Journal of Optoelectronics and Advanced Materials Vol. 3, No. 1, March 2001, p. 75 - 81

INVESTIGATIONS OF PYROELECTRIC PROPERTIES OF PURE AND ALANINE DOPED TGS CRYSTALS

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Pyroelectric measurements were performed on pure and on L or D alanine doped TGS. Crystals were grown in paraelectric phase (~52 °C) from solutions by slow evaporation of the solvent. Pyroelectric current was measured by, crossing the Curie point, both on heating and cooling. Spontaneous polarization $P_S(T)$ was also recorded using the charge integration method. The pyroelectric current of pure TGS samples along with the spontaneous polarization were detected only on heating, using a poling procedure similar to those applied to ceramic ferroelectrics. The remarkable asymmetry of measured pyroelectric coefficient of D and L alanine doped samples suggests a non-equivalent substitution of glycine in the host lattice.

(Received December 15, 2000; accepted February 22, 2001)

Keywords: TGS, Alanine doped TGS, Pyroelectric coefficient

1. Introduction

Triglycine sulphate single crystal (TGS) with the formula $(NH_2CH_2COOH_3)H_2SO_4$ is a ferroelectric material used for pyroelectric detector applications. The temperature dependence of Gibbs free energy expansion coefficients of pure TGS single crystals were determined according to the thermodynamic theory, by two methods [1,2]. Some ferroelectric parameters of pure and doped TGS single crystals were previously investigated [3-5]

The structure of alanine is similar to that of glycine molecule in TGS, except the CH_3 asymmetric group. The mechanical tension induced by alanine dopant in the crystal structure allows only a limited substitution concentration, usually less than ~1 %. The segregation coefficient of L-alanine in TGS crystal was estimated [6] to be about 0.01 versus the solution concentration. Doped crystals show a distorted habits versus pure TGS. Mirror external shapes of L versus D alanine doped crystals, suggest an equivalent substitution of the glycine GI molecule in the lattice [7]. However, ferroelectric properties of racemic (L+D) alanine doped TGS crystals suggest a non-equivalent substitution of L/D alanine in the host lattice [3, 5]. So far, only L-alanine doped crystals were intensively studied [4, 6-9].

2. Crystal growth and doping

Growing solution was prepared using previously synthesized and purified TGS substance [10]. The initial concentration of L or D alanine in solutions was x = 50 mol % versus TGS and equivalent stoichiometric H_2SO_4 was added. Solution preparation and treatment was similar to the procedure described in refs. [3, 9]. Crystals were grown in similar conditions by slow evaporation of the solvent in paraelectric phase at ~ 52 °C. The thermostating system ensured ± 0.1 °C accuracy control during the growth period of 40-50 days. Crystals with linear dimensions of 3-5 cm were obtained. Well faceted crystals were selected for measurements. Up to 10 samples were cleaved from one crystal and samples thickness of 0.5-0.7 mm were prepared by polishing. Silver-paint electrodes were used.

3. Experimental procedure

A variety of techniques were described [11] in the measurement of the pyroelectric coefficient (by measuring the voltage, the charge or the d.c. current appeared during the temperature variation of the crystal).

The pyroelectric coefficient defined as:

$$p = \frac{dP_s}{dT} \tag{1}$$

was obtained from the pyroelectric current, see Fig. 1, according to the equation[12]:

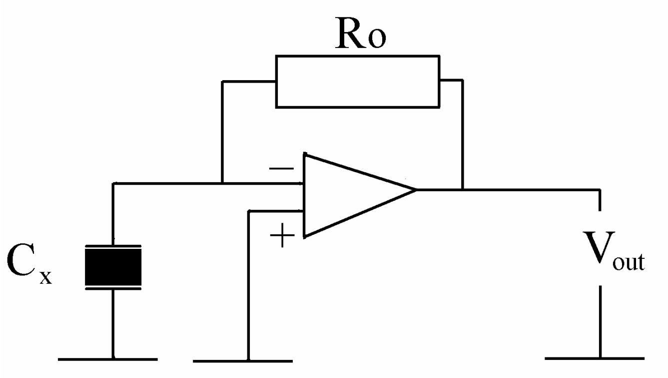

Fig. 1. General scheme for the measurement of the pyroelectric coefficient.
C_x - sample, R_o - resistance, V_{out} - output voltage.

$$p = \frac{V_{out}}{R_0} \cdot \frac{1}{A(dT/dt)} \tag{2}$$

In eq.(2), (dT/dt) is the heating rate and A is the sample area.

