THE EFFECT OF DOPING CRYSTALS OF TGS WITH SOME DI- AND TRIVALENT IONS ON ITS: (II) POLARIZATION AND PIEZOELECTRICITY

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ABSTRACT

The polarization, coercive field, piezoelectricity and electromechanical coupling for pure and doped single crystals of TGS are investigated in the temperature range 77–325 K. The influence of the divalent ions Ni$^{2+}$, Cu$^{2+}$ and Co$^{2+}$ and the trivalent ions Cr$^{3+}$ and Fe$^{3+}$ on the temperature of phase transition, the hysteresis loops of polarization and the second coefficient in the expansion of the free energy in powers of polarization is examined. The temperature dependence of the spontaneous polarization, coercive field and the piezoelectric and electromechanical coupling coefficients are studied and the results obtained are compared. The existence of a new ferroelectric phase transition in the low temperature range is also discussed.

INTRODUCTION

Ferroelectrics with appropriately high pyroelectric coefficients and low dielectric permittivity are optimal materials for the construction of pyroelectric detectors of infrared radiation. Detector materials such as mercury cadmium telluride and lead tin telluride are only useful in the temperature range from 77
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to 90 K. The need for cooling to these temperatures leads to complexity of both the detector mounting and the ancillary equipment required for cooling. Thus, one has to look for other materials which have their optimum working conditions at temperatures as close as possible to room temperature. This class of materials comprises Triglycine sulphate (TGS) crystals as well as their isomorphous crystals TGSe and TGFB (Krajewski 1966 and Hadni et al. 1969). However, a drawback of TGS as a detector arised from their spontaneous depolarization with time. A counter-measure has been sought in the stabilization of their structure by doping such crystals with some foreign (organic or inorganic) ions. In some cases, however, doping may cause a decrease of the pyroelectric coefficient which considerably lowers the detection parameters of the crystal.

Doping affects almost all the physical properties of ferroelectric crystals especially in the vicinity of the phase transition. Some physical properties of TGS crystals admixedtured with some organic compounds were studied, e.g the thermal diffusivity (Krajewski et al. 1976), dielectric permittivity, spontaneous polarization and pyroelectric coefficient (Keve et al. 1972) as well as the piezoelectric and elastic coefficients (Fotchenkov and Zaitseva 1962). In all cases a strong internal electric field, biasing the hysteresis loop, was found to exist due to the high measuring electric field used. The influence of inorganic ions on TGS was studied by many workers: e.g. the effect of doping TGS with Cu$^{2+}$ and Cr$^{3+}$ was studied by Stankowska (Stankowska 1967). Moravec (Moravec et al. 1973) studied crystals of TGS doped with Ni$^{2+}$, Cu$^{2+}$, Pd$^{2+}$ and Fe$^{3+}$ with different concentrations. The data reported by different authors on pure as well as doped TGS crystals diverse considerably. This diversity leaves much to be studied, and hence an investigation of some of the physical properties of doped TGS is needed.

The effect of adding some di- and trivalent ions to the solution of growth of TGS on the spontaneous polarization, coercive field, piezoelectric coefficient and the electromechanical coupling coefficient was studied in this work. Such a study is particularly important because it can shed some light on the behaviour of TGS crystals in pursue of some dopants which develop the intrinsic characteristics of such material for suitable technological applications. Also the existence of the new low temperature phase transition which was detected by Al–Eithan (Al–Eithan et al. 1982), using Raman spectroscopy of TGS, will be discussed.
Pure single crystals of triglycine sulphate, \((\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4\), as well as crystals admixed with \(\text{Co}^{2+}\), \(\text{Ni}^{2+}\), \(\text{Cu}^{2+}\), \(\text{Fe}^{3+}\) and \(\text{Cr}^{3+}\) were grown from an aqueous solution in the ferroelectric phase by the slow cooling technique (Gaffar et al. 1984). The starting temperature of crystallization was \(\sim 44^\circ\text{C}\). The admixed crystals were grown under identical conditions from solutions containing 1% by weight of the dopant. The admixture content in the samples was determined using the microprobe technique to be about 200 ppm.

The samples were prepared for measurement by cleavage. Only crystals with good faces, containing no visible defects and far from the seeding area were considered for measurements. The plates obtained in this way were ground, then polished to the exact orientation and dimensions. Conducting electrodes of silver solution were painted on the surfaces perpendicular to the ferroelectric \(b\)-axis. The final form of the sample was square in shape with an area of about 1x1 cm\(^2\) and a thickness of about 1.5 – 2.5 mm. The samples, without exposure to neither preliminary thermal nor electrical effects, were then placed in a crystal holder. Sample temperature was measured by means of a copper–constantan thermocouple and the temperature was controlled to \(\pm 0.1^\circ\text{C}\). All the measurements were taken under rough vacuum of about \(10^{-3}\) Torr.

