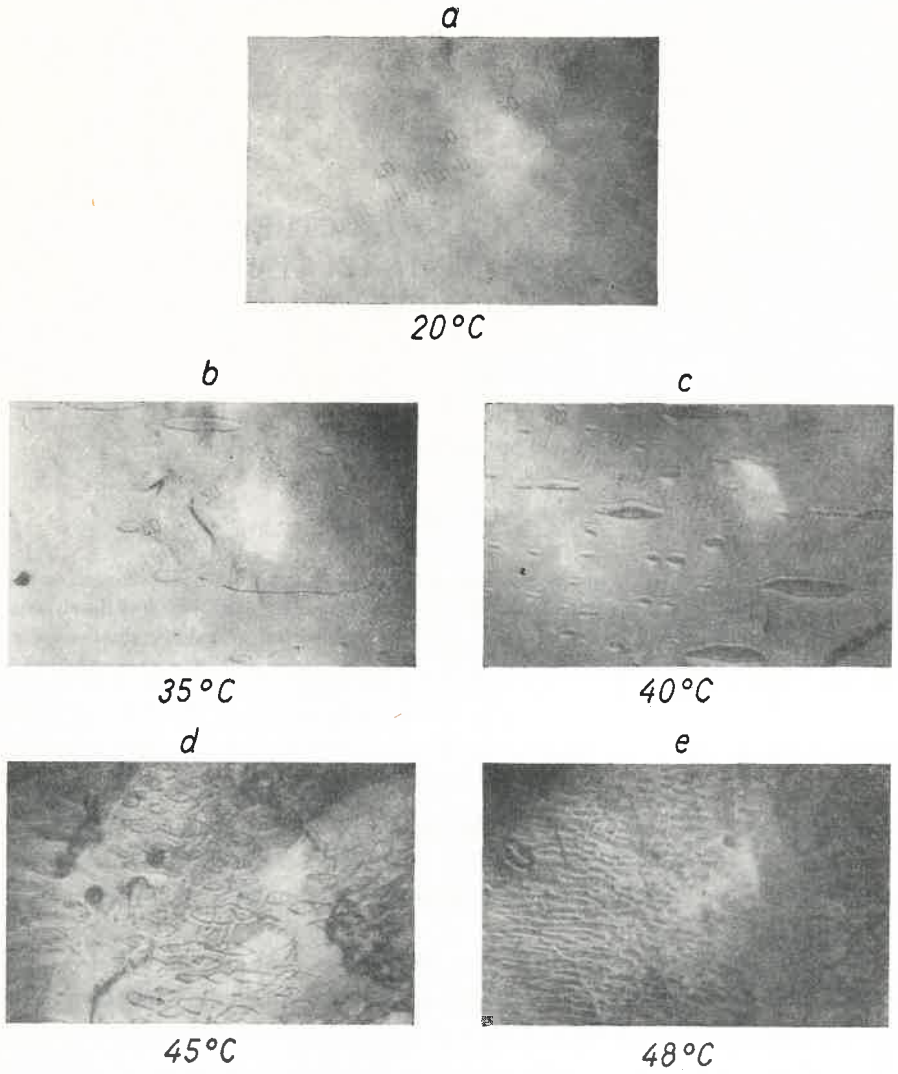

Fig. 1. Domain structure of TGS as dependent on temperature (magnification 35×)

crystal was single-domain in the observed micro-region (Fig. 1*a*). At 35°C several domains appeared (Fig. 1*b*). At 40°C, the micro-region broke up into more domains (Fig. 1*c*). The strongest frittering of the domain structure was observed at 45 and 48°C (Fig. 1 *d*, *e*). It is thus to be concluded that frittering of domain structure occurs already at temperatures below the Curie point and does not require heating above it.

The number of domains per unit surface area varies *vs* the temperature like the electric permittivity ε, which increases in the 30–40°C range *i. e.* at the temperatures at which the domain structure begins to break up. A further, steep rise in ε occurs between 45 and 48°C, where the domain structure becomes fine. The value of ε at a given temperature thus seems to be proportional to the number of domains per unit area of the crystal surface.

