5. *FLUX 2D, Version 7.1. CAD Package for electromagnetic and thermal analysis. User's Guide. CEDRAT 1994.*
6. *Złonkiewicz Z.: Wytwarzanie i właściwości powłok przewodzących palladowo-niklowych w technice słaboprądowej. Wydawnictwo Naukowe Lublin 1998r.*
7. *Złonkiewicz Z: Palladium-Nickel Conductive Coating in Low Current Engineering. 8th International Conference on Switching Arc Phenomena on Electrical Technologies for Environmental Protection, Łódź, 3-6.09.97, pp. 222-225*
8. *Złonkiewicz Z.: "Modelowanie przestrzeni stykowej metodami numerycznymi". IV Konferencja Naukowo -Techniczna: ZASTOSOWANIA KOMPUTERÓW w ELEKTROTECHNICE - ZkwE'99, Poznań/ Kiekrz 12-14 kwietnia 1999, str. 185-188*
9. *Złonkiewicz Z.: "Modele matematyczne - fizyczne wykorzystane do obliczeń rezystancji przejścia zestyków słaboprądowych" V Konferencja Naukowo - Techniczna: Zastosowania Komputerów w Elektrotechnice, Poznań/Kiekrz, 10 - 12 kwietnia 2000, str. 675-678*
10. *Złonkiewicz Z.: "Triple-Layer Contact Simulations" Electromagnetic Devices and Processes in Environment Protection ELMECO, Nałęczów, 04 - 06 czerwca 2000, pp. 231-237*
11. *Złonkiewicz Z.: "The Performance Analysis of Low-Current Contacts Modelled by Numerical Methods" Proceedings of 20th International Conference on Electrical Contacts, Stockholm Sweden, 19 - 23 June 2000, pp. 251-254*
12. *Złonkiewicz Z.: "Computer Simulation of Low Current Contacts". 9th International Conference*
13. *Switching Arc Phenomena, Łódź, September, 17-20, 2001, pp. 241-246*

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RELATION BETWEEN DOMAIN STRUCTURE DISTORTION AND COERCIVE FIELD IN L-LYSINE DOPED TGS SINGLE CRYSTALS.

1. INTRODUCTION

Triglycine Sulphate (TGS) is one of the most intensively examined ferroelectric material, finding wide application, as active element of the IR sensors, in the range of room temperature. Temperature of the Curie point for TGS is 49ºC and the material shows second order phase transition. Structure of the crystal lattice is monoclinic, both below, and above the Curie point. Cleavage plane is perpendicular to the ferroelectric b axis (0,1,0). One of the most important disadvantage of TGS is depolarisation process, influencing the electric parameters and performance of the detectors based on this material. Well known method for improvement of electric properties and elimination of depolarisation process is doping pure TGS with optical active particles [2,3,4].

TGS single crystals doped with l-lysine (TGSL10) were grown below Curie point with use of static method, by evaporation of the solvent. Morphology changes were observed in new grown single crystals in comparison to pure TGS. Parameters of the crystal lattice were determined with use

of powder X-ray diffraction method [7, 8] and compared with parameters of pure TGS. Temperature characteristics of spontaneous polarisation Ps were measured, after observations of domain structure of new material and theoretical model of correlation between domain structure parameters and spontaneous polarisation was developed and verified by measurements [10]. Samples were divided into three groups with different domain structure distortion parameter. Measurements of coercive field [9] were conducted within mentioned groups and compared with each other.

2. EXPERIMENT

CRYSTAL GROWTH

TGS was obtained in reaction of sulphuric and amino-acetic acids. Chemical formula of TGS is: $(NH_2CH_2COOH)_3 \cdot H_2SO_4$. Solution of TGS was obtained by mixing proper amounts of distilled water and mentioned above acids. Such obtained solution was filtered and left for crystallisation. Crystals were dissolved in distilled water and left for successive crystallisation, in order to eliminate impurities.

Pure crystals of TGS were dissolved in distilled water and after addition proper amount of l-lysine (10 % by weight) left for the crystallisation. In the moment when spontaneous crystallisation occurred at the bottom of the crystallisation vessel, small single crystals were taken off and treated as the seeds for the regular crystal growth. Seeds were mounted on the end of the rotative handle, plunged in the solution. Handle was rotating with speed 60 rev./min. Evaporation speed was adjusted experimentally.

CHARACTERISTIC OF THE SINGLE CRYSTAL

Obtained crystals were investigated with use of powder diffraction method [7,8] (apparatus DRON 2.0 with goniometer GUR5, quartz monohromator and Cu lamp), in order to confirm the change of parameters of the unit cell, as a result of doping process. Unit cell parameters were calculated with use of DHN-Powder Diffraction System software.