The spontaneous polarization was studied by a circuit similar to that used by Sawyer–Tower with a measuring field of about 400 V/cm and a frequency of 50 Hz. The hysteresis loops of polarization were displayed on a Tektronix DM 44 oscilloscope. The piezoelectric constant and the electromechanical coupling coefficient of the samples were measured by the resonance and antiresonance method (Mason 1950). The frequencies were accurately detected using a digital frequency counter with measuring range 10 Hz – 120 MHz.

RESULTS AND DISCUSSION

(I) Spontaneous Polarization

The spontaneous polarization, \(P_s\), of the pure and admixed TGS crystals was studied throughout its ferroelectric hysteresis loop. Fig. (1) shows the temperature dependence of \(P_s\) from liquid nitrogen temperature up to the transition temperature. The hysteresis loops of polarization were studied
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carefully around 173K looking for any phase transition that may exist in this region. Neither the loop disappeared nor the shape or the area of the loops was found to change abruptly. This was the case for all crystals which were studied in the present work. These observations do not support the existence of a phase transition as reported by Al–Eithan (Al–Eithan et al. 1982). The most common physical property used for detecting and studying phase transitions in ferroelectrics is the spontaneous polarization. Accordingly, the new phase transition proposed by Al–Eithan (Al–Eithan et al. 1982), as a conclusion for his experiments on the Raman spectrum of TGS, could not be experimentally verified in the present study. The results obtained by Al–Eithan may probably be related to the anomalies of dielectric constant of TGS at low temperature as reported by Itoh (Itoh and Mitsui, 1967).

The presence of Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cr$^{3+}$ and Fe$^{3+}$ in TGS crystals decreases the value of the spontaneous polarization but the behaviour of $P_s$ with $T$ is still as that of the pure samples. $P_s$ exhibits a drastic decrease in the vicinity of the phase transition becoming negligible at $T_c$, Fig. (2). This is in agreement with the results of other workers (Krajewski et al. 1968). The maximum decrease in spontaneous polarization is due to the existence of Cr$^{3+}$ in TGS. At room temperature $P_s$ for Cr$^{3+}$ – doped sample is only about 22% that of the undoped sample.

Hoffmann (Hoffmann et al. 1977) proposed a mechanism to account for the dependence of $P_s$ on $T$ in TGS crystals. According to this model the $P_s - T$ dependence is correlated with molecular and orientational changes, depending on temperature changes, in the skeleton of glycine I and the C–N bond respectively. A decrease in temperature leads to an increase of the projection of the dipole moment on the $b$–axis of the C–N bond in glycine I. Such increase appears microscopically as an increase in $P_s$, as in the case of nitroaniline–doped TGS crystals (Krajewski and Breczewski 1980). On the other hand, the observed decrease in the value of $P_s$ under the influence of Ni$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ and Fe$^{3+}$ may be understood in the light of a partial restriction of the vibrational motion of the C–N bond where the dopant is probably attached.

In a temperature region of about 10°C below $T_c$, a straight line relationship exists between $P_s^2$ and $T$ for all the samples. The second coefficient of the thermodynamic expansion, $\xi$, was calculated and it was found to be in good agreement with the data reported for the pure crystal by Tello (Tello and
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Hernandez, 1973). The maximum variation in $J$ was found to be about 15 times that of pure crystals for samples doped with $\text{Fe}^{3+}$. Table (1) gives some values describing spontaneous polarization of pure and doped TGS samples.

![Graph 1: Temperature dependence of the spontaneous polarization $P_s$ of pure crystals of TGS from liquid nitrogen temperature up to the transition temperature.](image1.png)

**Fig. 1:** The temperature dependence of the spontaneous polarization $P_s$ of pure crystals of TGS from liquid nitrogen temperature up to the transition temperature.

![Graph 2: Spontaneous polarization $P_s$ of pure and doped TGS crystals between room temperature and the transition point.](image2.png)

**Fig. 2:** Spontaneous polarization $P_s$ of pure and doped TGS crystals between room temperature and the transition point.

