

**THE EFFECT OF DOPING CRYSTALS OF TGS WITH SOME
DI- AND TRIVALENT IONS ON ITS:
(1) DIELECTRIC CONSTANT AND A.C. CONDUCTIVITY**

By

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ABSTRACT

The problem of the existence of a new ferroelectric phase transition at low temperatures in TGS crystals is discussed. The influence of some inorganic divalent and trivalent ions presented in the lattice of TGS on dielectric and a.c. conduction is examined. The internal biasing field caused by the existence of dopants in TGS crystals is found to have an effect similar to the effect of an external biasing field working on the crystal. A small thermal hysteresis in the dielectric behaviour is detected at the transition temperature. Both a.c. conductivity and activation energy change as a result of the existence of the distorted lattice caused by the dopants. The consistency between the results of the dielectric constant and the a.c. conductivity is quite noticeable.

INTRODUCTION

The discovery of ferroelectric properties in triglycine sulphate, TGS, is referred to Matthias (Matthias *et al.*, 1956) while the earliest studies on the temperature characteristics of the dielectric constant is attributed to Hoshino (Hoshino *et al.*, 1957). Latter, the measurements of the dielectric permittivity

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in the direction of the polar axis, b-axis, revealed a phase transition at about 323 K. Kazuyuki (Kazuyuki and Toshio, 1967) reported that the dielectric constant of triglycine sulphate displayed anomalous behaviour at low temperature. Recently, Al-Eithan (Al-Eithan *et al.*, 1982) observed drastic changes at about 173 K for TGS and at about 133K for DTGS in experiments on Raman spectrum. These drastic changes have been attributed to the existence of a new ferroelectric phase transitions for TGS and DTGS at low temperatures.

The study of the effect of doping TGS with inorganic ions on the physical properties of such crystals is tremendous in the published literature; nevertheless, there is a lot of discrepancy in the reported results. Some publications reported that there is no significant variations in the constants essentially characterizing the ferroelectric properties of triglycine sulphate under the influence of small concentrations of inorganic dopants (Silver *et al.*, 1975 and Polovinko *et al.*, 1980). On the other hand, some other publications which deal with the dielectric properties of TGS reported that the incorporation of inorganic ions in the lattice of TGS causes: 1- a shift in the temperature of transition, 2- a variation in the value of both the Curie constant C_0 and the maximum value of the dielectric permittivity ϵ_{\max} . and 3- a change in the temperature dependence of ϵ (Moravec *et al.*, 1973, Dikant *et al.*, 1976 and Bhalla *et al.*, 1984).

In this work, an examination of the existence of the new ferroelectric phase transition reported by Al-Eithan (Al-Eithan *et al.*, 1982) was performed, by studying the dielectric constant and the a.c. conductivity of pure and doped TGS crystals. A similar investigation was carried out by the authors (Gaffar *et al.*, 1987) through experiments on the polarization and piezoelectricity of such crystals. The influence of doping TGS crystals with some di- and trivalent ions on the dielectric constant and the a.c. conductivity was also studied.

EXPERIMENTAL

Triglycine sulphate single crystals were grown in the ferroelectric phase from saturated solutions by slow cooling technique (Gaffar and Abu El-Fadl, 1984). Crystals with admixture of Cu^{2+} , Co^{2+} , Ni^{2+} , Fe^{3+} and Cr^{3+} were obtained from solutions containing 1% by weight of salts of these ions in the form of sulphates. The concentration of the dopants in the samples was