Single crystals were cut into 2mm slices, with use of wire saw, perpendicular to the ferroelectric b axis. After mechanical treatment samples were formed in a shape of rectangular parallelepiped, measuring 6mm x 6mm x 2mm. Observations of the domain structure were performed after ageing of the samples i.e. after 200 hours after last phase transition [5, 6]. This method was chosen because active elements of the pyroelectric detectors, working at room temperature, have no possibility to rejuvenate in nominal conditions. Polished surface of the samples were then etched with amonium water in order to visualise the domain structure. In order to increase the contrast thin layer of the liquid crystal was deposited on the samples' surface. Two kinds of different liquid crystals were used (MBBA, PCB).

Images of domain structure in polarised light were registered by CCD camera, with video output connected to the PC. After the observations of the domain structure silver electrodes were attached to the samples (b surfaces of the samples were covered by silver conductive paste).

Previous works confirmed that basing on observations of the domain structure one can perform preselection of the samples and „predict" values of spontaneous polarisation [10]. In order to do this distortion coefficient Wsp has to be calculated according to the formula (1).

$$W_{sp} = 1 / n \left[\sum_{1}^{n} \left(\frac{\pi \left(\frac{2 P_i}{O_i} \right)^2}{P_i} \right) \right] \tag{1}$$

Estimated values of Wsp [10] were taken as boundary values in the process of samples classification. Samples were classified into three groups, after observations of domain structure in (110) growth pyramid and after calculation of the average value of Wsp coefficient, for domain patterns observed in these areas of the samples.

Table 1

Values of Wsp coefficient calculated for three types of assumed domain structure

Type of the domain structure	Wsp value
I	0,83
II	0,53
III	0,15

GR I contains samples with Wsp higher then 0,83. GR II contains samples with Wsp reaching values between 0,83-0,53 and GR III samples with Wsp reaching values between 0,53-0,15. Exemplary temperature dependencies of coercive field in particular groups are presented in Fig. 4.

3. RESULTS

Morphology of the new obtained TGSL10 single crystal differs from the morphology of pure TGS. Dimensions of the b (0,1,0) surface are larger, which makes this material more attractive from the point of view of technology and its application in IR detection devices. Parameters of the unit cell were changed. Unit cell parameters for pure TGS and TGSL10 are presented in Table 2. Morphology of the new obtained TGSL10 is presented on Figure 1. Figure 2 contains the diffraction peaks for TGSL10.