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A small shift in the transition temperature, $T_c$, under the influence of the dopants was observed. The shift is almost identical (about 0.8°C) in the case of the three divalent ions used; this is in good agreement with the results of Lösch (Lösch and Windsch 1965). Again, the presence of Cr$^{3+}$ in TGS was found to give the maximum variation in $T_c$, about 2.2°C. This result is not unexpected since Cr$^{3+}$ forms coplaner complexes with glycine I and glycine II in contrast to the simple planer complexes formed with divalent ions.

(II) Coercive Field

Fig. (3) shows the behaviour of the coercive field, $E_C$, with temperature for pure and doped TGS samples. From the figure it is obvious that the coercive field decreases rapidly in the vicinity of the transition as one approaches $T_c$. The value of $E_C$ at room temperature (see Table II) is in a good agreement with the literature (Mansingh et al. 1979). These values, however, differ by more than two orders of magnitude from the calculated values using the usual free energy phenomenological expansion as those given by Jona (Jona and Shirane 1962). According to Landolt-Bornstein (1969) the disagreement between the calculated and observed values could be due to the random microscopic switching and the forward and side-wise motion of the domain wall.

It is well known that the coercive field of a ferroelectric depends markedly on thickness, frequency and amplitude beside its strong dependence on temperature especially in the vicinity of the Curie point. According to Hadni (Hadni et al. 1983) the value of $E_C$ for pure TGS crystals of thickness 1.3 micron is about two orders of magnitude that of crystals of thickness 95 micron at all temperatures from 20°C to 48°C while the thickness effect becomes negligible for thicknesses greater than 0.1 mm. This behaviour was attributed to the formation of a surface layer which lead to an internal electric bias field. The effect of the bias field becomes more stronger for thinner samples.

Table I

Parameters describing the spontaneous polarization of TGS, pure as well as doped crystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_c$ °C</th>
<th>$P_s$ (μC/cm$^2$), at 30°C</th>
<th>$\chi$ (e.s.u./cm$^2$)$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGS, Pure</td>
<td>49.8</td>
<td>2.6</td>
<td>8.5 x 10$^{-10}$</td>
</tr>
<tr>
<td>TGS + Cu$^{2+}$</td>
<td>49.0</td>
<td>2.0</td>
<td>15.3 x 10$^{-10}$</td>
</tr>
<tr>
<td>TGS + Co$^{2+}$</td>
<td>49.5</td>
<td>1.2</td>
<td>36.3 x 10$^{-10}$</td>
</tr>
<tr>
<td>TGS + Ni$^{2+}$</td>
<td>49.8</td>
<td>0.9</td>
<td>79.0 x 10$^{-10}$</td>
</tr>
<tr>
<td>TGS + Fe$^{3+}$</td>
<td>49.4</td>
<td>0.62</td>
<td>127.0 x 10$^{-10}$</td>
</tr>
<tr>
<td>TGS + Cr$^{3+}$</td>
<td>47.6</td>
<td>0.60</td>
<td>93.9 x 10$^{-10}$</td>
</tr>
</tbody>
</table>
Fig. 3: Coercive field strength $E_C$ of pure and doped TGS crystals as a function of temperature from liquid nitrogen temperature up to the transition temperature.

Table II
Parameters describing the coercive field properties of TGS, pure as well as doped crystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$(E_C)_{\text{at R.T.}}$ V/cm</th>
<th>$(E_C)_{\text{max.}}$ V/cm</th>
<th>$T$ of $(E_C)_{\text{max.}}$ °K</th>
<th>$(s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGS, Pure</td>
<td>600</td>
<td>910</td>
<td>238</td>
<td>0.77</td>
</tr>
<tr>
<td>TGS + Cu$^{2+}$</td>
<td>475</td>
<td>596</td>
<td>275</td>
<td>1.48</td>
</tr>
<tr>
<td>TGS + Co$^{2+}$</td>
<td>710</td>
<td>825</td>
<td>276</td>
<td>0.66</td>
</tr>
<tr>
<td>TGS + Ni$^{2+}$</td>
<td>775</td>
<td>875</td>
<td>281</td>
<td>1.15</td>
</tr>
<tr>
<td>TGS + Fe$^{3+}$</td>
<td>525</td>
<td>525</td>
<td>298</td>
<td>0.78</td>
</tr>
<tr>
<td>TGS + Cr$^{3+}$</td>
<td>750</td>
<td>975</td>
<td>265</td>
<td>0.91</td>
</tr>
</tbody>
</table>
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In the vicinity of the Curie point, the dependence of $E_c$ on temperature takes the form $E_c \propto (T_c - T)^{s}$. The theoretical value of $(s)$ is equal $3/2$ according to both the phenomenological and microscopic mean-field theories. However, the experimental values of $(s)$ for the pure samples are different in the reported literature.

