

## THE EFFECT OF DOPANTS ON THE GROWTH AND PROPERTIES OF TGS CRYSTALS\*

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Triglycine sulphate (TGS) crystals were grown from pure and doped solutions. The results referring to the influence of the dopants on the growth, the domain structure, the lattice parameters and the different dielectric parameters are reported and discussed.

### Introduction

Triglycine sulphate (TGS) is well known as a ferroelectric material [1]. Its properties are generally known [2]. Because of its low Curie temperature of about 49 °C TGS is a convenient ferroelectric model material from which single crystals of good quality can be grown. The crystals are also used in the practice as pyroelectric displays and infrared detectors. The technical applications demand single crystals of high quality. Therefore, the study of the relation between the growth conditions and the properties of these crystals are of practical importance, too. The aim of the present paper was to give some contributions to the effect of dopants on the growth in macroscopic scale and to the ferroelectric behaviour of the TGS crystals.

### Experiments

#### *Chemical preparations*

The triglycine sulphate was synthesized from hot aqueous solutions containing in stoichiometric composition glycine and sulphuric acid of high purity [3]. In order to decrease the unwanted metal impurities, first of all that of the Fe ions, the glycine raw material was prepurified by recrystallizing two times. The steady composition of the starting material was controlled by potentiometric titration [4]. As dopants pure  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  and  $\text{KCr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ , respectively, were used whose concentrations within the solutions were varied between 2 and 25 mole% in order to grow crystals of rather large dopant contents.

\* Dedicated to Prof. I. Tarján on his 70th birthday.

The concentrations of Cu dopants incorporated into the TGS crystals were determined by complexometric titration [5]. As reagent  $10^{-3}$  M solution of SELECTON C (Complexon IV) produced by Reanal were used in specimen solutions of constant 0.5 M TGS concentrations and at constant 5.8 pH values. As indicator PAN was applied. The concentrations of Cr dopants within the crystals were measured spectrophotometrically [6, 7] using 0.1 M solutions of SELECTON B2 (EDTA) produced by Reanal in specimen solutions of constant 0.5 M TGS concentrations, at constant 6.00 pH values. The Cr concentrations were determined from the absorption peak heights measured at 548 nm.

For revealing the domain structure on the {010} cleavage faces of the crystals instead of the usual water (e.g. [3, 8]) cc. propion acid doped with a small amount of  $\text{BaCO}_3$  was used as etchant.

### *Crystal growth*

The crystals for the investigations were grown from pure and doped aqueous solutions by the well-known techniques of the solvent evaporation at constant temperature or of a program regulated decreasing of the temperature. The growth processes of two steps occurred below the Curie temperature of the crystals, that means, the growth history took place in the ferroelectric state. In the first step going out from rod-like seeds nearly uniform small crystals of dimensions of about 2  $\mu\text{m}$  were grown from pure solutions. They were usually bordered by {001} and {110} habit faces and {100}, {111}, {121}, {011} and {010} faces of small sizes. In the second step these small crystals were grown on.

### *Measurements of the dielectric parameters*

From the crystals small specimens were cleaved out the {010} cleavage faces of which were covered with silver paste as electrodes. Then at an electric field strength of  $100 \text{ Vm}^{-1}$  and a frequency of 1 kHz the relative dielectric permittivity ( $\epsilon_r$ ) and the dielectric loss ( $\text{tg } \delta$ ) of the specimens were measured as function of the temperature between about 20 and 60 °C with an accuracy better than  $\pm 0.1$  °C.

The ferroelectric hysteresis loops were measured in a modified Sawyer-Tower circuit at an electric field strength of  $2 \cdot 10^5 \text{ Vm}^{-1}$  and a frequency of 50 Hz. In this way the spontaneous polarization  $P_s$  and the coercitive force  $E_k$  belonging to the temperature of 20 °C were determined.

### *Measurements of the lattice parameters*

On powder specimens prepared from pure and copper doped crystals the lattice parameters were measured with Debye-Scherrer method. On cleavage pieces of the pure and doped crystals precision lattice parameter measurements were carried out with the Bond method [9, 10].