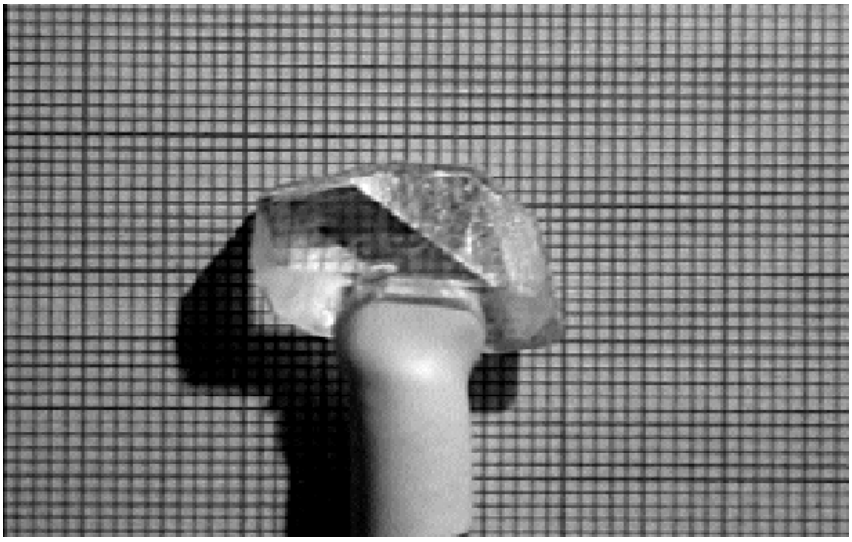

Fig. 1. Morphology of the new obtained TGSL10

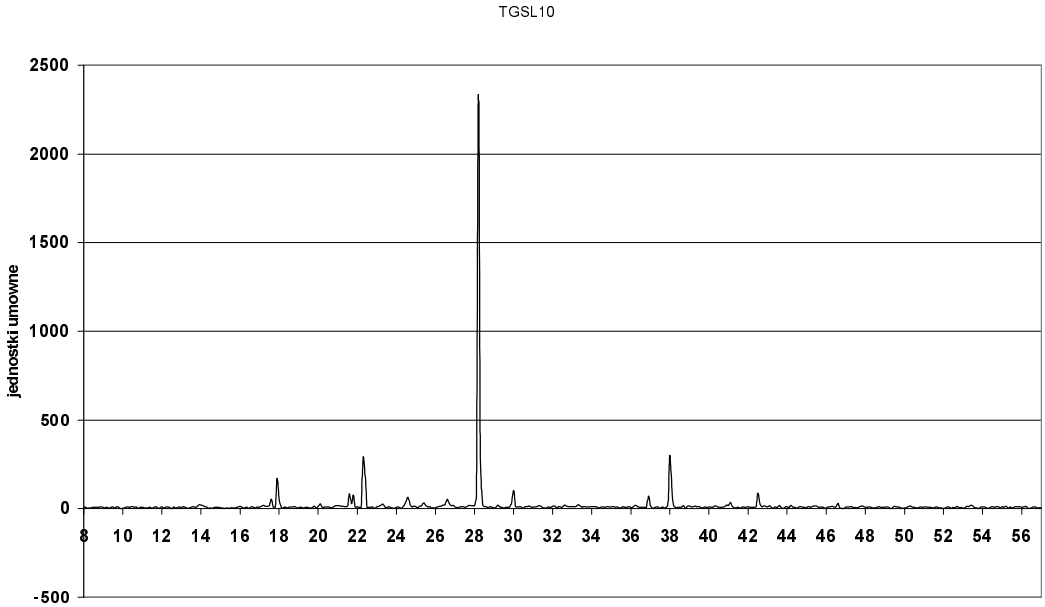

Fig. 2. Diffraction peaks for TGSL10

Table 2

Unit cell parameters for TGSL10 and TGS

Material	a, Å	b, Å	c, Å	ß	V, $Å^3$
TGSL10	9.481	12.643	5.721	110.414	642,721
TGS	9.401	12.633	5.719	110.259	637.239

where a, b, c, ß are parameters of the unit cell in notation of monoclinic system and V is the volume of the unit cell.

Diffraction diagram presents intensity of the diffraction peaks as a function of position angle 2θ in the range of 8º to 56º. Observations were made in the range of 5º to 125º with step 0.1º. Beyond the range of 2θ, presented on picture 1, diffraction peaks were not observed. Most of the domains observed in (110) growth pyramid were lenticular and elongated in direction perpendicular to c (0,0,1) axis of the crystal. Because the concentration of the dopant was not high, significant differences of domain amount were not observed when compared with pure TGS. Domains observed in TGSL10 were more elongated. Images of domain structure of TGSL are presented on Figures 3a and 3b.

