FERROELECTRIC PROPERTIES OF PURE AS WELL AS Cu^{++} AND Cr^{+++} DOPED TRIGLYCINE FLUOROBERYLATE

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Single crystals of triglycine fluoroberylate, pure as well as doped with the foreign ions Cu^{++} and Cr^{+++}, were obtained. Their dielectric properties, namely the temperature-dependence of dielectric permittivity, spontaneous polarization and coercive force, were determined.

Measurements of domain structure by etching were performed. Likewise to TGS, the domain structure of TGFB changes during rejuvenation and ageing.

1. Introduction

Triglycine fluoroberylate (TGFB) is a crystal of the glycine group, the chief representative of which is triglycine sulphate (TGS).

The ferroelectric properties of TGFB were discovered in 1957 by Pepinsky, *et. al.* [1]. Various authors report [1–3] a Curie point of TGFB crystal between 70°C and 75°C. The influence of a DC electric field on the dielectric properties of TGFB was studied by Wieder and Parkerson [3]. Brezina studied the properties of deuterized DTGFB crystals [4] as well as of mixed TGS+TGFB crystals [5], exhibiting a Curie point varying from 49°C to 72°C according to composition. The earliest observations of domain structure in TGFB crystal are due to Safrankova, Fousek and Kaczér [6] using the dew method.

In this paper, we report results on the ferroelectric properties of TGFB crystals, both pure and doped with Cu^{++} and Cr^{+++} ions, taking into account the domain structure of aged and rejuvenated crystals.

2. Experimental

TGFB is obtained by synthesis of fluoroberylate and aminoacetic acids [7]:

$$3\,NH_2CH_2\,COOH + H_2B_eF_4 = (NH_2CH_2\,COOH)_3\,H_2B_eF_4$$

the former stemming from the reaction of beryllium carbonate and hydrofluoric acid:

$$B_eCO_3 + 4\,HF = CO_2 + H_2O + H_2B_eF_4$$

The salt thus obtained is repeatedly recrystallized for purification.

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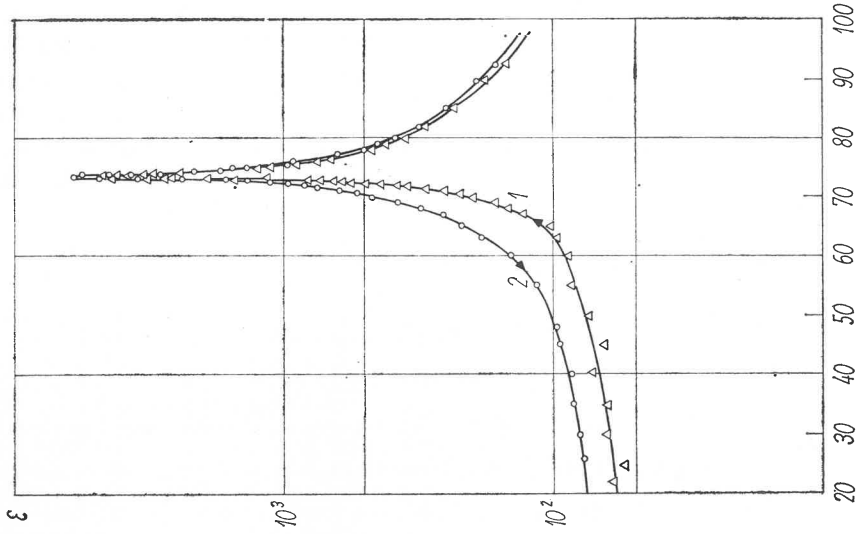