In Fig.(4) log $E_c$ is plotted versus log $(T_c - T)$ where $T_c$ is the value of the transition temperature as obtained from the spontaneous polarization measurements. The results follow a relationship of the form $E_c = \text{Const.} \times (T_c - T)^{s}$ with $(s)=0.77$ for pure samples. This is about half the theoretical value but it is not far from the experimental value given by Okada (Okada et al. 1980). Okada found the value of $(s)$ to be equal to 1 from measurements obtained by means of the hysteresis loop method at a fixed field amplitude and at low frequency. The value of $(s)$ obtained in this work for the pure sample, however, is different from that obtained by Martinez (Martinez and Gonzalo 1982). Martinez measured $E_c$ within one degree from $T_c$ while, at each measurement, care was taken of the amount of polarization reversal as a function of the square pulse amplitude. Although the value of $(s)$ obtained from these measurements was $1.45 \pm 0.10$, which is quite close to the theoretical value, their results are still under discussion.

Table III
Parameters describing the piezoelectric and electromechanical coupling coefficients of TGS, pure as well as doped crystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>at $28^\circ$C</th>
<th></th>
<th>at $T_c$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d_{22}$</td>
<td>$K$</td>
<td>$d_{22}$</td>
<td>$K$</td>
</tr>
<tr>
<td>TGS, Pure</td>
<td>$50 \times 10^{-8}$</td>
<td>0.21</td>
<td>$710 \times 10^{-8}$</td>
<td>0.34</td>
</tr>
<tr>
<td>TGS + Cu$^{2+}$</td>
<td>$70 \times 10^{-8}$</td>
<td>0.17</td>
<td>$179 \times 10^{-8}$</td>
<td>0.26</td>
</tr>
<tr>
<td>TGS + Co$^{2+}$</td>
<td>$245 \times 10^{-8}$</td>
<td>0.32</td>
<td>$1280 \times 10^{-8}$</td>
<td>0.44</td>
</tr>
<tr>
<td>TGS + Ni$^{2+}$</td>
<td>$110 \times 10^{-8}$</td>
<td>0.25</td>
<td>$310 \times 10^{-8}$</td>
<td>0.35</td>
</tr>
<tr>
<td>TGS + Fe$^{3+}$</td>
<td>$45 \times 10^{-8}$</td>
<td>0.21</td>
<td>$203 \times 10^{-8}$</td>
<td>0.35</td>
</tr>
<tr>
<td>TGS + Cr$^{3+}$</td>
<td>$160 \times 10^{-8}$</td>
<td>0.18</td>
<td>$530 \times 10^{-8}$</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Data for both Cu$^{2+}$ – and Ni$^{2+}$ – doped samples gave results for $(s)$ near the ideal value (see Table II) while the Fe$^{3+}$ – doped sample show no significant change in the value of $(s)$ with respect to the pure sample. From these results one may conclude that the presence of either Cu$^{2+}$ or Ni$^{2+}$ in the lattice of TGS improves its behaviour towards the ideal case, with respect to this property, in contrast to the Co$^{2+}$ in TGS which causes deviation from the ideal behaviour.
Fig. 4: Relation between log $E_C$ and log $(T_C - T)$ for pure and doped crystals of TGS near $T_C$.

(III) Piezoelectric Constant
The piezoelectric constant $d_{22}$ in the direction of the polar axis was investigated as a function of temperature for pure and admixed TGS crystals. The resonance $f_r$ and antiresonance $f_a$ frequencies were clearly marked. The frequencies at which $f_r$ and $f_a$ occur decrease with increasing temperature which is essentially due to the decrease in elasticity with temperature. Both $f_r$ and $f_a$ disappear at all temperatures greater than $T_C$ for pure, Co$^{2+}$ and Ni$^{2+}$-doped crystals. The resonance and antiresonance are still detected at temperatures slightly greater than $T_C$ for Cu$^{2+}$, Fe$^{3+}$ and Cr$^{3+}$-doped crystals.