2. Effect of an applied DC electric on the domain structure

Plates 3 mm thick were prepared by cleavage perpendicularly to the ferroelectric axis and were etched in an aqueous solution of 10% NH_4OH. The specimen was then coated with glycerine electrodes, and a DC electric field was applied to it along the *b*-axis. With the aim of observing domain wall motion, after each application of the field the specimen was etched in a manner to reveal the new interdomain boundaries maintaining, however, the old ones.

In aged TGS specimens, motion of domain walls was observed already in fields of the order of 50 V/cm (Fig. 2). Total vanishing of domain structure (consequently, a single-domain state) was found in fields of about 300 V/cm. In copper or chromium doped TGS crystals, the field strength required for producing a single-domain state increased considerably with the admixture content. In the case of TGS crystal obtained from a solution

TABLE I

Polarizing field strength *vs* admixture content of the solution, for aged and rejuvenated TGS specimens

Admixture content in the solution	Polarizing field E_p (in V/cm)	
	Aged specimens	Rejuvenated specimens
0%	300	80
	285	100
	300	80
	300	100
$CuSO_4$ 1%	1525	800
	1500	825
	1460	770
	1500	800
2%	2500	1550
	2520	1600
	2500	1570
	2520	1600
10%	10140	9200
	10160	9150
	10210	9200
	10210	9200
$Cr_2(SO_4)_3$ 0.5%	3550	1900
	3400	1950
	3350	1950
	3330	1950
1%	3500	2350
	3560	2380
	3570	2380
	3570	2400

