

# Influence of conduction on the dielectric properties of pure TGS crystal

N. VINETICU<sup>a</sup>, C. MINDRU<sup>a</sup>, D. MARINEL<sup>a</sup>, H. V. ALEXANDRU<sup>b</sup>

<sup>a</sup>Faculty of Physics, University of Bucharest, Romania

<sup>b</sup>Academy of Romanian Scientists, 54 Splaiul Independentei, Ro-050094, Bucharest, Romania

Triglycine sulphate crystal (TGS for short) is a ferroelectric with a Curie point around 49 °C. In pure state it has a metastable state in ferroelectric state, crossing down the transition point. TGS crystals were grown around 52 °C, in the paraelectric phase, where no mechanical tensions due to domains were present. Dielectric properties of a pure TGS sample were measured vs. 1 Hz ÷ 10 MHz frequency range during the temperature decrease from 60 °C towards the room temperature, at a constant rate of 0.6 °C/min. The Influence of conduction on the dielectric parameters, like the relaxation times and the Cole-Cole constants of the two main component of permittivity were evaluated. Strikingly, the parameters have particular dependences on several ranges of temperature. The main temperatures ranges, where the parameters change are around 35-37, 40-41 and 45-46 °C. These temperatures seem to be related with the lattice dynamic.

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## 1. Introduction

Ferroelectric materials are studied both on fundamental aspects and for electronic device applications like pyroelectric devices, nonvolatile memories, storage devices and nanofabrication. Studies were made on the relaxation phenomena of the ferroelectric domains [1-3], dielectric relaxation [4, 5], lattice dynamics [6, 7], ionic conduction and space charge polarization at low/very low frequencies [8-10].

We have previously presented the single crystal growing conditions in the paraelectric phase and important properties of the ferroelectric crystals [11, 12]. Some other important parameters we have recently analyzed [13-15].

Here, we present the influence of conduction on the assembly of experimental data on a large frequency range (1-10<sup>7</sup> Hz), down the Curie point till the room temperature.

## 2. Experimental

TGS single crystal was grown in a thermostated oven in paraelectric phase at 54 °C. Basic TGS substance was synthesized from the components and refined by fractional recrystallization [14]. Samples were cleaved from a quality single crystal, perpendicular on the ferroelectric axis “b” and polished samples were silver painted as electrodes.

Measurements were automatically measured by the dielectric spectrometer Alpha-A Novocontrol. The temperature control and the constant pace decrease was electronically monitored, using a flux of the thermostated

nitrogen according to the temperature program, from 60 °C toward the room temperature.

Both component of permittivity were automatically registered by the computer system on the frequency range 1 Hz ÷ 10 MHz, considering five equidistant measurements points in log scale, on every frequency decade. The temperature range considered here will be around and down the Curie point.

## 3. Results

The Cole-Cole dependence  $\epsilon''$  versus  $\epsilon'$ , with and “NO losses” considered, was drawn directly from the experimental data, at several temperatures around the Curie point and down. For every temperature, the three curvatures zone where fitted with arcs of circles LOW, MIDDLE and HIGH, as corresponding to the three relaxations zone (see fig.3). NO correction for arcs superposition was made, because we intended to see which parameter is more affected. For each arc of circle the relaxation time of LOW and HIGH frequencies were evaluated vs. temperature and Cole-Cole  $\alpha$ -parameter also (fig.3). Some other parameters shall be considered elsewhere.

### 3.1. Dielectric parameters around the Curie point

We have tested the dielectric parameters around the transition temperature. In fig.1 we have represented both dielectric components at 49.4 °C, in paraelectric phase, than at 48.5 °C and 47.6 °C i.e. in the ferroelectric phase.

All components show clearly an increase towards the lower frequencies, due to conductivity.

