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GROWTH AND CHARACTERIZATION OF PURE AND ALANINE DOPED TGS CRYSTALS

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Growth and characterization are presented for pure and alanine doped TGS crystals. Permitivity and losses of pure TGS show a peculiar behaviour in the ferroelectric phase, crossing up and down the Curie point, in two successive runs between room temperature and 60 °C. There were found for alanine doped crystals reproducible values of permittivity which are lower than those from pure TGS crystals, thus pointing to much higher figures of merit of this material for IR detectors. TGS:(L+D)alanine doped crystals show peculiar ferroelectric hysteresis loop, composed of three elementary cycles. The bias field and the coercive field of the two pined components show different behavior both for increasing a.c. field and temperature, suggesting a non-equivalent substitution of alanine in the crystal lattice. Doped TGS:(L) alanine crystals show stable permittivity versus temperature and much smaller losses than in pure ones. Asymmetrical hysteresis loops of highly pined ferroelectric domains and the bias field much larger than the coercive field have been also observed.

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1. Introduction

Triglycine sulphate crystal (TGS) with the formula $(NH_2CH_2COOH)_3\ H_2SO_4$ is a ferroelectric material used for pyroelectric detector applications. Growing conditions of pure crystal were intensively studied [1-5]. Crystal purification by fractional recrystallisation, peculiar growth kinetic and the influence of impurities have been studied previously [6]. The temperature dependence of the Gibbs free energy expansion coefficients of pure TGS crystals was determined according to the thermodynamic theory, by two methods [7,8]. Some ferroelectric parameters of pure and doped TGS crystals were investigated [9-11].

Alanine dopant is similar to glycine, except the CH_3 asymmetric group (see below). Alanine doped crystals show a distorted habitus versus pure TGS. Mirror external shapes of L versus D alanine doped crystals [12], suggest an equivalent substitution of the glycine GI molecule in the lattice [13], but no reliable data are available. It is the purpose of this paper to show that TGS:(L+D) alanine doped crystals do not display symmetrical properties and the bias field introduced by the two components are remarkably different. TGS:L alanine doped crystals show more stable values of the permittivity and losses versus temperature, show strongly pined polarization and the bias field much higher than the coercive field. For higher level of doping much lower polarization values are recorded and the distorted hysteresis loops show irregular creeping of the ferroelectric domains by switching in the a.c. field.

2. Crystal growth and doping

Pure TGS crystals and crystals doped by racemic mixture of (L+D) alanine were grown in the same conditions by slow solvent evaporation at 45 and 35 ^{o}C, i.e. in the ferroelectric phase.

In the experiment 4$^{\#}$, the growth solution was prepared using previously purified TGS substance [9] and x = 25 mol % (L+D)-alanine pro mol TGS, (concentration c = 7.5 %) and the equivalent stoechiometric H_2SO_4 , according to the hypothetical equation [12b]:

$$(1-c)\,[G_3\,H_2\,SO_4] + c\,[al_3\,H_2\,SO_4] = [G_{3(1-c)}\,al_{3c}\,H_2SO_4] \qquad (1)$$

c is molar fraction alanine, in the mixture alanine and glycine, where "G" is the glycine (NH_2 CH_2 COOH) and "al" is alanine (NH_2 CH CH_3 COOH). The relation between the two concentrations according to the formula $[G_{3-x}\,al_x\,H_2SO_4]$ are $x = 3\,[1/c - 1]^{-1}$. Crystals in this experiment were grown for a temperature decrease from 45 to 35 ^{0}C.

In the experiments TGS:(L) noted 7 $^{\#}$ and 8 $^{\#}$, L alanine concentration in solution was x = 75 % (c ≈ 20 %). The solubility of the basic substance was somewhat higher, but at pH = 2.5 according to the stoechiometric equation (1), did not agree with the literature data [12b]. The crystals were grown by slow evaporation at 38 ^{0}C during 40 and 60 days, respectively.

In the experiment TGS:(L) alanine 9 $^{\#}$, crystals were gown at 54 ^{0}C (i.e in the paraelectric phase), by slow solvent evaporation. The initial concentration in solution was: x ≈ 120 %, (c ≈ 28 %). Heavy doping in this case produced strained crystals which cracked spontaneously during handling and presented distorted hysteresis loops.