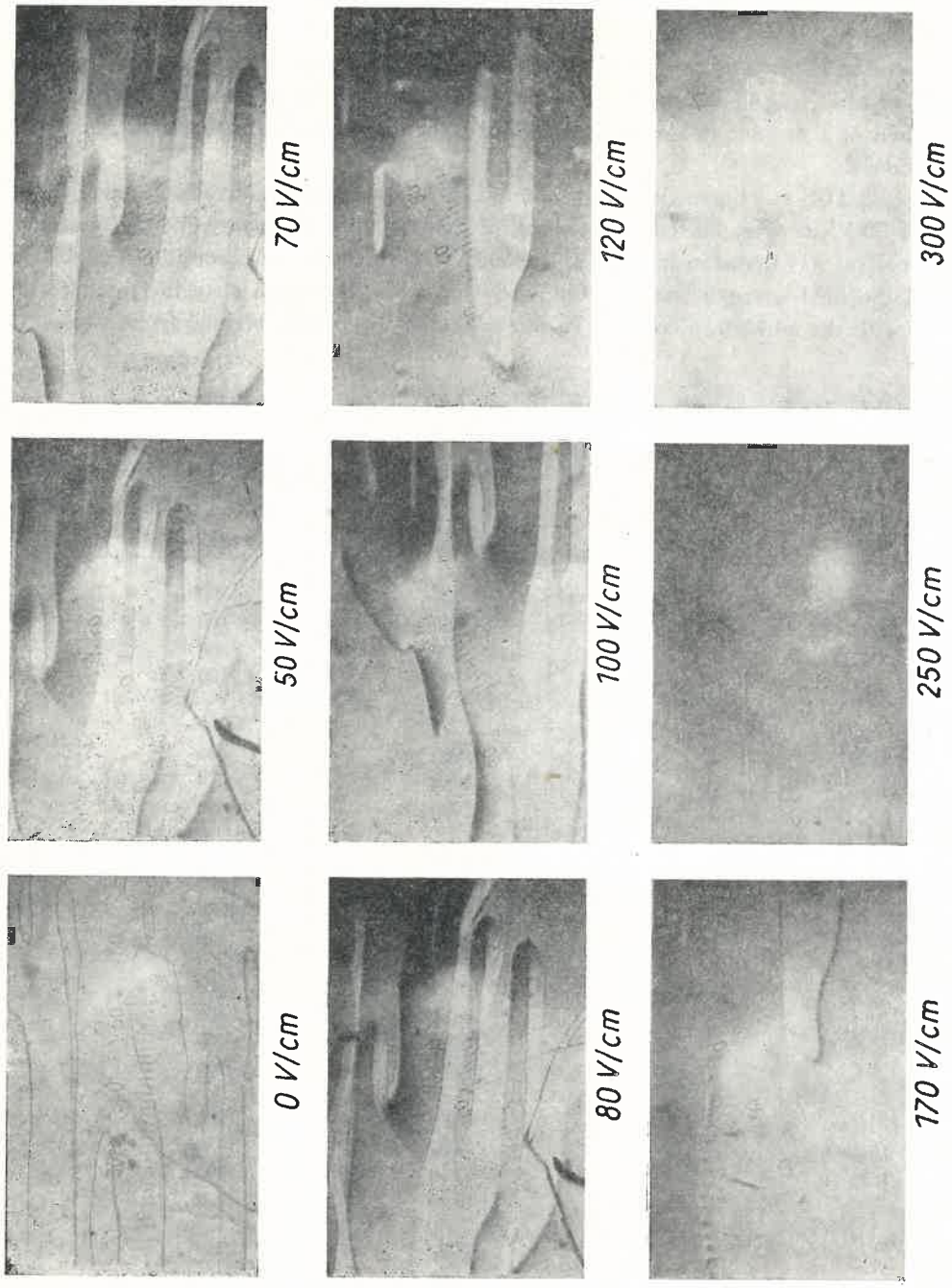

Fig. 2. Changes in domain structure due to a DC electric field (magnified 35 times)

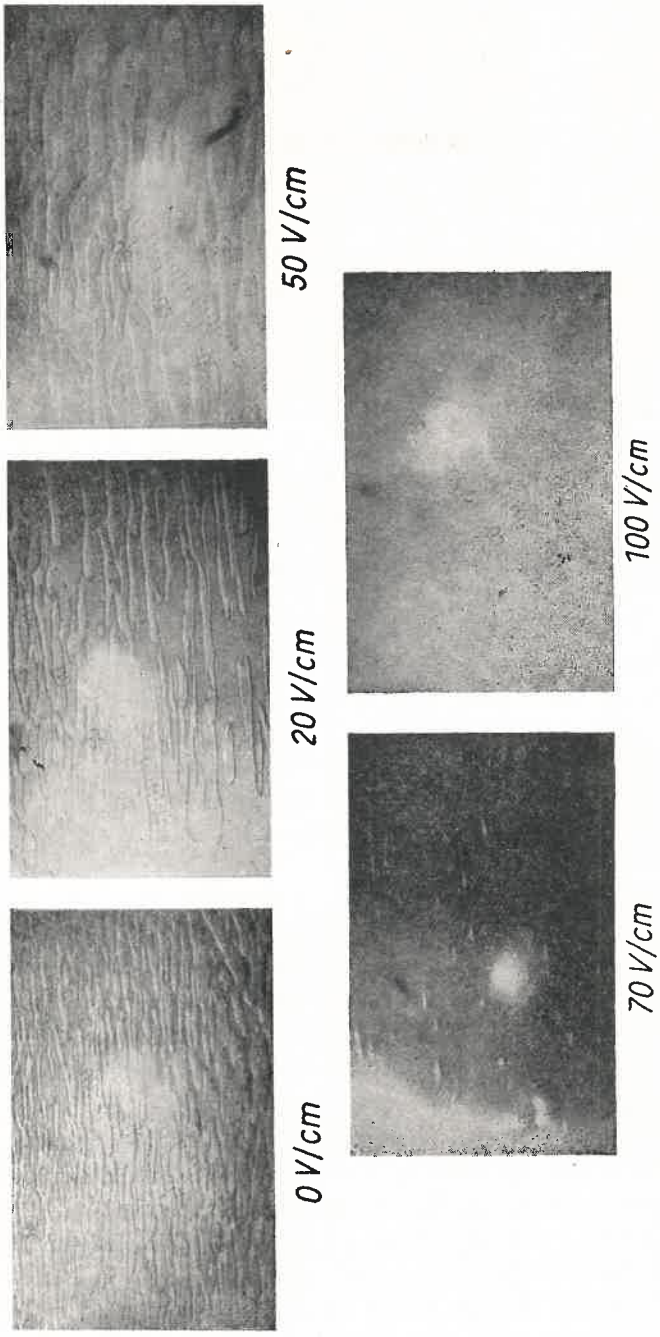

Fig. 3. Changes in domain structure of a rejuvenated TGS specimen due to a DC electric field (magnified 35×)

containing 10% $CuSO_4$, the field strength needed for eliminating domain structure amounted to 10 kV/cm.