examined and it was found to be nearly equal 200 ± 20 ppm for all the dopants. Samples for the present investigation were rectangular in shape (about 1cm^2 area, 1.5–2.5 mm thick) and were cut perpendicular to the ferroelectric *b*-axis from the most clear and transparent parts of the grown crystals. After polishing and etching, the samples were dried and conducting silver paste was painted on the two opposite surfaces of the sample. The dielectric permittivity was measured with an accuracy of about 1% by the resonance method at a constant frequency of 1 KHz using RCL bridge (Philips type PM 6302) with a.c. field of strength of about 30V/cm. The measurements were performed while heating as well as while cooling with a rate of about $0.5^\circ\text{C}/\text{min}$. In the region of the phase transition or in the region where it is probably may exist, the rate was decreased to about $0.05^\circ\text{C}/\text{min}$. The temperature was measured with an accuracy of about $\pm 0.05^\circ\text{C}$ using a copper-constantan thermocouple and a precision microvoltmeter (Keithley model 177 DMM). The a.c. conductivity was calculated from the measurement of the voltage drop across a standard resistor (10^4 ohm) connected in series with the sample. An applied field strength of 30 V/cm was used throughout the measurements. Both the dielectric permittivity and the a.c. conductivity were measured within the temperature range 90–360 K on freshly prepared samples (i.e. samples were not yet subjected to any thermal cycling). All the measurements were carried out under a vacuum of about 10^{-3} Torr.

RESULTS AND DISCUSSIONS

Dielectric constant

The temperature dependence of the dielectric constant ϵ and its inverse ϵ^{-1} of pure and doped TGS single crystals are presented in Figures 1 and 2. Each curve of Fig. (1) may be divided into two parts. The first part of each curve represents the results of the measurements below room temperature. The value of ϵ for all crystals containing dopant is higher than that for pure crystals. ϵ exhibit the same behaviour with temperature for all crystals except that small flat peaks were detected at about 110 K for Cr^{3+} – and at about 150 K for both Co^{2+} – and Ni^{2+} – doped crystals as could be seen from Fig. (1). Such flat peaks were observed in the behaviour of the dielectric constant at about 170 K for pure TGS and at about 100 K for ice crystals doped with KOH (Kazuyuki and Toshio, 1967). In the latter case the peak was attributed to the orientation polarization of KOH molecules while in the first case it was related to the

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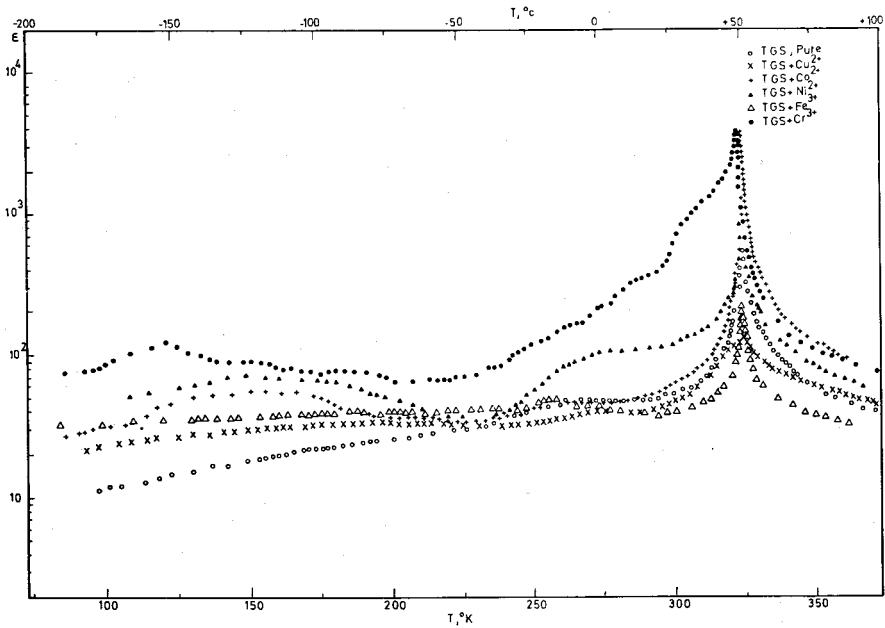


Fig. 1 : The temperature dependence of the dielectric constant of pure as well as doped TGS crystals. (The measuring field frequency is 1 KHz).