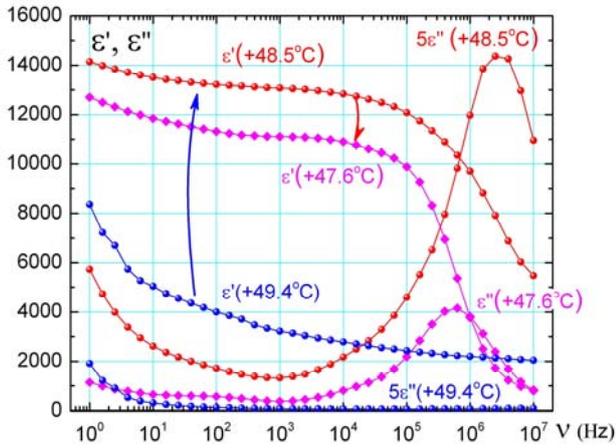


Fig.1. Real and the imaginary components of permittivity around the transition point

In the ferroelectric temperature range, the two components of losses (at 48.5 and 47.6 °C) shows maxima around  $10^6$  Hz of several intensities. The real component shows abrupt decreases in the same frequencies range. This shows the fundamental  $\epsilon''$  component of the dielectric relaxation is typically related with the ferroelectric transition. Almost no losses can be seen in paraelectric phase at 49.4 °C. Than, decreasing the temperature, at 48.5 °C a jump of the real component value of about four time and appearance of the maxima of losses can be noticed in fig.1. Further decreasing the temperature both component of permittivity decrease.

### 3.2. Influence of conductivity versus the measured frequency

The two components of permittivity in the Debye concept, taking into consideration the conductivity of the sample are:

$$\epsilon' = \epsilon_{\infty} + \frac{(\epsilon_{st} - \epsilon_{\infty})}{1 + \omega^2 \tau_{\epsilon}^2} \quad (1)$$

$$\epsilon'' = \frac{\omega \tau_{\epsilon} (\epsilon_{st} - \epsilon_{\infty})}{1 + \omega^2 \tau_{\epsilon}^2} + \frac{\sigma}{\epsilon_0 \omega} \quad (2)$$

Here  $\epsilon_{\infty}$  and  $\epsilon_{st}$  are the extreme values vs. frequency of the real component of permittivity in the Cole-Cole [16, 17] representation. However, the last term of the imaginary component in eq. (2), is usually considered as  $[\sigma/\epsilon_0\omega]^N$  because N is not always one.

The program associated with the dielectric spectrometer Alpha-A Novocontrol was used to find out the components of the imaginary component of permittivity at the temperature of 45.5 °C, i.e. in ferroelectric phase, as in fig.2. At that temperature we have found  $N = 0.205$ .

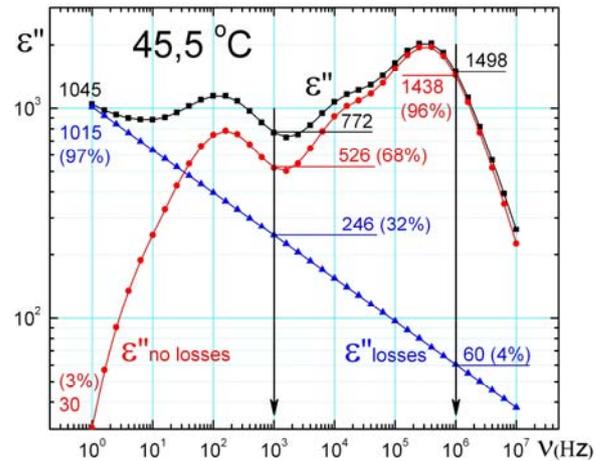


Fig.2. Estimation of conduction component at 45.5 °C vs. frequency.

The conductivity component of  $\epsilon''$  at 1 Hz, as seen in fig.2, is about 97%. Even at 1 kHz and at 1 MHz the conductivity component are about 68% and 4 % respectively. Thus, the influence of the conductivity component might be considerable, particularly at lower frequencies. Besides, in fig.2 we notice the three component of relaxation, as discussed in ref. [13-15].

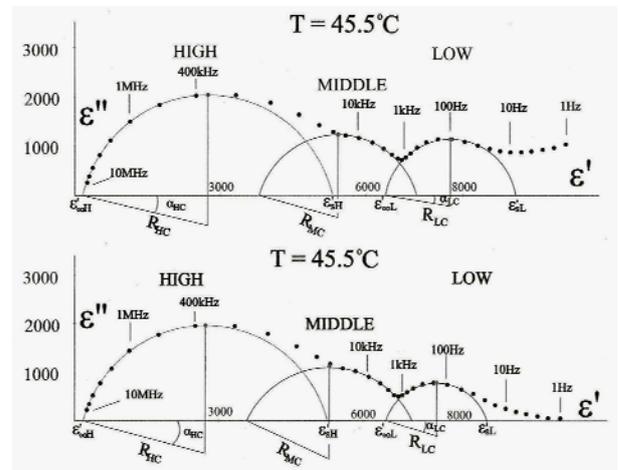


Fig.3. Cole-Cole representation of permittivity components with and with NO losses conduction estimation in the ferroelectric phase at 45.5 °C.