The field strength producing the single-domain state will be referred to as the polarizing field E_p. Measurements of E_p were performed in aged and rejuvenated specimens [9], pure and doped with copper or chromium.

Aged specimens (*i. e.* ones never heated above the Curie point) were rejuvenated by heating at 100°C for 1h and cooled to room temperature at a rate of 0.1°C per minute. With this cooling procedure, the specimens remained above the Curie point for 5 hrs and were subjected to etching 8 hrs after transition through it. Fig. 3 shows pictures of domain structure in a rejuvenated specimen and its variations under the influence of an external DC electric field. In the case of rejuvenated specimens, a field of about 20 V/cm sufficed for producing domain wall motion, and 100 V/cm produced a single-domain state (total vanishing of domain structure).

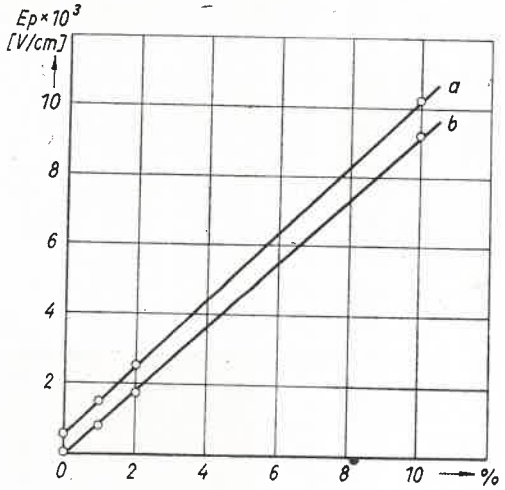

Fig. 4. Polarizing field E_p *vs* $CuSO_4$ concentration in the solution: *a*) aged specimens, *b*) rejuvenated specimens

In order to check the reproducibility of the results, measurements were performed on various specimens cut from the same crystal and belonging to the same pyramide of growth. The results are assembled in Table I, where the polarizing field strength is given for aged and rejuvenated specimens *vs* the concentrations of copper and chromium admixture in the solution.

For the rejuvenated specimens, E_p was by several orders smaller than for the aged ones. Hence, rejuvenation is seen to cause a higher mobility of the domains, as proved by the considerable decrease in polarizing field strength on rejuvenation.

The introduction of admixtures acts to stabilize the domain structure, as shown by the considerably higher field strength required for moving a domain wall and by the increase in E_p with larger admixture content. Fig. 4 shows graphs of E_p *vs* the $CuSO_4$ admixture content of the solution from which the crystal had been grown, for aged and rejuvenated specimens.

3. Effect of an AC electric field on the domain structure

Aged TGS specimens, pure and doped with Cu^{++} and Cr^{+++}, exhibiting asymmetric dielectric hysteresis loops, were rejuvenated in an AC field of frequency 50 Hz. Graphite electrodes were imposed on multi-domain regions (Figs 5*a*, 6*a*, 7*a*) and an AC field of strength 2500 V/cm was applied, according to the type and amount of the admixture, for 6–48 hrs, *i. e.* until symmetric hysteresis loops and normal current loops appeared (Figs 5*e*, *f*; 6*e*, *f*; 7*e*, *f*) pointing to rejuvenation of the specimen in the AC field. On removing the field and electrodes, the specimens were etched and observations of domain structure were made (Figs 5*d*, 6*d*, 7*d*). In pure and copper doped TGS specimens the AC field was found to cause a vanishing of the domain structure and total symmetrization of the dielectric hysteresis loop. In TGS doped with chromium, a domain structure remained and even 48 hrs in the AC field failed to yield a symmetric hysteresis loop (Figs 7*d*, *e*, *f*).

After 50 hrs outside the field, when the specimens were etched again for domain structure (Figs 5*g*, 6*g*, 7*g*), and the hysteresis was measured (Figs 5*h*, *i*; 6*h*, *i*; 7*h*, *i*), they once more exhibited such a structure and the loop was asymmetric. In the case of chromium doped crystal, the loop reverted to its previous shape.