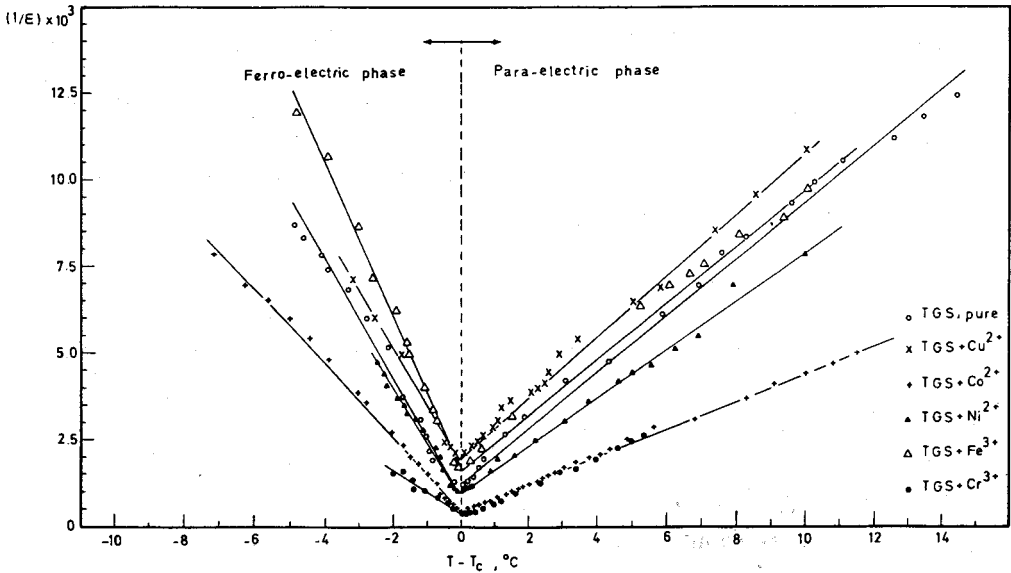


Fig. 2 : Relation between inverse of the dielectric constant and temperature in the vicinity of the Curie temperature for pure and doped TGS crystals.

domain wall motion rather than to the piezoelectric resonance effect. Special considerations were given to the measurements performed around 170 K on the pure and doped crystals; however, no marked changes in the dielectric constant were observed in this temperature range. This suggest that there is no evidence for any phase transition at low temperature in contrast to the conclusion of Al-Eithan (Al-Eithan *et al.*, 1982).

According to Hoshino (Hoshino, 1962) and Blinc (Blinc *et al.*, 1961), the second moment of the proton magnetic resonance spectrum of TGS decreases with increasing temperature up to a maximum at 225 K and 150 K respectively. The spin-lattice relaxation time of protons in TGS has its maximum value at about 185 K (Blinc *et al.*, 1966). These results lead to a conclusion that NH₃ groups rotate more freely above this temperature range than below it. These variations could results in a change in the domain wall configuration which leads to an easier motion for the domain walls around these temperatures. This could be the reason for the drastic changes observed by Al-Eithan (Al-Eithan *et al.*, 1982) and this is not a ferroelectric phase transition. Hence, we intend to believe that the technique used by Al-Eithan is not suitable for detecting the phase transitions in ferroelectric materials.

The second part of the curves representing ϵ versus T show the results between 300 K and 360 K. A relatively finite sharp peak exists at the transition temperature for all crystals. This could be attributed to either inhomogeneities in temperature, stress distribution, partial clamping of the crystal by the electrodes or by saturation of polarization against an applied field as suggested by Kamysheva (Kamysheva *et al.*, 1974).

From Fig. (1) it is clear that ϵ is very sensitive to the type of dopant. Cr³⁺ - and Co²⁺ - containing crystals exhibit the highest ϵ_{\max} . at the transition temperature, it is about 210% higher than that for pure crystals. Tsedrik (Tsedrik *et al.*, 1976) reported an increase of about 250% owing to the existence of Co²⁺ or Cu²⁺ in TGS. In the present work the presence of Cu²⁺ lowered ϵ_{\max} . by about 90% relative to the pure samples which is in agreement with the results reported by Batra (Batra and Mathur, 1978).