### Results and discussion

In growing the crystals using the seeds mentioned before in pure solutions the bordering, the so-called *growth form* of the crystals remains the same as that of the seeds (Fig. 1a). After the growth from solutions doped with copper or chromium and potassium, respectively, a change in the size ratios of the faces were observed (Fig. 1b). In the bordering the  $\{001\}$  and  $\{110\}$  faces remain the habit faces, but the other ones become relatively smaller or some of them even disappear. This growth form modification caused by the selected effect of the dopants on the growth of the crystallographically different faces is bigger in the case of the Cr and K dopants than in that of Cu dopants.

Depending on the growth conditions the dopant particles present in the solutions are incorporated into the crystals during the growth. By measuring the dopant concentrations in the crystals the effective segregation coefficients of Cu and Cr dopants were determined. Increasing the growth rate from 0.2 up to 10 mm/day measured in the  $\langle 010 \rangle$  direction the effective segregation coefficients have shown a rising tendency between  $5.0 \cdot 10^{-3}$  and  $3.6 \cdot 10^{-2}$  in the case of Cu dopants and between  $2 \cdot 10^{-2}$  and  $2.3 \cdot 10^{-1}$  in the case of Cr ones. The segregation coefficients for both kinds

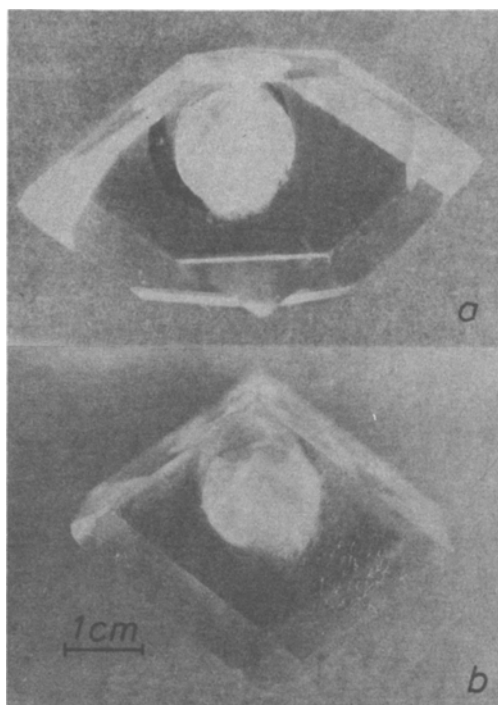
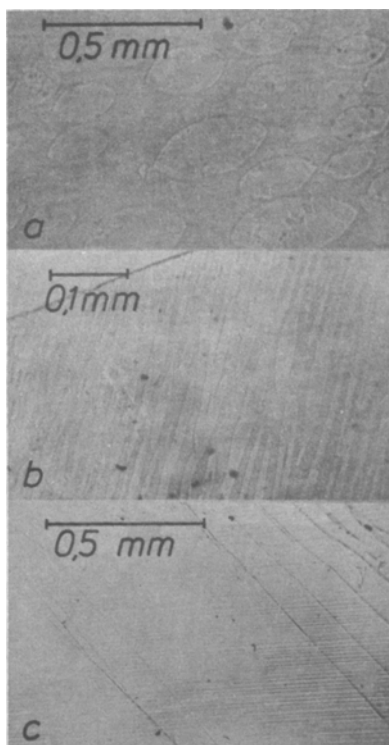


Fig. 1. The growth forms of TGS crystals grown from a pure solution (a) and from that doped with 10 mole% Cu (b)

of dopants are smaller than unity, and their values lie in that order of magnitude which was found also by other authors [11].

According to the etching experiments the crystals in the as-grown state consist only of a few of the ferroelectric domains. After a thermal treatment above the Curie temperature the number of the newly formed domains, especially in the case of the doped crystals, increases significantly. The domain form appearing by etching on the  $\{010\}$  cleavage faces of the crystals shows certain differences according to the dopant species. As Fig. 2 demonstrates on the faces of the pure crystals the domains are generally lens-like (Fig. 2a) and on those of the doped crystals they have generally elongated forms (Fig. 2b). In the case of Cr dopants whisker forms were also observed (Fig. 2c).