TABLE II

Spontaneous polarization of TGS crystal *vs* the type of admixture

Type and content of admixture	$P_s\left(\frac{\mu c}{cm^2}\right)$	
	Aged specimens	Rejuvenated specimens
TGS	2.10	2.86 (6)*
TGS+Cu^{++} (1%)	1.33	2.33 (12)
TGS+Cr^{+++} (1%)	1.02	1.10 (48)

* Time (in hrs) of rejuvenation in a 2.5 kV/cm AC field.

As results from the measurements, the AC field causes a reorientation of most domains in the direction of the 50 Hz field. However, some of the domains do not participate in polarization switching because of their strong stabilization in the crystal, as is the case in crystals doped with chromium. Nevertheless, the AC field produces a loosening of the domain structure, as proved by the symmetrization of the hysteresis loop and the emergence of single-domain regions. Rejuvenation with an AC field is not permanent; after a time, the specimen again exhibits the original structure and loop. In admixtured TGS crystals, owing to stronger stabilization of the domains, the time necessary for rejuvenation is much longer than in pure TGS (Table II).

The hysteresis loops were resorted to for determining the spontaneous polarization of the aged and AC field-rejuvenated specimens. The results are assembled in Table II. Aged specimens exhibit a spontaneous polarization much lower than rejuvenated ones. Similarly, in admixtured specimens, the spontaneous polarization is less than in pure TGS. The spontaneous polarization value can be taken as a measure of the purity of the crystal — the purer the crystal the larger is the spontaneous polarization.