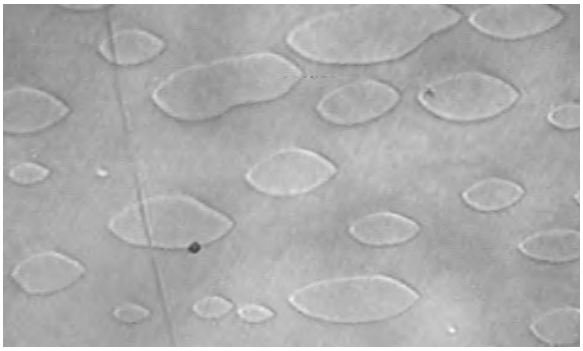

Fig. 3a. Domain structure of TGSL10 observed after etching

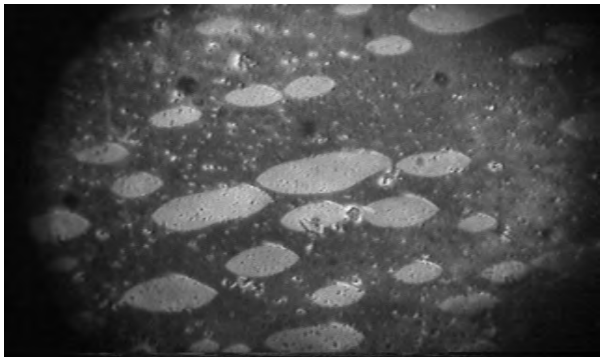

Fig. 3b. Domain structure of TGSL10 observed after deposition of liquid crystal

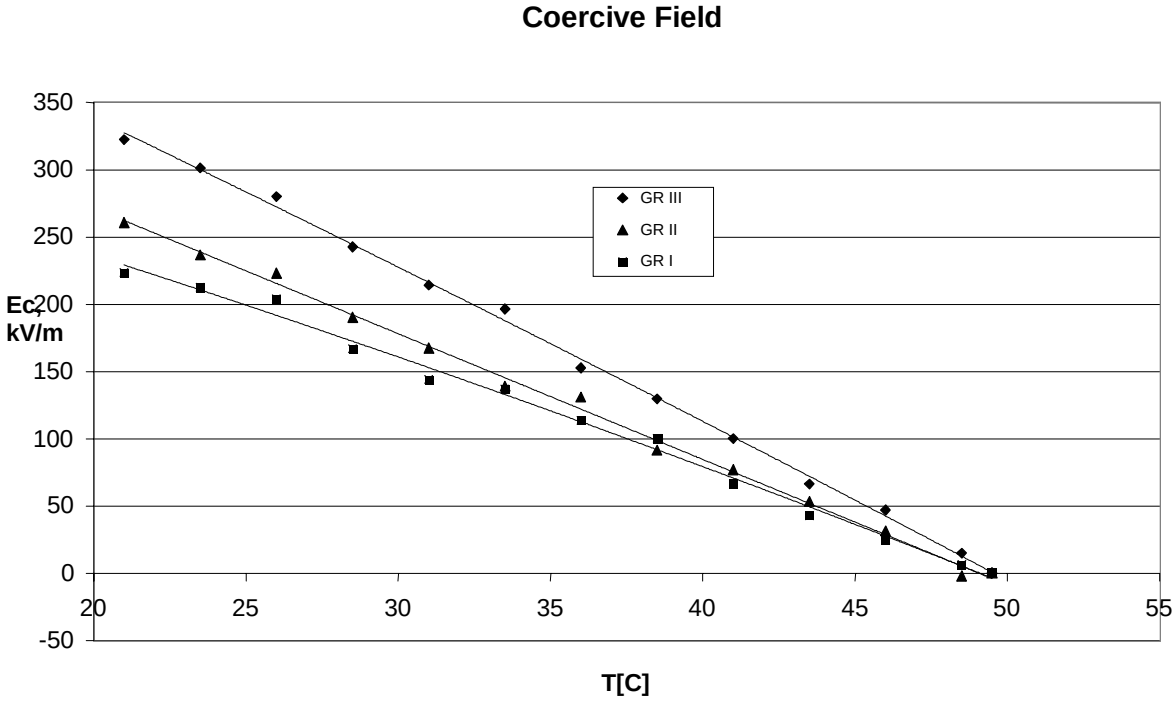

Fig. 4. Temperature dependencies of spontaneous polarisation measured for the samples belonging to different groups

4. CONCLUSION

New pyroelectric material TGSL10 was obtained. Dopant has significant influence on the morphology, electric properties and domain structure of the material. Influence of the dopant was also confirmed in case of the unit cell parameters. Increase of Ec was observed as well as higher linearity of this parameter, when compared with pure TGS. Growth plane b(0,1,0) was wider, what makes new obtained material more attractive from the point of view of its application. It was proven, that simplified mathematical model found confirmation in case of the real single crystals and let us predict the values of the spontaneous polarisation and coercive basing on observation of

the domain patterns. The higher is distortion of the domain structure (low value of Wsp coefficient) the higher are coercive field values. This makes possible preparation of the simplified method of samples classification based on optical observations.

5. REFERENCES

1. *P. Rosakis, Q. Jiang, „On the Morphology of Ferroelectric Domains", Int. J. Energy Sci. 1995, vol. 33, no. 1 pp. 1-12.*
2. *X. Sun, M. Wang, Q-W. Pan, C-S. Fang, „Study on the growth and properties of guanidine doped Triglicine Sulphate crystal", Crystal Research & Technology 1999, vol. 34, no. 10, pp. 1251-1254*
3. *J. Stankowska, E. Peter, A. Czarnecka, „The effect of D-phenylalanine admixture on dielectric properties and domain structure of TGS crystals", Ferroelectrics*
4. *W. Shi, M. Wang, X. Sun, C. Fang, „Properties of LUTGS crystal grown above Curie temperature", Ferroelectrics 1999, vol. 221, pp. 123-127*
5. *J.W. Hong, K.H. Noh, „Surface charge density and evoluation of domain structure in TGS determined by electrostatic-force microscopy", Physical Review B 1998, vol. 58 no. 8*
6. *VA. Gunyakov, AM. Parshin, BP. Khrustalev, VF. Shabanov, „Detrmining the orientation of the director of a nematic liquid crystal on the surface of a ferroelectric crystal", Optiko-Mekhanicheskaya Promshlennost 1997, vol. 64, no. 5, pp. 96-98*
7. *W. Paszkowicz, „Aplication of Optimisation to Powder Pattern Indexing", J. Apl. Cryst. 1987, 20, 3, 166-172*
8. *W. Paszkowicz, „On the Estimation of Unit Cell from Powder", J. Apl. Cryst. 1987, 20, 3, 161-165.*
9. *B. Woś, W. Proszak, M. Trybus „Komputerowe stanowisko do pomiarów parametrów pętli histerezy dielektrycznej w oparciu o ideę mostka pomiarowego Diamanta-Drecka", MKM 2000 – materiały konferencyjne, pp. 613-618*
10. *M. Trybus, W. Kalita, W. Proszak "Relation Between Domain Structure Distortion and Spontaneous Polarisation in l-lysine Doped TGS Single Crystals", ICSS Zakopane 2002*