In fig. 3 are presented the Cole-Cole representation of three relaxation processes “as measured” (upper representation) and “NO losses” curve with the conduction term drawn out (lower part of fig.3). As seen, the low (around 100 Hz) and middle (around 40 kHz) frequency, arcs Cole-Cole relaxations are depressed and the  $\alpha$  Cole-Cole parameters have substantially larger values in the lower part of fig.3. We shall present further the influence of conduction on several dielectric parameters.

### 3.3 Low and high relaxation times

The estimation of the relaxation times was made according to the eq.  $\omega \cdot \tau = 1$ , where  $\omega$  correspond to frequency at the maximum of  $\epsilon''$  in the Cole-Cole diagrams, versus temperature like in fig.3, on the vertical lines.

In fig. 4 is presented the relaxation time for lower frequency. The difference between the two types of estimations on the most part of the temperature range is no more than 12 %. However, around the temperature 41 °C the curve “NO losses” changes the slope, making this temperature remarkable. Then, around 46 °C both curves switches drastically, the slope and the relative difference between the two curves become about 50%. Why this temperature is so special is not clear yet.

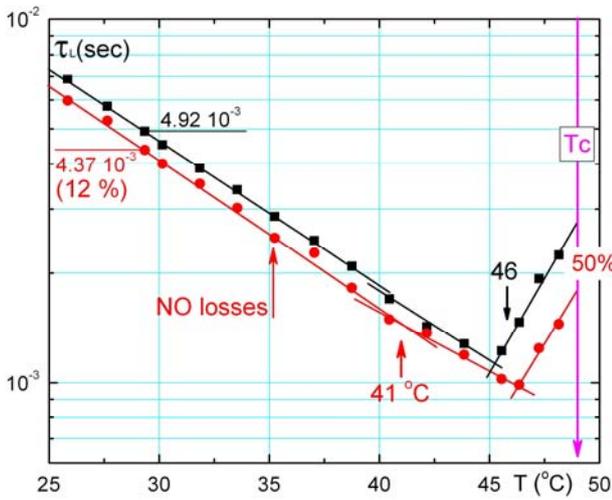


Fig.4. Low relaxation time presented in two versions, versus temperature.

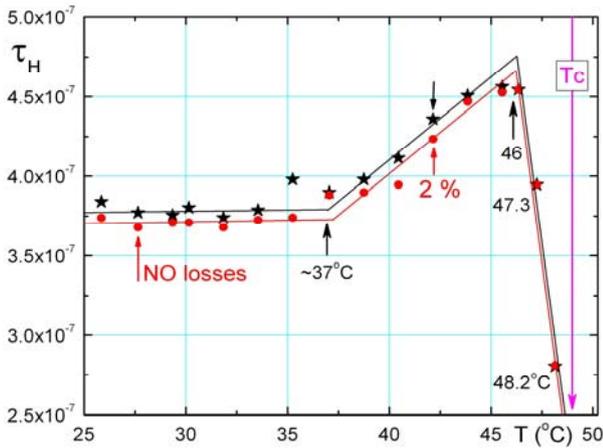


Fig.5. High relaxation times presented versus temperature.

The high relaxation time appears as constant up to about 37 °C. The difference between this relaxation time for the two components versus temperature is quite small, i.e. not larger than about 2% in fig.5. However, it is quite remarkable the slope increase around 37 °C and again drastically reversed slope around 46 °C. There is no relation between the two types of relaxation time. Close to

the transition point, the low relaxation time increases, while the higher relaxation time drastically decreases.

### 3.4. Alpha Cole-Cole paramètres versus temperature

In the Cole-Cole representation:

$$\epsilon' = \epsilon_{\infty} + \frac{(\epsilon_{st} - \epsilon_{\infty})}{1 + (j\omega\tau)^{1-\alpha}} \quad (3)$$

the coefficient  $0 < \alpha < 1$  descends the centre of Debye semicircle under the  $\epsilon'$  axis and adjust the experimental data to the model. Using the experimental data and the “NO losses” data we have represented the temperature dependence of Lower and Higher frequency components versus temperature in figs. 6 and 7.