Excluding Cr³⁺ - doped crystal, there is a small shift in the transition temperature under the influence of the dopants. The maximum shift is about 0.8 K which is in agreement with the results of Lösche (Lösche and Windsch, 1965). According to Lösche the complexes formed by Glycine II and Glycine III

groups with the divalent foreign ions were so simple that the influence of the distorted lattice on T_c was small, not more than 1 K. The lowest T_c value in the present study is due to Cr^{3+} - doped crystals, shifted about 2.2 K from that of the pure samples. This could be attributed to the co-planer complexes formed by Cr^{3+} in TGS lattice and its high ionization activity. Evidence for the formation of diglycinate - Cr^{3+} chelate in TGS solution has been reported by Nishimura (Nishimura and Hashimoto, 1973). The results of the present investigation give rise to a difference between Fe^{3+} - complexes in doped TGS and complexes formed in the presence of Cr^{3+} in contrast to the suggestion of Silver (Silver *et al.*, 1975).

In a limited temperature range around T_c , the temperature dependence of the reciprocal dielectric constant is practically linear for pure and doped samples, Fig. (2). In the paraelectric phase, the Curie - Wiess law holds though the slopes of the lines are rather different indicating a dependence on the type of the ion involved. In the ferroelectric region, the difference in the slopes could be attributed to the difference in the domain structure of the crystals as a result of inserting the foreign ions. Such a difference has been confirmed since Zhukov (Zhukov *et al.*, 1976) found that the existence of Ni^{2+} or Cr^{3+} ions in the lattice of TGS strongly changed the configuration of its ferroelectric domains.

Taking into account the difference between adiabatic and isothermal dielectric constant; according to the theory, the slope of the straight line representing ϵ^{-1} versus T in the ferroelectric region, is 2.4 times that in the paraelectric region. In the present study, the ratios of the slopes are in good agreement with the theory for all crystals except the case of Cr^{3+} - doped crystals which gives a different result from the predicted value.

According to Wieder (Wieder, 1959), the relation:

$$\epsilon_{\max.} (T_{\epsilon_{\max.}} - T_0) = 0.5 C_0,$$

holds for a second order phase transition under the influence of an external biasing field.

In such a case, $\epsilon_{\max.}$ is affected by two factors. The first is the relaxation of interaction of crystal defects which leads to the decrease of $T_{\epsilon_{\max.}}$. The second is the appearance of internal fields causing the maximum shift of the position of $\epsilon_{\max.}$ towards higher temperatures and it is accompanied by a decrease in the magnitude of $\epsilon_{\max.}$.

The structural or chemical defects could create an internal biasing field which possibly has an effect analogous to that of the external biasing field. The results of the present work confirm the straight line behaviour suggested by Wieder (Wieder, 1959). However, the straight line representing our results has an intersection with the y-axis and could have the form:

$$\epsilon_{\max.} (T_{\epsilon_{\max.}} - T_0) = 0.56 C_0 + 580 ,$$

this behaviour is illustrated in Fig. (3).

The above equation suggests that the effect of the biasing field created by the dopants could be divided into two parts. The first part depends on the type of ion involved, i.e., the type of complexes formed, the ionization activity of the ion, its valency and ionic radii. The second part is independent of the type of dopant and it could be related to the dimensions of the existed distorted lattice, i.e., the concentration of the foreign ions involved which is constant in the present study. Thus, one may conclude that doping TGS crystals with inorganic ions could create internal biasing field which has about the same effect on the value of the dielectric constant produced by an external biasing field.