Fig. 1

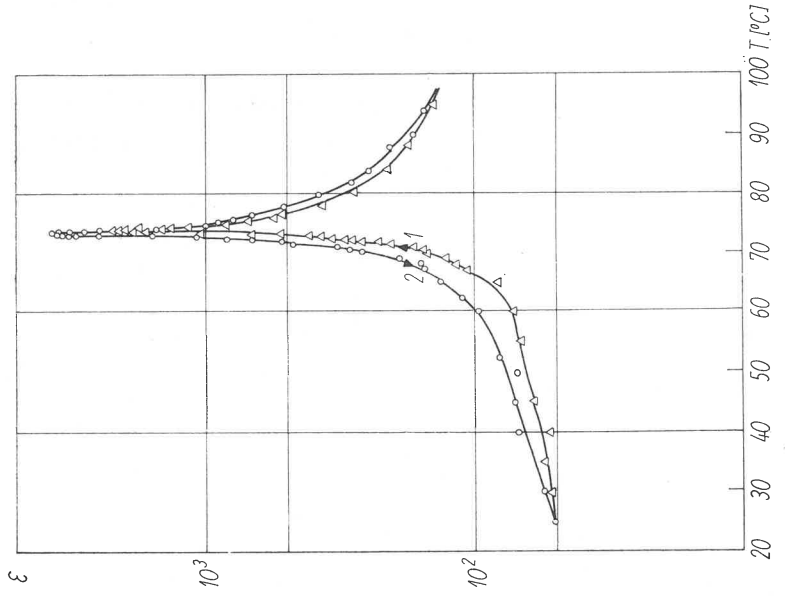

Fig. 2

Fig. 1. Electric permittivity of TGFB *versus* the temperature
Fig. 2. Electric permittivitty of Cu^{++} doped TGFB *versus* the temperature

TGFB single crystals were obtained by crystallization from aqueous solutions. In order to obtain doped crystals, a 2% admixture of cupric chloride $CuCl_2$ or, respectively, chromium carbonate, was added to the TGFB solution. Copper doped crystals are tinted blue, whereas chronium doped ones are tinted green and differ strongly in shape from the pure ones. Chromium doped single crystals grow fewer walls, and are flattened in the direction of the *z*-axis but elongated in that of the *b*-axis; moreover, they are by no means easy to grow, and attain no considerable size.

Samples for the measurements were cleaved perpendicularly to the ferroelectric axis, polished, and coated with silver electrodes. Figs 1, 2 and 3 show the temperature-dependence of electric permittivity measured in pure, copper doped, and chromium doped TGFB crystals. Curve *1* was obtained when raising the temperature and curve *2* when lowering

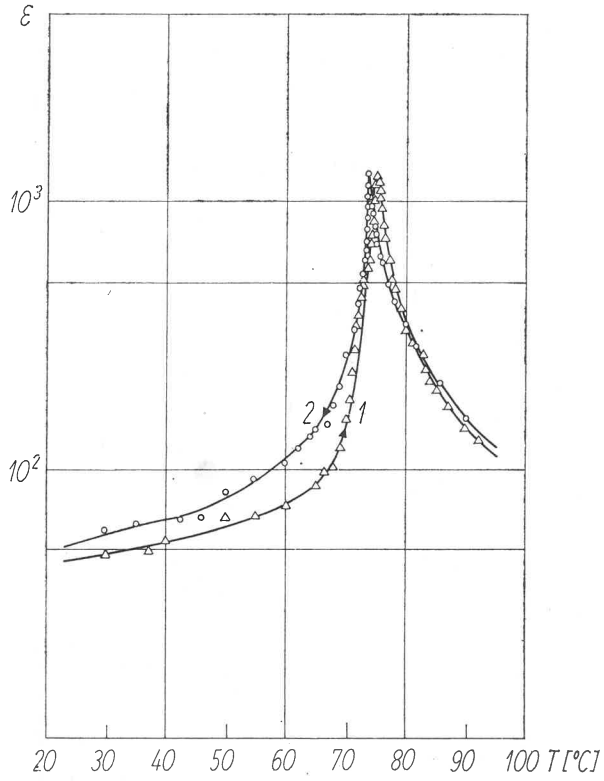

Fig. 3. Electric permittivity of Cr^{+++} doped TGFB *versus* the temperature

it. Previous to lowering the temperature, the sample was maintained for 5 hrs at 100°C. In Table I, the Curie point temperatures obtained when raising the temperature, T_c^{ag}, and when lowering it, T_c^{rej}, as well as the corresponding ε_{max}^{ag} and ε_{max}^{rej} values, are listed. Noteworthy is the marked temperature hysteresis of permittivity and the decrease in ε for the copper and chromium doped crystals.