The lattice parameters measured on TGS crystals doped with Cu in concentrations between 0.05 and 0.6 mole% were:  $a=(0.942\pm 0.010)$  nm,  $b=(1.262\pm 0.010)$  nm, and  $c=(0.573\pm 0.007)$  nm. They do not differ from those measured on the pure crystals and given in the International Tables. That means that the possible changes of the parameters are within the given limit of error. The precision



**Fig. 2.** Some typical forms of ferroelectric domains after a thermal treatment, revealed by etching on the  $\{010\}$  cleavage faces of different TGS crystals: a — in a pure crystal, b — in a Cu doped crystal, and c — in a Cr and K doped crystal

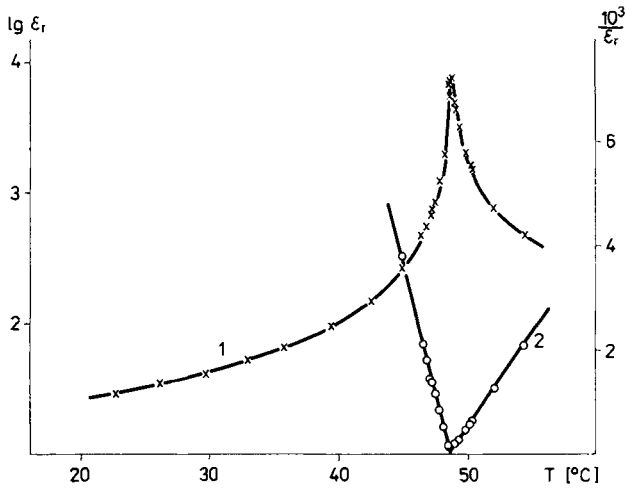


Fig. 3. The temperature  $T$  dependence of the relative dielectric permittivity  $\epsilon_r$  of a Cu doped TGS crystal: 1 — in a  $\lg \epsilon_r$  versus  $T$  representation; 2 — in a  $1/\epsilon_r$  versus  $T$  representation

measurements of the parameter  $b$  show, however, certain differences: in the undoped crystal  $b = (1.264\,824\,9 \pm 5 \cdot 10^{-7})$  nm, in the crystal doped with 0.1 mole% Cu  $b = (1.264\,828\,7 \pm 5 \cdot 10^{-7})$  nm and in the crystal doped with 0.2 mole% Cr (together with K in unknown concentration)  $b = (1.264\,732\,3 \pm 5 \cdot 10^{-7})$  nm. From this especially the Cr and K dopants seem to be effective in decreasing the parameter  $b$  of the TGS crystals.

The relative dielectric permittivities of the crystals have shown the well-known temperature dependent course. This is demonstrated by the curve 1 in Fig. 3 for the case of a TGS crystal doped with Cu in a heating course. At the phase transition temperature  $T_m$  a very high maximum ( $\epsilon_{r,\max}$ ) appears as compared with the starting

Table I

The dielectric parameters of TGS crystals, measured at heating (h) and cooling (co), respectively.  $C^-$ ,  $C^+$  are the Curie constants in ferroelectric and paraelectric phase, respectively.  $\epsilon_{r,\max}$  is the maximum relative dielectric permittivity at the phase transition temperature  $T_m$ .  $T_c$  is the Curie temperature

Dopant	$C^-$ [ $10^3$ °C]		$C^+$ [ $10^3$ °C]	$\epsilon_{r,\max}$ [ $10^3$ ]	$T_m$ [°C]	$T_c$ [°C]
—	$0.90 \pm 0.01$	(h, co)	$3.03 \pm 0.04$	$8.6 \pm 0.2$	$48.9 \pm 0.1$	$48.6 \pm 0.1$
			(h, co)			
Cu	$1.06 \pm 0.02$	(h)	$2.87 \pm 0.02$	$7.7 \pm 0.1$	$48.8 \pm 0.1$	$48.4 \pm 0.1$
	(0.9...1.7)	(co)	(h, co)			
Cr (and K)	$0.90 \pm 0.01$	(h)	$2.63 \pm 0.03$	$8.0 \pm 0.1$	$49.1 \pm 0.1$	$48.7 \pm 0.1$
	(0.9...1.75)	(co)	(h, co)			