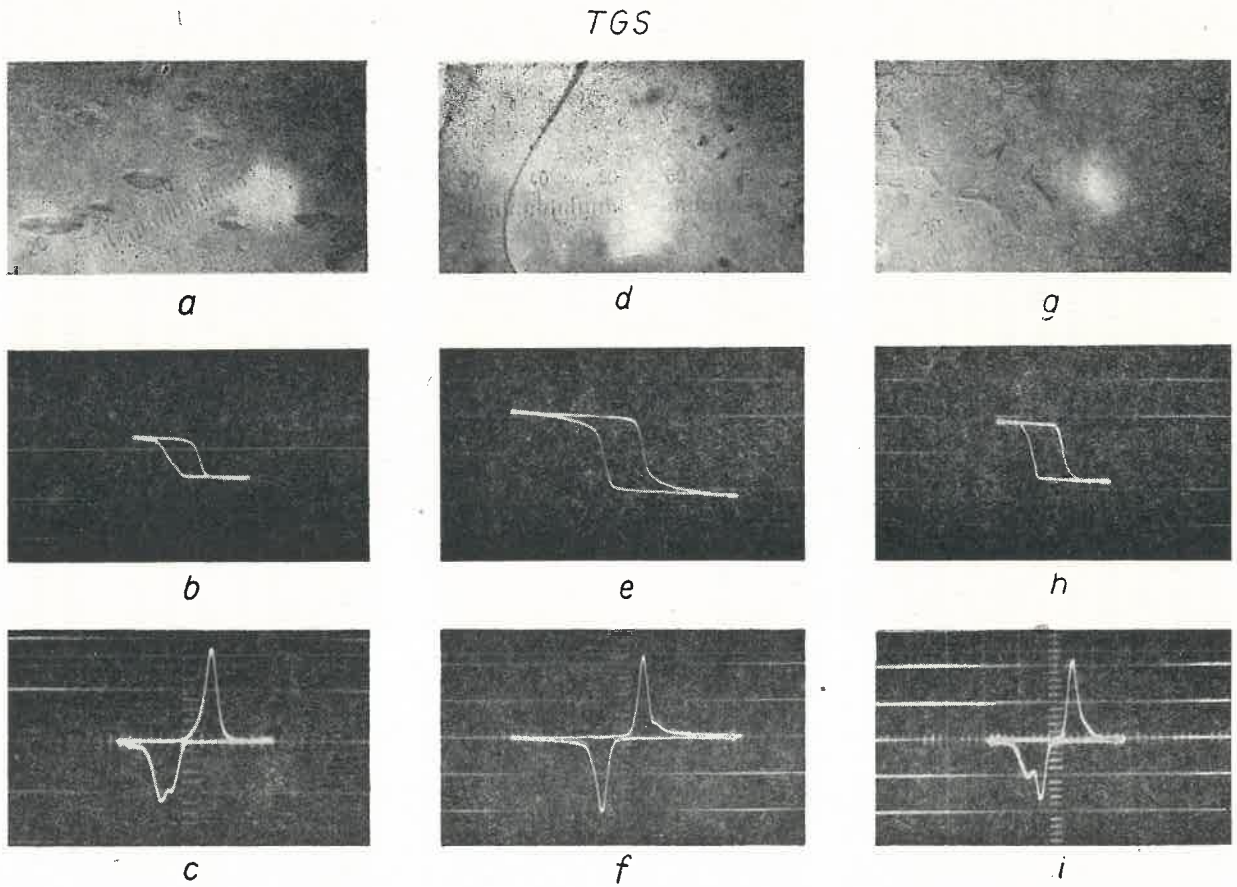

Fig. 5. Effect of an AC electric field on the domain structure of TGS: *a*) domain structure previous to applying the field, *b*) dielectric hysteresis loop with structure *a*, *c*) current loop, *d*) domain structure after 6 hrs of applying an AC field of strength 2500 V/cm, *e*) dielectric hysteresis loop after 6 hrs of applying AC field, *f*) current loop after 6 hrs applying AC field, *g*) domain structure 50 hrs after switching off the field, *h*) dielectric hysteresis loop 50 hrs after switching off the field, *i*) current loop 50 hrs after switching off the field