In general, the numerical values obtained in the present investigation for the dielectric constant of TGS crystals are, to some extent, different from the corresponding values obtained by some other authors (Polovinko *et al.*, 1980, Tsedrik *et al.*, 1976 and Stankowska, 1967). One reason to explain this difference is the temperature of growing TGS crystals. For each growth temperature there is certain domain configuration to which the dielectric constant is sensitive. This problem was discussed by Stankowska (Stankowska, 1967) giving a graph showing the variation of $\epsilon_{\max.}$ with the temperature of crystal growing. It is important to mention that all crystals used in the present investigation were grown under the same conditions to establish a good base for comparison between the results. Another possible reason is the, relatively large thickness of our samples which we preferred to use in order to avoid the effect of the surface layer on the dielectric constant as detected by Chynoweth (Chynoweth, 1960). According to Kamysheva (Kamysheva *et al.*, 1974) the dielectric constant increases linearly with sample thickness and the increase becomes much pronounced near the transition temperature.

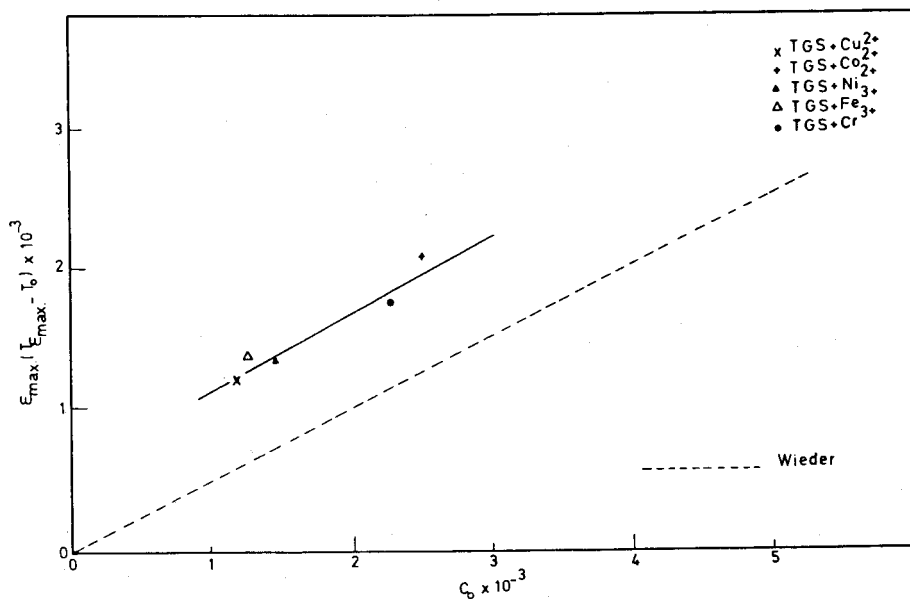


Fig. 3 : Relation between $\epsilon_{\max.} (T_{\epsilon_{\max.}} - T_0)$ and the Curie constant C_0 for TGS crystals doped with some di- and trivalent inorganic ions.

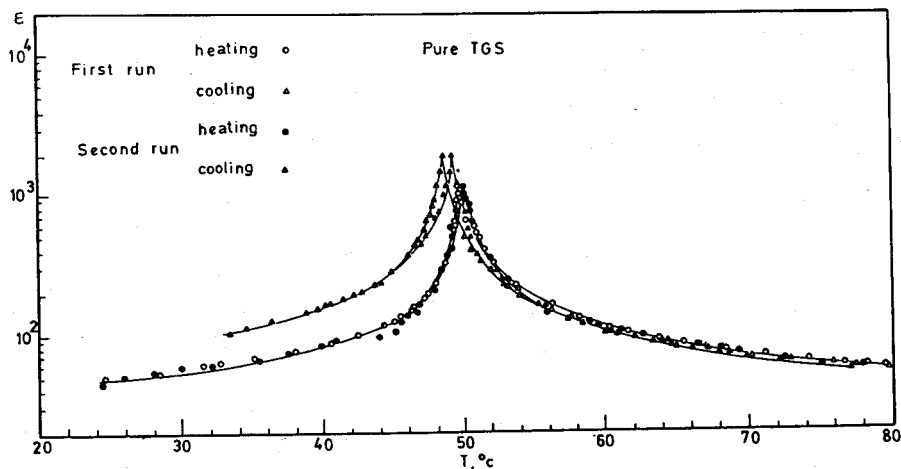


Fig. 4 : Experimental results showing thermal hysteresis in the dielectric constant of pure TGS crystals.