In rejuvenated crystals, the hysteresis loop was measured *versus* the temperature;

TABLE I

Numerical values of parameters describing the dielectric properties of TGFB crystals, pure as well as Cu^{++} and Cr^{+++} doped

	T_c^{ag} [°C]	T_c^{rej} [°C]	ε_{max}^{ag}	ε_{max}^{rej}	P_s 20°C $\left[\frac{\mu C}{cm^2}\right]$	E_c 20°C $\left[\frac{v}{cm}\right]$
TGFB	73.6	73.4	4750	6050	2.76	1300
TGFB + Cu^{++}	73.8	73.5	2200	3720	2.52	1500
TGFB + Cr^{+++}	75.1	73.9	1226	1265	0.88	3000

this permitted the determination of spontaneous polarization P_s and coercive force E_c (Figs 4 and 5). The lowest P_s and highest E_c values are exhibited by the chromium doped crystals, pointing to the formation of a strong complex with TGFB stiffening the crystal lattice, as is the case with TGS [8].

Domain structure was rendered apparent by etching [9, 10]. TGFB plates several

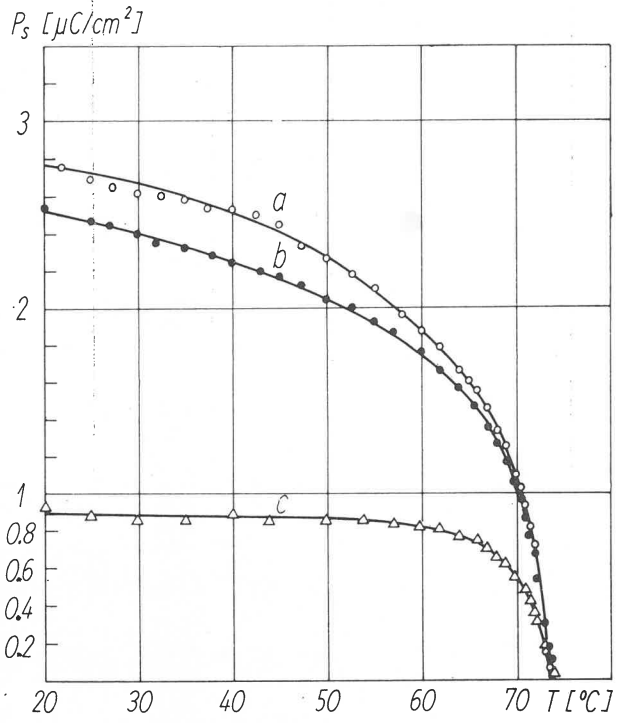

Fig. 4. Spontaneous polarization *versus* the temperature, in TGFB crystals: *a*) pure, *b*) Cu^{++} doped, *c*) Cr^{+++} doped

millimetres thick were etched in a 10% aqueous solution of NH_4OH. The domain structure was apparent under a MIN 8 microscope in reflected light at oblique illumination.

Investigation was conducted as follows: Firstly, the domain structure of aged crystals was observed; the sample was then rejuvenated in a thermostat at 100°C in an atmosphere of air, in the presence of concentrated sulphuric acid. The sample was maintained at 100°C for a period varying from 1 to 10 hrs and cooled at a rate of 0.1° per minute to room temperature. On cooling, the sample was etched at well-defined intervals of time, counted