3. Experimental

Several single crystals successively grown from the same solution were investigated. Taking into account [12,13] the segregation coefficient of ~ 0.01, the dopant concentration in our crystals was estimated to be no more than 0.5 mol %, except in the experiment 9 $^{\#}$.

Samples of sizes d = 1.0-1.5 mm, S = 0.6 - 0.8 cm^2 were cleaved from the crystals grown from solution. Silver paste was used as electrodes. The sample holder was mounted in to a special furnace that allowed temperature sliding at about 0.2 ^{o}C/min.

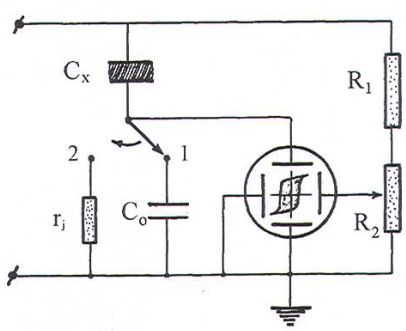

Fig. 1 Sawyer-Tower experimental scheme. Switching on r_j position the recharging current of the sample can be displayed as in Fig.2.

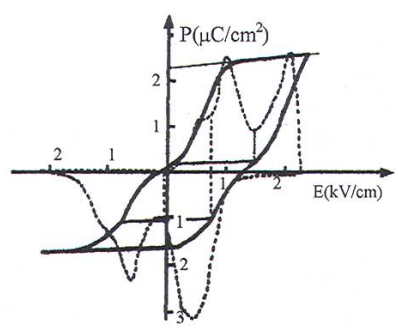

Fig. 2 Typical images of the hysteresis loop and the recharging current loop, for TGS:(L+D) alanine doped sample.

The permittivity ε_r and dielectric loss tgδ were measured with a self-acting bridge at 1 kHz as a function of temperature, which was ran up and down between room value and 70 ^{0}C. Polarization components P^+, P^-, coercive field components E_C^+, E_C^- and the bias field E_B have been measured versus temperature and intensity of the applied a.c. electric field, E_{ac}, up to 6-8 kV/cm. It has been used a modified Sawyer-Tower circuit (Fig. 1), which allowed to record sequentially on the oscilloscope screen the hysteresis loop (HL) and its derivative (i.e. the recharging current loop). This last procedure was particularly very useful in the decomposition of the HL of TGS:(L+D)alanine.

The boundary between the elementary cycles of that hysteresis loop has been set-up at the minimum values of the recharging current loop, as in Fig. 2.

4. Results

a/ Pure TGS samples show unstable values of the relative permittivity and dielectric losses after an intended or accidental excursion of temperature through the Curie point ($T_C = 49.2$ ^{0}C). Large differences of ε_r (and $1/\varepsilon_r$) values can be noticed in Fig. 3-a, particularly in the ferroelectric region, running up and down the temperature of pure TGS samples. This effect appears to be related to the changes of topography and the number of ferroelectric domains, due to a transient stage towards the minimum of the free energy of the system [14]. In L-alanine doped samples both ε_r and tgδ decrease about one order of magnitude versus pure TGS samples. Besides, both parameters are much more stable against large variations of the temperature (see Fig. 3-b). This effect can improve appreciably the figure of the merit of material used in a pyroelectric device [15].

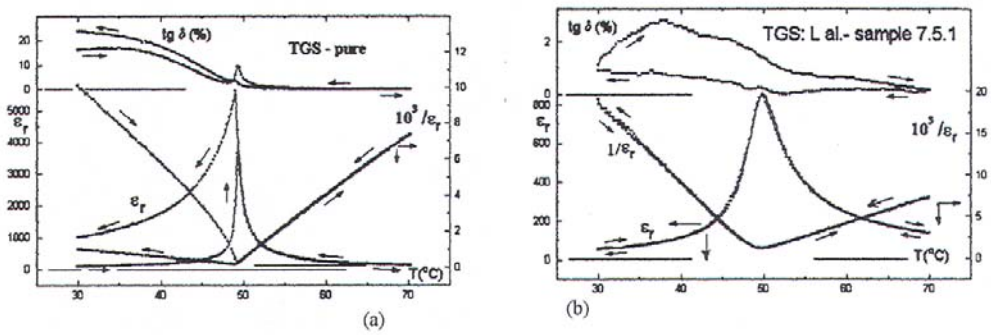

Fig. 3 Permittivity and losses for pure TGS (a) and for TGS:L alanine doped crystals (b). The reverse of the permittivity $1/\varepsilon_r$ shows large differences for pure TGS in the ferroelectric phase crossing up and down the Curie point. TGS:L alanine doped samples shows more stable, reproducible and smaller values of permittivity ε_r and losses tgδ.