We have measured also the spontaneous polarization by charge integration method [12]. The output voltage (V_{out}) in Fig. 2 is given by:

$$V_{out} = \frac{1}{C_0}\int_0^t idt \tag{3}$$

were i(t) = A p (dT/dt) is the pyroelectric current.

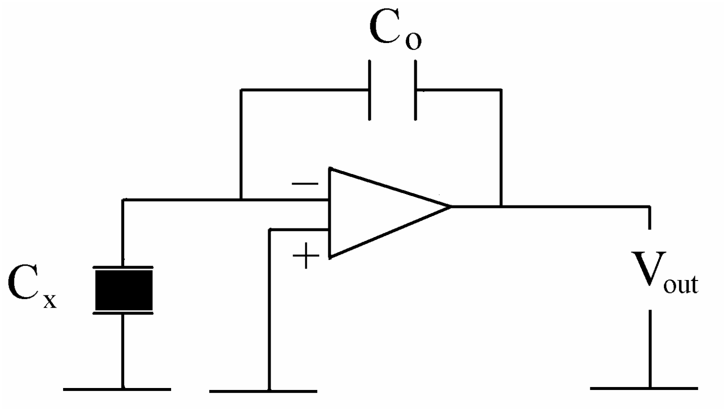

Fig. 2. General scheme for the measurement of the spontaneous polarization by charge integrated method. C_x - sample, C_o - integration capacitor, V_{out} - output voltage.

Spontaneous polarization $P_S(T)$ can be calculated according to the equation:

$$V_{out} = \frac{A}{C_0}\left[P_S(T_C) - P_S(T)\right] \qquad (4)$$

were $P_S(T_C)$ is usually kept as zero reference.

The charge integration method is very useful for P_S determination at low temperatures (where polarization reversal may not be possible), provided that calibration of the polarization at one temperature be possible. The change of spontaneous polarization as a function of temperature is easily obtained by integration of the pyroelectric charge (eqs.3 and 4).

4. Experimental results

Pyroelectric measurements were performed on pure and L/D alanine doped TGS crystals. The samples were mounted in a cryostat and the pyroelectric current was recorded with a computer controlled Keithley 6517 electrometer, both on heating and on cooling. The experimental data were handled with Origin 3 program and the results are presented below.

4.1. Pure TGS

Pyroelectric coefficient (PC) and spontaneous polarization could be measured only on the first heating experiment of a sample. Data are presented in Fig. 3 and Table 1. Peak value of the PC on this heating run is comparable with Landolt Börstein data [13] and L/D doped TGS samples (see Table 1).

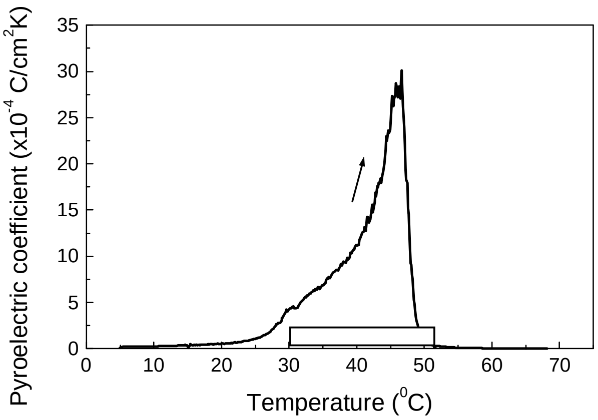

Fig. 3. Temperature dependence of the pyroelectric coefficient for pure TGS crystal. The curve was obtained on heating after poling the sample by applying a d. c. electric field of E = 2 kV/cm at room temperature. The heating rate was 0.2 K/sec.