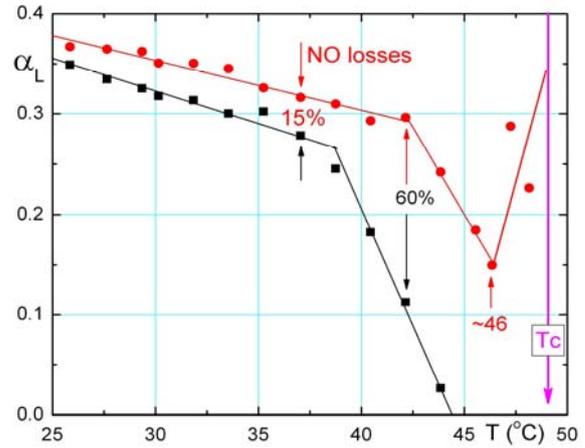


Fig.6. Alpha low representation in the two versions versus the temperature.

In fig.6 the difference between the two representations with conduction and NO conduction is very important. Up to about 40 °C the difference is about 15 %, but further the difference exceed 60 %. It is remarkable the slope change around 40-41 °C and the rivers of the slope of the curve “NO losses” around 46 °C.

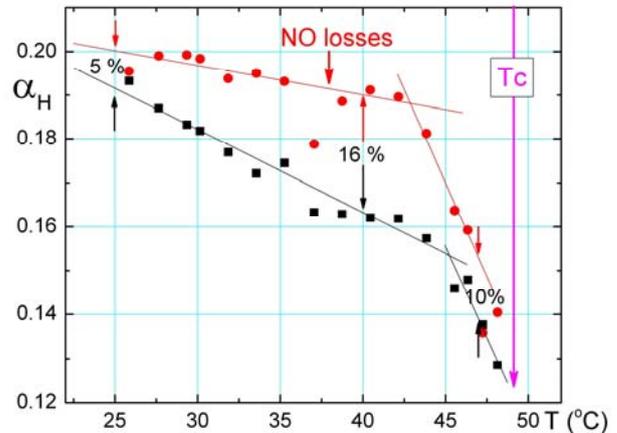


Fig. 7. Alpha high representation versus the temperature.

In fig. 7 important differences of about 16 % appear up to about 45 °C, where both curves increase the slope towards the Curie point. The difference between the two curves is still about 10 %, between 45 °C and  $T_c$ , but no reverse of the slopes take place.

#### 4. Discussions

A jump of  $\epsilon'$  take place crossing down the Curie point and the losses component appears. Than,  $\epsilon'$ ,  $\epsilon''$  decreases (fig.1), on the account of temperature decrease in the ferroelectric phase.

The decomposition of  $\epsilon''$  in double log scale (as in fig.2), is very useful. At lower frequencies the contribution of conductivity is very high. It is about 97 % from the measured values at 1 Hz, still 68 % at 1 kHz and about 14 % at 10 kHz. It is still a few percent even at the frequency of 1 MHz. It is very important, measuring the dielectric constant at lower frequencies, at least up to 1 kHz (which is the standard), to decompose the measured data and to analyze the behavior of the components with temperature.

In fig. 3, at lower frequencies up to about 40 Hz, a "tail", probably of losses is still visible. The frequency of the maximum of  $\epsilon''$  LOW in fig.3 is displaced from 100 Hz to about 150 Hz, i.e. about 50 %, which agree with the estimation from fig.4, between 46 °C and  $T_c$ . The displacement of  $\epsilon''$  HIGH which is almost negligible in fig.3, was estimated as 2 % in fig.5.

What is very strange in fig. 4 and 5, there are the slope changes and the slope switching of the relaxation times. The Low relaxation time  $\tau_L$  which vary, between  $10^{-3}$  and  $10^{-2}$  sec, fig.4, has two "accident" on the 25- $T_c$  temperature range: the slope change around 40-41 °C and the unexplained slope switch from "normal" negative to positive values around 46 °C. The activation energy on 25-45 °C temperature range was about 0.7 eV as previously estimated [14].