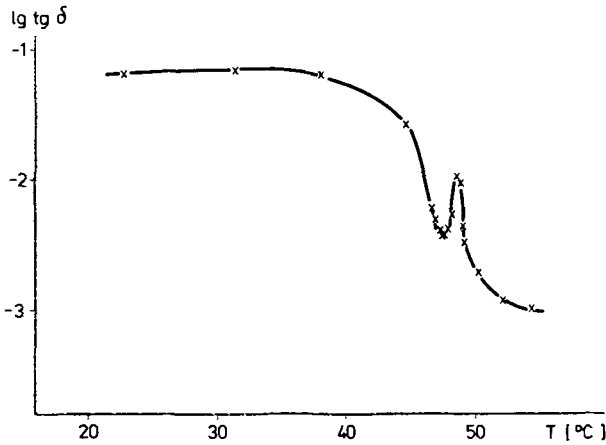


Fig. 4. The temperature  $T$  dependence of the logarithmic dielectric loss  $\lg \operatorname{tg} \delta$  of a Cu doped TGS crystal

value of the dielectric permittivity at room temperature. In the as-grown crystals having a prehistory only below the Curie temperature these starting values were found to be about 30. Both the ferroelectric and the paraelectric parts of the temperature  $T$  dependence of the dielectric permittivity in the vicinity of the Curie point  $T_c$  may be described by the Curie—Weiss law:  $1/\epsilon_r = (T - T_c)/C$ , where the Curie constant  $C$  for the ferroelectric phase  $C^-$  differs from that for the paraelectric phase  $C^+$ .

The dielectric parameters found are summarized in Table I. The data of Table I present the following details. The Curie constants measured in the paraelectric phase are reproducible independent of the heating or cooling course of the thermal treatment. The Curie constants measured in the ferroelectric phase show generally a larger or smaller practically irreproducible hysteresis. Such hystereses were already found on TGS by other authors [12].

Both in the undoped and doped TGS crystals the dielectric loss showed a strong decrease with an increasing temperature, and a sharp maximum appeared around the ferroelectric phase transition temperature (Fig. 4). The values of the spontaneous polarizations and the coercitive forces determined from the measurements of the hysteresis loops of the crystals are listed in Table II.

Considering that the maximum of the dielectric permittivity and the Curie temperature can be influenced by the defects within the crystals [13] the values of  $\epsilon_{r,\max}$ ,  $T_m$  and  $T_c$  listed in Table I are in good agreement with those mentioned in the literature [14, 15]. The hysteresis and the differences in Tables I and II or found in the literature are believed to lead back to the complex interactions between the lattice defects, e.g. impurities, and the domain structure. As it was already mentioned the as-grown domain structure can differ considerably from that after thermal treatments. Consequently, the reproducibility of the dielectric parameters is the question of the reproducibility of the domain structure of the ferroelectric crystals.

**Table II**

The values of the spontaneous polarizations  $P_s$  and the coercitive forces  $E_k$  at 20 °C, determined from the hysteresis loops investigated on (010) oriented cleavage pieces of pure and doped TGS crystals

Dopant	$P_s$ [ $10^{-2}$ Cm $^{-2}$ ]	$E_k$ [ $10^4$ Vm $^{-1}$ ]
—	$2.8 \pm 0.2$	$9.1 \pm 0.5$
Cu	$1.7 \pm 0.1$	$7.5 \pm 0.3$
Cr (and K)	$1.6 \pm 0.1$	$8.3 \pm 0.4$

### Summary

By measuring the dielectric parameters the crystals produced in our laboratory were controlled. Furthermore, the present investigations have given some new contributions to the close connection among the growth conditions, the real structure and the physical properties of the TGS crystals.

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