On cooling from the paraelectric phase the PC and P_S surprisingly have extremely small and non-reproducible values in Fig. 4. In successive runs the measured values of PC and P_S decreases continuously. The P_S values in Fig. 4 are about two orders of magnitude smaller than the P_S values usually measured by Sawyer-Tower method [1,3,8,13]. A long tail of the P_S curves in the paraelectric phase (Fig. 4), suggests the space charge in the body of the samples has an important contribution.

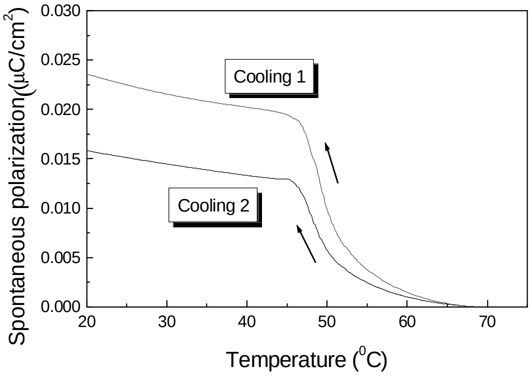

Fig. 4. The temperature dependence of the spontaneous polarization experimentally recorded for pure TGS crystal. The curves were obtained on cooling from paraelectric phase in two successive runs.

4.2. L alanine doped TGS

Data are presented in Figs. 5, 6 and in Table 1. Spontaneous polarization at room temperature has comparable values with pure TGS (Fig. 6, Table1). Sawyer-Tower measurements show distorted hysterezis loops (samples TGS:(L al) -30 A, crystal 3, plate 1 and plate 2.2), having the bias field E_B comparable with the coercive field E_C and $P^+ > P^-$. A standard dependence of this last parameters $(P_S)^2 \sim (T - T_C)$ was noticed at $T \geq 40\ ^0C$ (data not presented here).

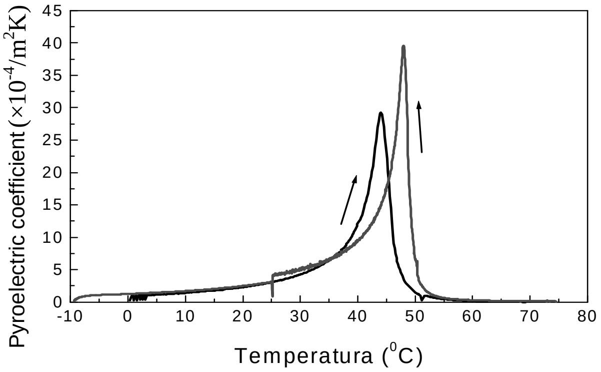

Fig. 5. The temperature dependence of the pyroelectric coefficient for of L-alanine doped TGS crystal. The arrows show the results obtained on heating (0.24 K/s) and on cooling (0.06 K/s).

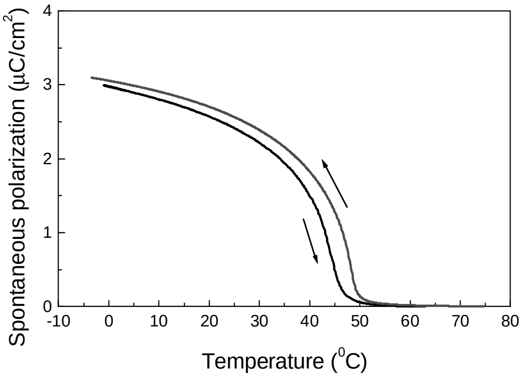

Fig. 6. The temperature dependence of the spontaneous polarization experimentally recorded for L-alanine doped TGS crystal (see Fig. 2). The arrows show the data obtained on heating / cooling.

4.3. D alanine doped TGS

The temperature dependence of the PC values for these samples apparently seems to be quite similar to that from L alanine doped samples (Figs. 5,7). However, significantly higher values of PC and of the spontaneous polarization were recorded (by charge integration technique) for D alanine doped samples (see Figs. 6, 8 and Table 1). The peak values of the PC on heating and cooling do not coincide for both types of samples. A small temperature hysteresis in the samples, versus thermocouple recordings, might not be excluded (heating rates ~0.2 ^{o}C/s, cooling rates ~0.05 ^{o}C/s). However, the smaller peak of the PC on heating is displayed in opposite directions versus the higher peak on cooling (at 48 ^{o}C), in D and L alanine doped samples. This strange effect, specially tested in several samples, could not be satisfactorily explained. A space charge effect is probably involved (see also the temperature dependence of the spontaneous polarization in Figs. 6 and 8).