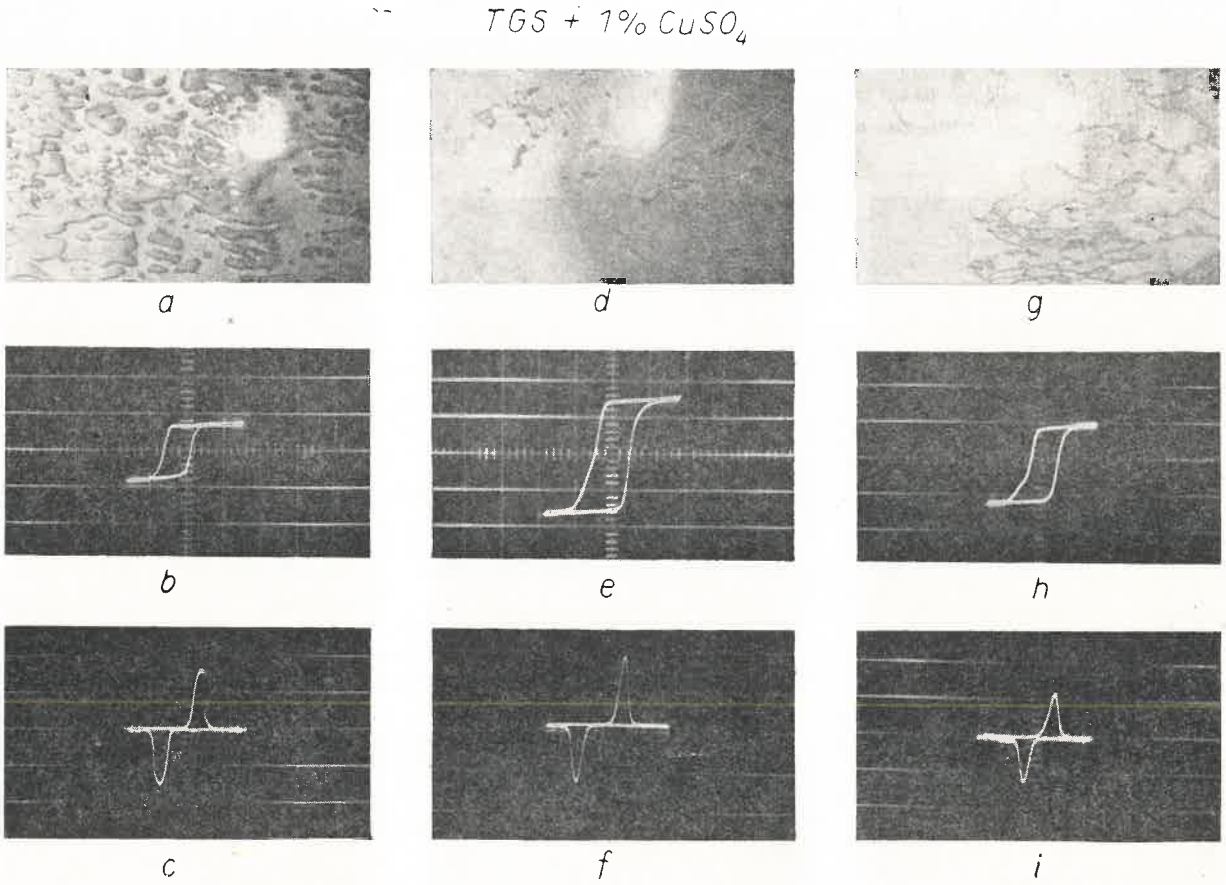

Fig. 6. Effect of an AC electric field on the domain structure of TGS crystal grown from a solution containing 1% $CuSO_4$ admixture: *a*) domain structure previous to applying the field, *b*) dielectric hysteresis loop with structure *a*, *c*) current loop, *d*) domain structure after 12 hrs of applying a 2500 V/cm AC field, *e*) dielectric hysteresis loop of crystal with structure *d*, *f*) current loop, *g*) domain structure 50 hrs after removing the field, *h*) dielectric hysteresis loop of crystal with structure *g*, *i*) current loop 50 hrs after switching off the field