b/ TGS:(L+D)alanine samples show distorted HL, built up of three elementary cycles due to a switching component P' and two other nonequivalent components P^A and P^B pined by dopants in opposite directions. They change their shares in the HL, versus the a.c. electric field. The pinned components represent about 20% of the polarization for pure TGS at saturation of the HL. This ratio is much larger than the dopant concentration in the crystal, which is less than 0.5 %. The dependence of these components on temperature is presented in Fig. 4a. One observes a different behaviour as a function of type of alanine substitution of L or D in the TGS lattice. The temperature dependence of the coercive field components E_C^+, E_C^- in Fig. 4b shows large differences. The polarization components P^+ and P^- are almost equal for this sample. These facts suggest [9,16] that the substitution of L and D alanine components in the TGS crystal lattice is not equivalent.

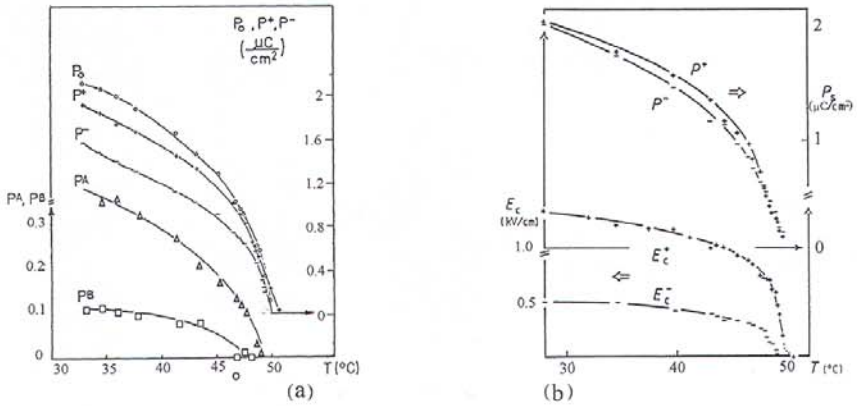

Fig. 4 The temperature dependence of several polarization components of TGS:(L+D) alanine doped crystals. The polarization components P^+ and P^- were measured in the opposite direction of the hysteresis loop. a) P^A and P^B correspond to estimated values of the polarization components pined by dopants. b) Another sample showing polarization components P^+ and P^- almost equal and having the same temperature dependence. The corresponding coercive field components E_C^+ and E_C^- behaves quite differently versus temperature.

c/ TGS:(L)alanine samples show a bias field of $E_b \cong 2\text{-}3$ kV/cm, much higher than the coercive field $E_c \cong 0.6\text{-}0.8$ kV/cm and a remarkable different behaviour versus temperature in Fig. 5b. Higher L-alanine doping ensures higher and asymmetrical pinning of the polarization. The component P^+ have a normal behaviour with temperature, while P^- component is considerably smaller and remains almost constant up to ~ 40 ^{0}C in Fig. 5a.

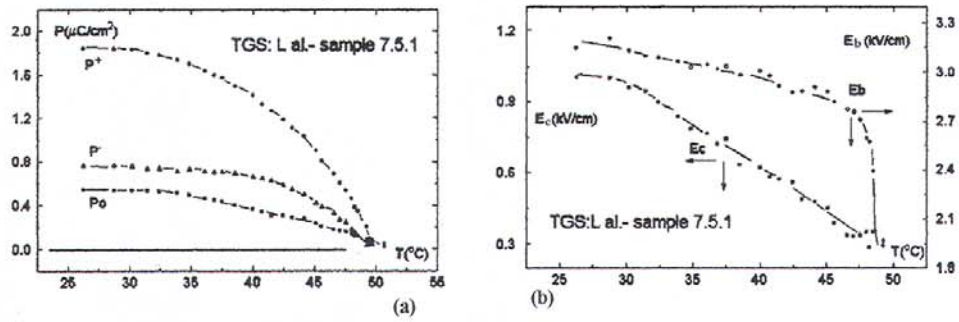

Fig. 5 Essential ferroelectric parameters versus temperature, measured on the saturated hysteresis loop, for TGS:L alanine doped crystals. a) Pined component P^+ have a normal behavior with temperature, while P^- component is almost constant up to about 40 ^{0}C. b) Bias and coercive field for the same sample has a significantly different behaviour versus temperature.