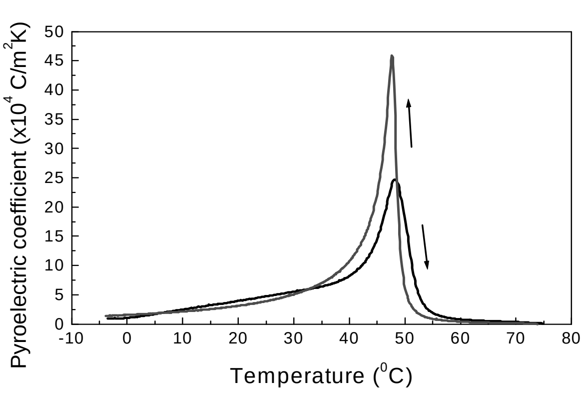

Fig. 7. Temperature dependence of the pyroelectric coefficient for of D-alanine doped TGS crystal. The arrows show the results obtained on heating (0.19 K/s) or on cooling (0.06 K/s).

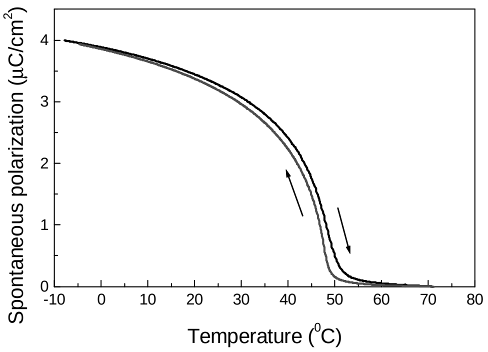

Fig. 8. The temperature dependence of the spontaneous polarization experimentally recorded for D-alanine doped TGS crystal (see Fig.2). The arrows show the data obtained on heating / cooling.

5. Discussion

Pyroelectric current of pure TGS samples was detected only during heating, following a poling procedure similar to those applied for ceramic ferroelectrics ($E^{DC} \approx E_{COERCIVE}$). The special behavior of ferroelectric parameters PC and P_S for pure TGS samples, crossing up and down the Curie point, can be explained on the basis of domain structure evolution. Coming from the paraelectric phase, a very large number of ferroelectric domains nucleate in the ferroelectric phase. Subsequently, the minimum of the free energy of the system is attained as a result of the balance of the number of opposite ferroelectric domains which decreases the free energy and the increase of this energy due to the increased length of the domain walls. There is a typical evolution of the domain topography, with a relaxation time of the order of one hundred of hours, described in the literature [7] and correlated with a typical evolution of the permittivity and losses, crossing up and down the Curie point [2,5].

L or D alanine doped TGS crystals show significant different behavior. Peak values occur around 44.5 - 49.1 °C, respectively on heating and close to 48.0 °C on cooling. Both type of doped samples show tails of the PC and P_S curves in the paraelectric phase due to space charges accumulated in the body of the samples. This effect (Fig. 4) is remarkable on cooling of pure TGS samples. The peak values displacement of PC curves versus temperature for the L/D doped TGS samples might be dependent on the heating/cooling rate, but it seems to depend also on the sample structure by doping. Experimental data of the PC for doped samples recorded on the computer have been analytically identified and separately integrated curves versus temperature were in very close agreement with the $P_S(T)$ curves experimentally measured by the charge integration method.

Alanine doped crystals present unipolarity (are monodomain), or have very few domains of opposite polarity. Usually they have much smaller and reproducible values of the permitivity and losses [2,3,5,14]. These crystals are much more suitable for IR detector applications [5,14].

An important asymmetry of L versus D alanine doped TGS crystals for PC and P_S was established in this paper. This fact supports the previously suggested supposition that L and D alanine substitution in the TGS lattice do not take place in the same glycine GI position [3].