Initial measurements of the dielectric constant were carried out on fresh samples. Subsequent measurements after heating and cooling of the samples gave different results. Typical behaviour of the dielectric constant through two successive heating and cooling cycles is shown in Fig. (4). The difference in the value of ϵ in the ferroelectric phase is significant, more than 45%, while it is within the experimental error in the paraelectric phase. Moreover, the value of ϵ_{\max} obtained during cooling is higher, by about 40% than that obtained during heating.

A temperature hysteresis effect was also observed when the sample was heated and then cooled through T_c . The width of the temperature hysteresis changed from 1.1K in the first run to 0.6K in the second run. The temperature hysteresis may be attributed to the fact that cooling through transition could produce strains in the lattice which would not be annealed out at lower temperatures.

The existence of the temperature hysteresis was previously noticed throughout the measurements of the electrical conductivity in TGS (Gurevich and Zheludev, 1961). The temperature hysteresis was still detected in spite of the successive heating and cooling treatments. Since the existence of such hysteresis is one of the characteristic features of the first order phase transition, it could be concluded that the transition in TGS may exhibit some features of the first order.

A.C. Conductivity

The temperature dependence of the a.c. conductivity of pure and doped TGS samples is presented in Fig. (5). From the figure the following remarks could be drawn:

- 1- Nothing is observed to indicate the existence of a new phase transition at 173 K or at any other temperature in the low temperature range.
- 2- A pronounced anomaly is observed at T_c . Similar anomalies were observed at the transition of TGS, barium titanate, Rochelle salt and potassium niobate (Zheludev, 1971).
- 3- The behaviour is considerably different in the ferroelectric phase according to the type of dopant, this is due mainly to the difference in the domain configuration - the resemblance between the behaviour of ϵ and $\sigma_{a.c.}$ is quite clear

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- 4- The values of the activation energy differ from one dopant to the other and also differ for the conduction around the transition temperature. The values of the activation energy are 0.05 e.V. in the ferro – and 0.39 e.V. in the paraelectric phases for the pure samples which is in good agreement with the literature (Zheludev, 1971).
- 5- The value of T_c for all crystals are consistent with those obtained from the measurements of the dielectric constant.