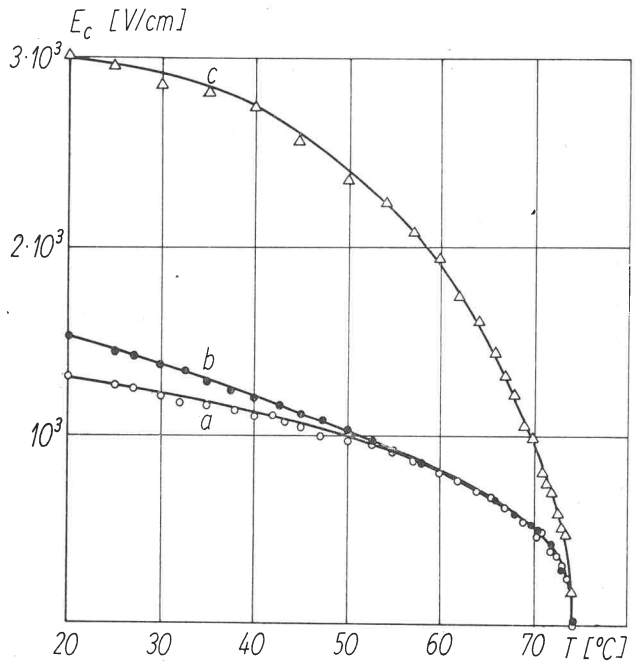

Fig. 5. Coercive force *versus* the temperature, in TGFB crystals: *a*) pure, *b*) Cu^{++} doped, *c*) Cr^{+++} doped

from the moment of transition through the Curie point. In TGFB, rejuvenation (as it is the case with TGS) causes a breaking up of the domain structure, which changes at first rapidly and then more and more slowly as a result of aging. In Fig. 6, this is illustrated by pictures of domain structure in TGFB previous to rejuvenation (*a*), and at a well-defined time after rejuvenation (*b* and *c*) in the two growth pyramids (110) (*A*) and (001) (*B*).

Figs 7 and 8 show the number of domains per 1 mm length in the growth pyramid (001) *vs* the time and logarithm of the time elapsed since transition through the Curie point, for two TGFB samples. For comparison, Figs 7 and 8 show the curve obtained for TGS single crystal [11]. The changes in domain structure during ageing are found to proceed quite similarly in the two isomorphous crystals. However, the domains differ in shape between the two. TGFB is more apt than TGS to exhibit 60° blocks which, even during rejuvenation, maintain their boundaries. In the growth pyramid (110), lens--shaped domains occur, of a shape more strongly irregular than in TGS.