Present data undoubtedly show that D alanine doped TGS crystals have higher pyroelectric coefficient than L alanine doped crystals and is more suitable for pyroelectric applications.

Table 1.

Crystal	Pyroel. Coefficient at 20 ^{0}C, ($\times10^{-4}$, C/m^{2}K)	Peak Pyroel. Coefficient ($\times10^{-4}$, C/m^{2}K)	Spontan. Polariz. at 20 ^{0}C, ($\times10^{-2}$, C/m^2)
TGS:Dal (heating)	↗ 3.0_1	33.7_1 (at 49.1_5 ^{0}C)	3.5_3
TGS:Dal (cooling)	↘ 3.2_6	52.8_1 (at 48.0_5 ^{0}C)	3.5_7
TGS:Lal (heating)	↗ 2.4_4	29.4_4 (at 44.5_5 ^{0}C)	2.6_0
TGS:Lal (cooling)	↘ 2.4_8	39.5_1 (at 48.0_5 ^{0}C)	2.7_0
TGS pure (heating)	↗ 0.32	31.4_8 (at 46.0_5 ^{0}C)	2.3_6

6. Conclusions

Pure TGS samples show the peak value of the pyroelectric coefficient (only on heating) in reasonable agreement with the literature data [13]. On cooling from paraelectric phase, partially or even totally compensated polarization, due to domain instability [3], gives very small and uncertain values.

The remarkable asymmetry of PC values for D and L alanine doped crystals suggests a non-equivalent substitution of glycine in the host lattice of TGS, in agreement with [3].

Higher pyroelectric coefficient values of D alanine doped TGS crystals versus L alanine doped TGS crystals show the doped crystal is more suitable for practical applications.

References

[1] H. V. Alexandru, C. Berbecaru, A. Popescu, Anal. Univ. Bucuresti-Fizica **45**, 73 (1996).
[2] H. V. Alexandru, C. Berbecaru, the 3-rd European Conference on Applications of Polar Dielectrics, Bled, Slovenia, ECAPD-3, Sept. 1996, Abstract Booklet pag.156.
[3] H. V. Alexandru, C. Berbecaru, Ferroelectrics, **202**, 173-182 (1997).
[4] J. Stankowska, A. Czarrecka, B. D. Gemi, Acta Phys. Pol. **83**, 485 (1993).
[5] H. V. Alexandru, Intern. Conf. on Crystal Growth XI, Hague, P 106.02, June 1995.
[6] E. T. Keve, K. L. Bye, P. W . Whipps, A. D. Annis, Ferroelectrics **3**, 39 (1971).
[7] B. Brezina, M. Havrankova, Cryst. Res. Technnol. (a) **20** (1995) 781, (b) **20,** 787 (1995).
[8] C. Berbecaru, H. V. Alexandru**,** B. Logofatu, A. Stanculescu, F. Stanculescu, ICCG XII, Jerusalem Israel, abstract pag 379, July 1998.
[9] H. V. Alexandru, C. Berbecaru, B. Logofatu, A. Stanculescu, F. Stanculescu, J. Optoel. Advanced Materials **1** (4), 57 (1999).
[10] H. V. Alexandru, C. Berbecaru, Crystal Res. Technol. **30**, 307 (1995).
[11] M. E. Lines, A. M. Glass, “Principles and Applications of Ferroelectrics and Related Materials”, Clarendon Press, Oxford (1977).
[12] W. M. Dolyle, “A User’s Guide to Pyroelectric Detectors”, Laser Prec. Corp., 1984.
[13] Landolt Borstein, vol.16, Ferroelectric and related substances, Springer-Verlag, p. 610, 1982.
[14] C. Berbecaru, G. Conache, H. V. Alexandru, L. Pintilie, B. Logofatu, M. Craciun, ROCAM 2000, Romanian Academy, 23-25 oct.2000, Abstract Booklet, pag. 29.
[15] M. Costache, I. Matei, L. Pintilie, H.V. Alexandru, C. Berbecaru, ROCAM 2000, Romanian Academy, Abstract Booklet, pag. 116, 23-25 oct. 2000.