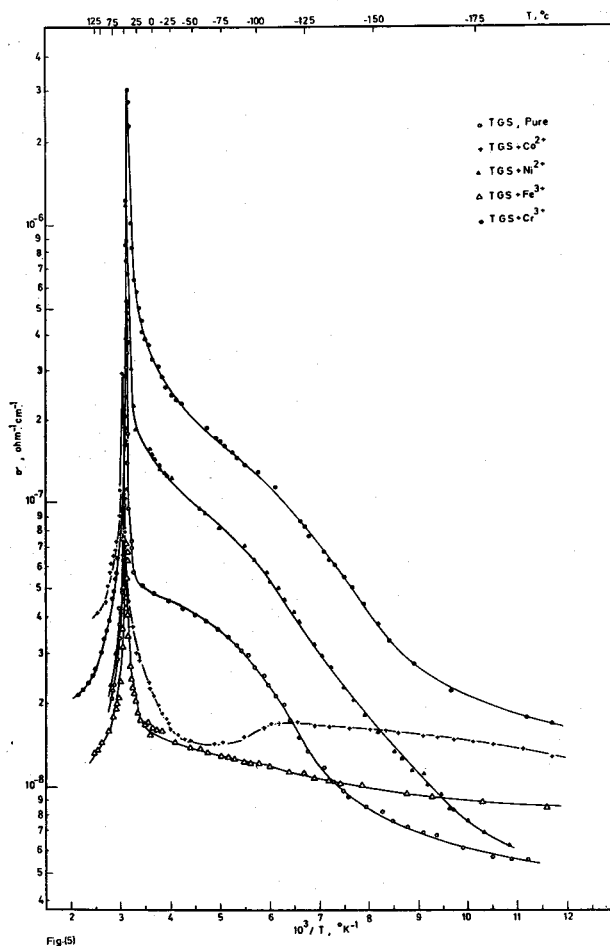


Fig. 5 : A.C. conductivity as a function of temperature of pure and doped TGS crystals. (The measuring field frequency is 1 KHz).

The conduction mechanism in TGS crystals is ionic in nature (Zheludev, 1971); a result which is confirmed by the fact that TGS are usually grown from solution containing excess amount of sulphuric acid. Accordingly, conduction in TGS crystals depends strongly on the growth condition, especially on the pH value of the growth solution. This could be one of the reasons for the diversity in the data reported for the activation energy and the anomalous behaviour at T_c . Another source for the diversity may be due to the frequency and strength of the measuring field applied in each case; it was as large as 10KV/cm. in the work of Michalczyk (Michalczyk and Hilczer, 1977) while it was as small as 1 V/cm. in the work of Dikant (Dikant *et al.*, 1977).

The a.c. conductivity of a normal dielectric may be related to its capacitance, C, through the relation:

$$\text{Tan } \delta = \frac{\sigma}{\omega C} \quad (1)$$

where $\tan \delta$, the dielectric losses, is the ratio of the imaginary to real parts of the dielectric constant and $\omega = 2\pi f$, f is the frequency of the measuring field.

If we neglect the effects due to any irregularity of the electric field at the boundaries of the material, equation (1) could be used to calculate σ since C and $\tan \delta$ are measurable quantities in the present investigation. σ was calculated as a function of temperature for all the samples, pure as well as doped ones. It was found that the general behaviour of calculated σ as a function of T is almost the same for all the samples. Hence, only the results obtained for the pure sample, as an example, is shown in Fig. (6). The figure includes also the temperature dependence of $\tan \delta$ for the pure sample.

The agreement between the measured, σ_m , and calculated, σ_c , values is evident in the paraelectric phase and in the low temperature range of the ferroelectric phase. Clear difference between σ_m and σ_c is observed in the temperature range 125° - 225 K. This difference could be related to the fact that dielectric constant measurement is sensitive to some factors which have no significant effect on the measurement of a.c. conductivity. One of these factors could be related to the configuration of the ferroelectric domains governed by domain wall motion. The reason for this motion around 185 K may be attributed to the variation in mode of rotation of NH_3 groups in the lattice of TGS at this temperature as suggested by Blinc (Blinc *et al.*, 1966).