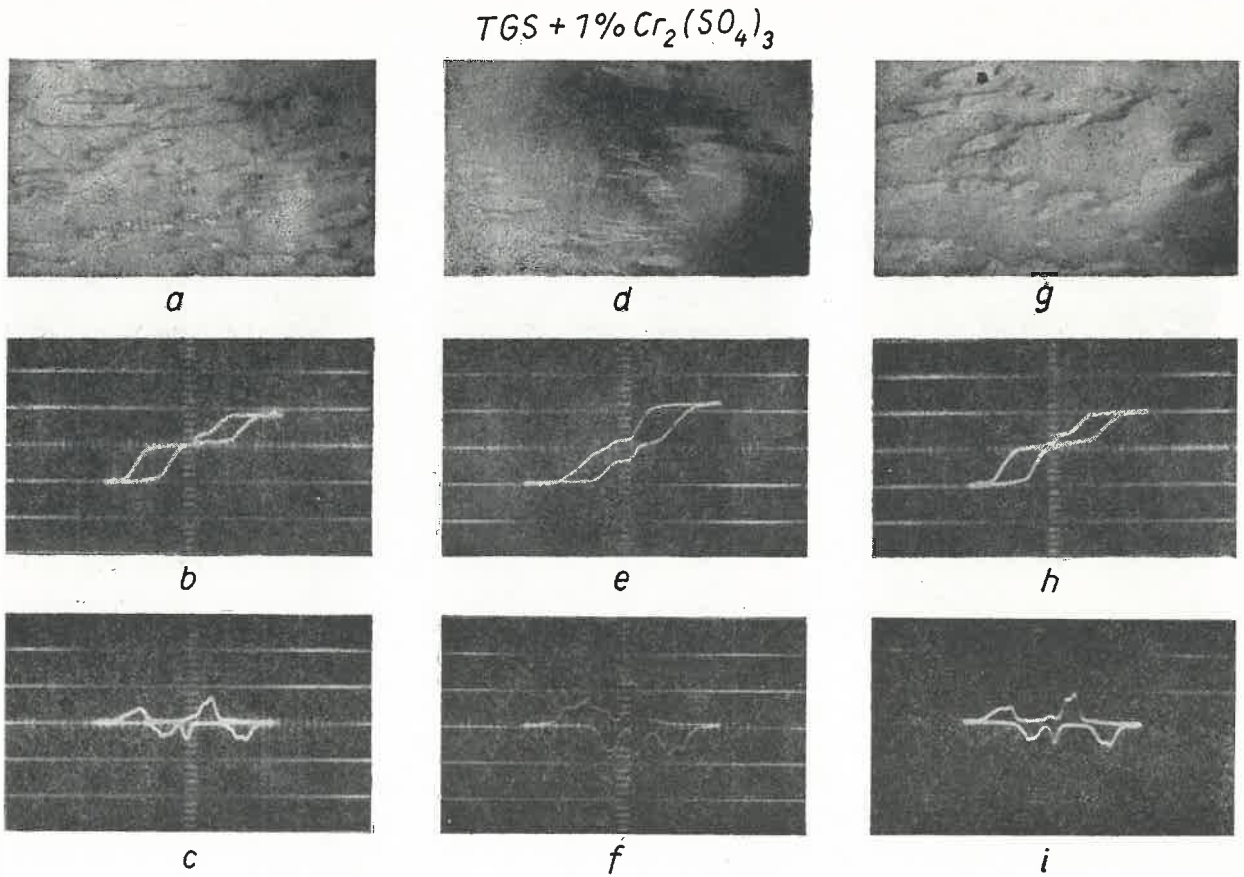

Fig. 7. Effect of an AC electric field on the domain structure of TGS crystal grown from a solution containing 1% $Cr_2(SO_4)_3$ admixture: *a*) domain structure previous to applying the field, *b*) dielectric hysteresis loop with structure *a*, *c*) current loop, *d*) domain structure after 48 hrs of applying a 2500 V/cm AC field, *e*) dielectric hysteresis loop of crystal with structure *d*, *f*) current loop, *g*) domain structure 50 hrs after removing the field, *h*) dielectric hysteresis loop of crystal with structure *g*, *i*) current loop 50 hrs after switching off the field

3. *Conclusions*

1. Frittering of the domain structure occurs already at temperatures below the Curie point, and the number of domains per unit area of the surface is proportional to ε.

2. Cu^{++} and Cr^{+++} admixtures stabilize the domain structure of TGS, as proved by the following experimental results:

a) the polarizing field E_p increases with higher admixture concentrations,

b) E_p is large in aged crystals and lower in rejuvenated ones.

3. Rejuvenation in an AC field causes:

a) a rise in spontaneous polarization,

b) a symmetrization of the dielectric hysteresis loop.

4. A well-defined difference exists between thermal rejuvenation and rejuvenation in a AC field:

a) thermal rejuvenation causes a frittering of the domain structure, which undergoes a change in the process of ageing, and a symmetrization of the hysteresis loop, which does not change appreciably;

b) AC field-rejuvenation produces a single-domain region which, after a time, breaks up into domains; the loop reverts to its original asymmetry.

REFERENCES

[1] G. L. Pearson, W. L. Feldman, *J. Phys. Chem. Solids*, **9**, 28 (1959).
[2] V. A. Meleshina, I. S. Zheludev, I. S. Rez, *Kristallografia*, **5**, 322 (1960).
[3] J. Stankowska, *Acta Phys. Polon.*, **31**, 527 (1967).
[4] V. P. Konstantinova, *Rost kristallov*, Izd. Nauka, **7**, 197 (1967).
[5] F. Moravec, V. P. Konstantinova, *Kristallografia*, **13**, 284 (1968).
[6] R. Toyoda, *J. Phys. Soc. Japan*, **14**, 376 (1959).
[7] V. P. Konstantinova, J. Stankowska, *Kristallografia*, **15**, 382 (1970).
[8] V. P. Konstantinova, J. Stankowska, *Kristallografia*, **16**, 158 (1971).
[9] A. G. Chynoweth, W. L. Feldman, *J. Phys. Chem. Solids*, **15**, 225 (1960).
[10] J. E. Petroff, *Phys. Status Solidi*, **31**, 285 (1969).
[11] V. P. Konstantinova, V. F. Miuskov, B. V. Maksimov, *Izv. Akad. Nauk SSSR*, **33**, 371 (1969).
[12] V. A. Meleshina, *J. Phys. Soc. Japan*, **28**, 357 (1970), Proc. of the Second International Meeting on Ferroelectricity (1969).