Some samples, cleaved on the +b direction from the crystal, show unusual higher saturation value of $P^+ \cong 4$ μC/cm^2 (as in Fig. 6), compared with the usual values for pure TGS of about 2.7 μC/cm^2 at room temperature.

L alanine doped crystals show also a noticeable anisotropy of growth along the ferroelectric axis, in good agreement with [12a, 17]. The shape of the HL has a different evolution increasing the a.c. electric field, for the samples sliced from the opposite direction of the ferroelectric axis, as in Fig. 6. We have to notice that the HL opens at a.c. electric field peak values larger than ~(Eb +Ec). The HL shows unipolarity at smaller a.c. field values on the pined direction P^+. Up to about 2 kV/cm

for +b sliced samples and up to about 4 kV/cm for -b direction sliced samples (along the ferroelectric axis), the HL does not show the P^- component. Numbers on several cycles in Fig. 6 show several stages of the HL, increasing the electric field.

We have to emphasize that on the –b direction of the ferroelectric axis, crystal growth rate is slower, the doping is higher and the polarization values are smaller. The tilted over shape of the HL for the sample 7.5.1, shown in Fig. 6 (right hand side), suggests the ferroelectric domains are much highly pinned by dopant for both P^+ and P^- components. There is some bending on these loops, suggesting that dislocations or some other kind of lattice defects might be involved [9].

d/ TGS:(L)alanine 9 #, highly doped crystals grown in the paraelectric phase, show heavily distorted HL, bias field of ~5 kV/cm and smaller and non-reproducible polarization values.

6. Discussion

It has been shown [7,11] that unreliable ε_r (T) values are recorded in the ferroelectric phase of pure TGS, crossing up and down the Curie point. The figure of merit of the pyroelectric materials $M = p / \rho C \varepsilon_0 \varepsilon_r$ increases on the account of the pyroelectric coefficient $p = (dP_S/dT)$ and decreases on the account of permittivity ε_r. The ferroelectric domain structure and its uncontrollable evolution with temperature, (which is responsible for non-reproducible values of permittivity) make pure TGS material less suitable for pyroelectric device applications.