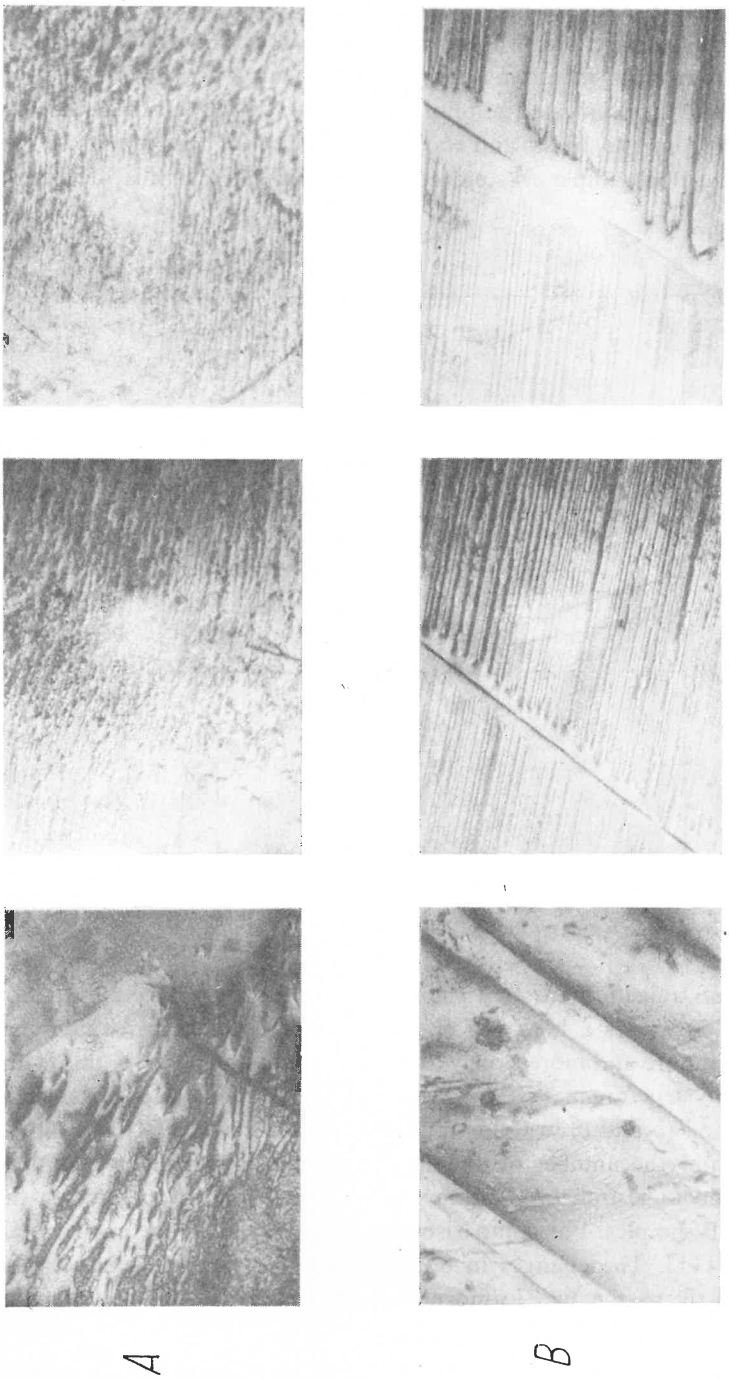

Fig. 6. Domain structure in TGFB crystals: a) previous to rejuvenation, b) 20 hrs and c) 45 hrs after transition through the Curie point. A — growth pyramid (110), B — growth pyramid (001)

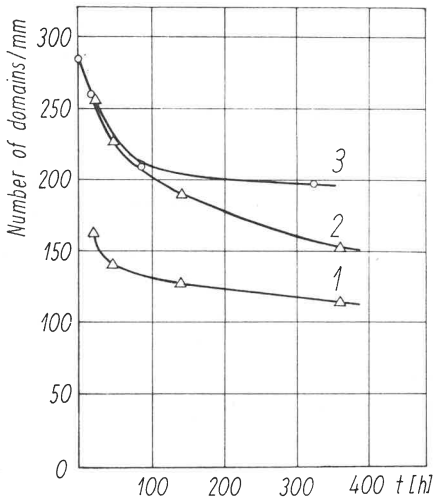

Fig. 7. Number of domains per 1 mm *versus* the time, in TGFB crystals (curves *1* and *2*) and TGS crystals (curve *3*) in growth pyramid (001)

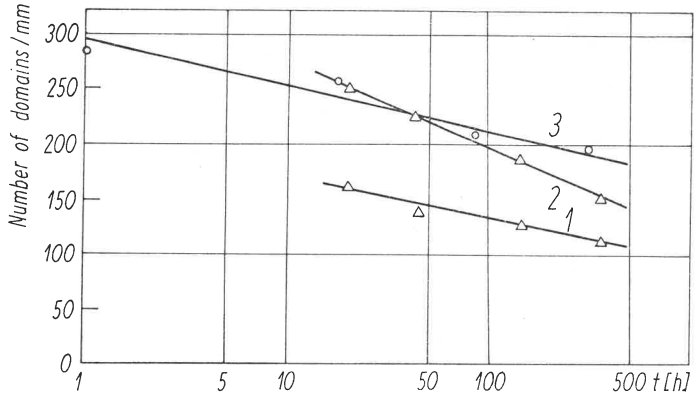

Fig. 8. Number of domains per 1 mm *versus* the logarithm of the time, in TGFB crystals (curves *1* and *2*) and TGS crystal (curve *3*), in growth pyramid (001)

3. Conclusions

1. TGFB crystals, both pure and doped, exhibit (like TGS) temperature hysteresis of electric permittivity.

2. Copper and chromium doped TGFB crystals exhibit a higher coercive force and lower spontaneous polarization and electric permittivity than pure crystals.

3. In TGFB, domain structure is irregular and fragmentary; often 60° blocks occur which, on rejuvenation, retain their boundaries.

4. The change in number of domains after rejuvenation is a linear function of the logarithm of the time.

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