The HIGH frequency relaxation time  $\tau_H$  in fig.5 is constant up to about 37 °C, which is NOT quite normal for the temperature activated processes. For the same reason the slope increase of the  $\tau_H$  between 37 °C and 46 °C is also abnormal (non-Arrhenius). On the temperature interval 46 °C and  $T_c$  the decrease of  $\tau_H$  is quite unexpected with high activation energy, approximated at about 2.4 eV.

The LOW and HIGH  $\alpha_{CC}$  coefficients show other puzzling effect.

The coefficient  $\alpha_L$  does change the slope around 40 °C and "NO losses" curve switch the slope at 46 °C. Between 46 °C and the Curie point, the centre of the arc Cole-Cole of the original curve with losses starting from around 45 °C rises over the X-axis. This region of the curve has no physical meaning.

The "NO losses" coefficient  $\alpha_H$  do change the slope around 40 °C and substantially decreases towards the

Curie point. The 10 % difference versus the original curve in the temperature range 45 °C and Curie point shoes the conduction are still important even at this frequencies.

#### 5. Conclusions

1/ Around the transition point, the real component  $\epsilon'$  increases with a jump and the  $\epsilon''$  appears as a maximum in the region of HIGHER frequency region. The corresponding relaxation time  $\tau_H$  is closely related to the transition [13-15].

2/ The influence of conductivity on the imaginary component  $\epsilon''$  is still very important at  $10^3$  Hz (about 30 %) where the standard measurements of the dielectric constant are made in the literature. We suggest the frequency standard, at least for ferroelectrics, to be  $10^4$  Hz where the losses are about 10 %, or at still higher frequencies.

3/ Both LOW and the HIGH relaxation times show important slope changes around 41 °C and at 46 °C switches, but in the opposite directions. The LOW relaxation time variation, cover about one order of magnitude ( $10^{-3}$ - $10^{-2}$  Hz) on the considered range of temperature.

4/ The HIGH relaxation time sensitivity to conduction is very low and vary approximately between  $2.5 \cdot 10^{-7}$  and  $510^{-7}$  Hz. on the considered temperature range. The increase of the HIGH relaxation time between 37 °C and 46 °C is abnormal for a temperature activated mechanism. On the other side between 46 °C and Curie point the estimated activation energy of about 2.4 eV is questionable.

5/ The Cole-Cole coefficients HIGH and LOW show as important temperature slope changes to be 41 °C and 46 °C. This temperature slope changes which appear on the parameter analyzed here shows possible changes in the lattice dynamic of the TGS crystal.

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#### References

- [1] J. Fusek, V. Janousek, Phys. Stat. Sol. **13**, 195 (1966).
- [2] J.Zang Phys. Stat. Sol. (a) **193**, 347 (2002).
- [3] J. Zang, Ferroelectrics **281**, 105 (2002).
- [4] K.Kuramoto, H.Motegi, E. Nalamura, K. Kosaki, J Phys Soc. Japan **55**, 377 (1986).

- [5] G.Luther, Phys. Stat. Sol. (a) **20**, 227 (1973).
- [6] Andrew P. Giddy et al J. Phys : Condens. Matter **1**, 8327 (1989).
- [7] Genowefa Slosareki et al, J. Phys: Condens. Matter **1**, 5931 (1989).
- [8] C.P. Ganea, Rom. Journ. Phys. **57**(3–4), 664 (2012).
- [9] Constantin P. Ganea, Cent. Eur. J. Phys. **11**(4), 497 (2013).
- [10] C.P. Ganea, Eur. Phys. J. Plus **129**, 238 (2014) .
- [11] H. V. Alexandru et al, Cryst. Res. Technol. **30**, 307 (1995).
- [12] H. V. Alexandru, Annals New York Academy of Sciences **1161**, 387 (2009).
- [13] R. Bacsei, C. Mindru, C.-P. Ganea, H. V. Alexandru, J. Optoelectron. Adv. Mat. **15**, 1360 (2013).
- [14] C. Mindru, C. P. Ganea, H. V. Alexandru, J. Optoelectron. Adv. Mat. **14**, 157 (2012).
- [15] H. V. Alexandru, C. Mindru, R. Bacsei, C.-P. Ganea, J. Optoelectron. Adv. Mat **16**, 457 (2014).
- [16] ] K.S. Cole, R.H. Cole, J. Chem. Physics **9**, 341 (1941).
- [17] Robert H. Cole, J. Chem. Physics **23**, 493 (1955).

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\*Corresponding author: horia@infim.ro