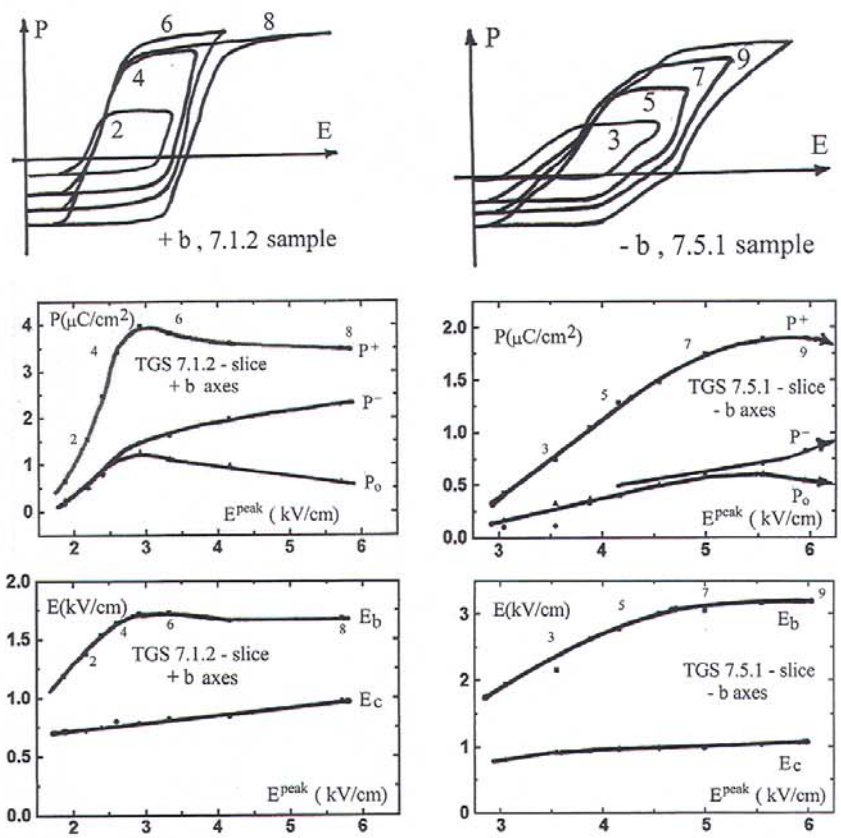

Fig. 6 The main ferroelectric parameters and the hysteresis loop evolution, versus the a.c electrical field, of TGS:(L) alanine doped sample(7#). On the –b ferroelectric direction crystal grows slower and acquires higher amount of dopant, presents higher bias field and much lower polarization values. The coercive field, however do not exceed 1 kV/cm. Figures on several hysteresis loops show several stages of the HL evolution with the a.c. electric field.

Lower and reproducible ε_r (T) values of alanine doped TGS crystals ensure higher and stable figures of merit for applications. The dielectric losses, related to the ferroelectric domain wall oscillations are about one order of magnitude smaller than those for pure TGS (Fig. 3), thus suggesting that the doped crystals seem to be mostly single-domain.

The role of the alanine molecule in the TGS lattice is related in terms of atomic motion of glycine GI group required to reverse the crystal polarity [13]. Using a simple model [16], we could estimate that about 20 % of the polarization were pined by (L+D)alanine, at the saturation of the HL, in the experiment $4^{\#}$. The polarization component P^A (associated to P^+ in Fig. 4), appears to be more firmly pinned in the TGS lattice. Usually P^A component has a larger associated bias and coercive field. Its associated cycle is much larger as a component in the HL (see also Fig. 2). Even for $P^+ = P^-$ (sample in Fig. 4b), the associated coercive field behaves significantly different versus temperature. Our experimental data suggest an asymmetrical strain field in the lattice, produced by a non-equivalent substitution of glycine by L or D alanine. This data are in contrast with the supposition according to which, the L or D alanine substitution of the glycine group GI is equivalent [13].

In fact, according to the crystal structure, investigated by Hoshino et al. [18], the planar molecule GI is located on the mirror plane at y=1/4 and 3/4 in the elementary cell and is responsible for the crystal polarization. The glycine molecules GII and GIII interchange their role as "zwitter-ion", every time the GI molecule switches the other position at the polarization reversal. The alanine molecule is both structurally and chemically similar to glycine, excepting the asymmetric position of the CH_3 group. L or D alanine substitution in the lattice "freezes" a particular structural configuration in the elementary cell. But so far, in the literature there is no evidence about the exact substitution position. The data we present here suggest a non-equivalent substitution.

TGS:(L) alanine doped crystals present interesting aspects related to the growth kinetic of the crystals from solutions. Pined polarization in the first layers grown on the seed, make an asymmetric growth kinetic of the crystal, accompanied by different doping levels and properties of the crystal in opposite direction along the ferrolectric axis. The HL has a significant bias field, much larger than the coercive field and shows unipolarity of the samples at lower a.c field intensity (Fig. 6). However, an optimum concentration of dopant is required. Lower concentration do not make the crystal single-domain, while at higher concentrations, the polarization in both directions are to strongly pined and get smaller values, decreasing the figure of merit of the material.

7. Conclusions

Pure and alanine doped TGS crystals were grown in similar conditions.

TGS:(L+D) alanine doped samples show distorted hysteresis loops, having three distinct cycles. Two opposite cycles were assigned to the domains pined in the crystal lattice by L and D components of the dopant. Their behaviour versus temperature and intensity of ac electrical field, suggests a non-equivalent substitution of glycine in the lattice.

TGS:L alanine doped crystals show growth asymmetry along the ferroelectric axis. Lower growth rate in the -b direction of the ferroelectric axis is related to higher doping, which involves lower polarization values and higher bias and coercive fields. Creeping of ferroelectric domains in the -b sliced samples (Fig. 6) are probably related to structural defects induced by higher concentration of the dopant. Spontaneous polarization of L alanine doped crystals measured with a Sawyer-Tower circuit shows different values in the opposite directions along the ferroelectric axis $P^+/ P^- > 2.5$. Some doped samples show unusual higher values of polarization ($P^+ \cong 4\ \mu C/ cm^2$), as compared to pure TGS samples ($P \cong 2.7\ \mu C/ cm^2$). The figure of merit of a pyroelectric material can be considerably increased on the account of pinned polarization which increases the pyroelectric coefficient and decreases the permittivity and losses. This is the case of our alanine doped crystals.

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