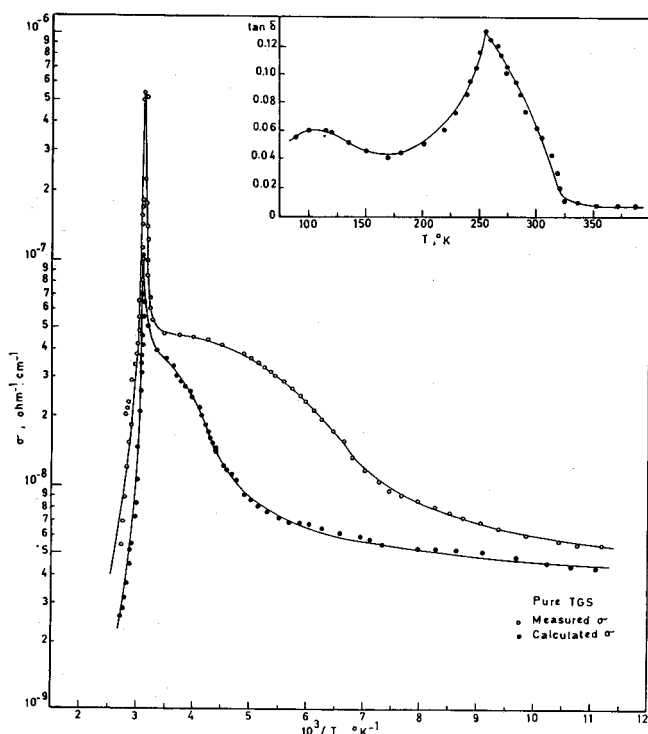


Fig. 6 : Temperature dependence of measured, σ_m , and calculated, σ_c , a.c. conductivity of pure TGS crystal. At the upper right, the temperature dependence of dielectric losses $\tan \delta$ of pure TGS is shown.

The activation energy of conduction in the paraelectric phase deduced from calculated σ is 0.35 e.V. which agrees with the value 0.39 e.V. estimated from measured σ while the activation energy in the ferroelectric phase obtained from σ_c is about twice the value obtained from σ_m which is to be expected due to deviation between σ_c and σ_m in the ferroelectric phase.

From the results of the dielectric constant and the a.c. conductivity, no evidence of the existence of the reported low temperature ferroelectric phase transition was observed. The effect of admixtures, even in low concentrations, on the measured properties in this work is quite evident.

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التغير الطوري عند درجات الحرارة المنخفضة وتأثير تطعيم بلورات كبريتات ثلاثي الجليسين على العزل والتوصيل الكهربائي تحت تأثير مجال كهربائي متردد

محمد عبد العزيز جعفر - لطيفه الحوطي - ميشه المريخي
وعبد العزيز علي محمد

بينت النتائج التي توصل إليها هذا البحث عدم ظهور دلائل تشير إلى وجود تغير في الطور عند درجات الحرارة المنخفضة سواء عند قياس ثابت العزل أو المقاومة الكهربائية تحت تأثير مجال كهربائي متردد وأيضاً سواء للبلورات النقية أو لتلك المطعمة بأيونات شائبة مما يؤكد عدم قدرة تجارب أطيف رامان على اكتشاف وجود التغيرات الطورية في المواد الفروكهربية .

توصلت النتائج أيضاً إلى أن قيم ثابت العزل تتغير تحت تأثير إضافة أيونات ثنائية وثلاثية التكافؤ أما سلوك ثابت العزل مع درجة الحرارة فإنه يبقى كما هو . الازاحة التي تنشأ في درجة حرارة كوري إزاحة لا تتعدى 0.8 درجة فيها عدا حالة البلورات المطعمة بالكروم حيث تصل الازاحة إلى 2.2 درجة . ينشأ عن وجود الأيونات الدخيلة مجال انحيازي داخلي له نفس السلوك الذي ينشأ عن مجال انحيازي خارجي ولكن بتأثير مضاعف على ثابت العزل لهذه البلورات . أثبتت التجارب وجود عروة تخلف حراري عرضها حوالي 1.1 درجة ووجود هذه العروة إنما هو من مظاهر التغيرات الطورية من الرتبة الأولى .

تم قياس المقاومة الكهربائية تحت تأثير مجال كهربائي متردد وقد لوحظ التشابه بين سلوك العزل والتوصيل الكهربائي مع تغير درجة الحرارة . تتغير قيم المقاومة الكهربائية وطاقة التنشيط من عينة لأخرى على حسب ما بها من أيونات شائبة كما تتغير تلك القيم لنفس العينة في طور الفروكهربية عنها في طور الباراكهربية . أمكن حساب التوصيل الكهربائي بمعلومية ثابت العزل وزاوية الفقد ووجد تطابقاً في النتائج مع القيم المقاسة عملياً في طور الباراكهربية بينما أمكن تفسير الفرق بين القياسات العملية والحسابات النظرية في طور الفروكهربية .