The temperature dependence of the piezoelectric constant of the studied crystals is shown in Fig. (5). It is quite clear that $d_{22}$ increases sharply as the
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Curie temperature is approached for all crystals except for Cr$^{3+}$-doped sample which shows a gradual increase. The sharp rise in the $d_{22}$-piezoelectric coefficient close to the phase transition was attributed by several authors (Silvestrova and Yurin 1963 and Shuvalov and Pluzhnikov 1961) to the increase in the mobility of domains on approaching the Curie point. Cr$^{3+}$ also tends to lower the value of $d_{22}$ at $T_C$. Samples doped with Cr$^{3+}$, Fe$^{3+}$ and Cu$^{2+}$ show a gradual decrease in the value of $d_{22}$ from its maximum value at $T_C$ before the disappearance of $f_r$ and $f_a$. This behaviour is similar to that of irradiated pure TGS crystals (Amin et al. 1976) which was attributed to the large uncertainty in the dielectric constant $\varepsilon_{22}$ in the anomalous region.

In the low temperature range, nothing was observed in the behaviour of $d_{22}$ to indicate the existence of a new ferroelectric phase transition as was reported by Al–Eithan (Al–Eithan et al. 1982).

Fig. 5: The temperature dependence of the piezoelectric constant $d_{22}$ for pure and doped crystals of TGS above room temperature.
Fig. 6: The electromechanical coupling coefficient $K$ of pure and doped TGS crystals as a function of temperature.

(IV) Electromechanical Coupling Coefficient

The electromechanical coupling coefficient $K$ of the samples used in this investigation was also calculated and its temperature dependence is given in Fig. (6). The electromechanical coupling coefficient for all samples increases first with increasing temperature up to a maximum, then it drops off abruptly while approaching $T_c$. The numerical values of $K$ for different samples are given in Table (III). The value of $K$ for the pure crystal is in a good agreement with the reported values (Amin et al. 1976 and Hausimi and Kataoka 1959). The highest value of $K$ was found in the case of Co$^{2+}$ doped crystals which means that such dopant increases the ability of TGS to convert mechanical energy to electrical energy. On the contrary, doping TGS with Cu$^{2+}$ decreases the value of the electromechanical coupling coefficient.
CONCLUSIONS

The following main conclusions may be drawn from the present study on the polarization and piezoelectricity of TGS pure and doped samples.

1- The existence of the low temperature phase transition suggested by Al-Eithan has not been confirmed by our measurements of spontaneous polarization and piezoelectricity. From our point of view, the technique used by Al-Eithan may be not suitable for detecting the phase transitions in ferroelectrics.

2- Although the concentration of impurities inserted in TGS crystals used for this study is almost the same, the effect on the studied physical properties is not the same. This could be attributed to the effect of the forces of chelate bond of the respective impurity inside the structure of the TGS lattice. It is to be noted that all crystals were grown under the same conditions.

3- The addition of Cu$^{2+}$, Co$^{2+}$, Ni$^{3+}$, Fe$^{3+}$ and Cr$^{3+}$ considerably affected the measured physical constants for pure TGS crystals. The degree of variation changed from one dopant to the other. There is no single dopant which affected all the measured physical properties towards the ideal behaviour.

REFERENCES


تأثير تطعيم بلورات كبريتات ثلاثي الجليسين بأيونات ثنائية وثلاثية التكافؤ على الاستقطاب التلقائي والبيزوكرهبية

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و عبد العزيز علي محمد

يهدف هذا البحث إلى دراسة تأثير إضافة أيونات ثنائية وثلاثية التكافؤ إلى محلول إنشاء بلورات كبريتات ثلاثي الجليسين على الاستقطاب التلقائي والبيزوكرهبية. كما يهدف إلى التأكد من وجود تغير في الطور عند درجات الحرارة المنخفضة أشار إلى وجود بحث أجرى لدراسة طيف رامان لهذه البلورات.

لدت النتائج على أن وجود الأيونات الثنائية تعمل على نقص الاستقطاب التلقائي في حين يظل سلوك تغير $P_0$ مع تغير درجة الحرارة مستقراً معتقلاً، حيث هو على عقب البلورات النقيّة. يضمن الاستقطاب التلقائي بسرعة بالقرب من درجة حرارة الانتقال الطوري وتكوين العلاقة بين $P_0$ ودرجة الحرارة في هذه المنطقة علاقة خط مستقيم أمكن منها تعدين المعامل الثاني في مفكوك الجهد كدالة في $P_0$ وقيمته في حالة العينات النقيّة تتفق مع نتائج الأبحاث المنشورة. لوحظ أن درجة حرارة الانتقال الطوري $T_C$ في حالة البلورات المطعمة بشواطئ ثنائية التكافؤ متساوية تقريباً وهي لا تختلف كثيراً عن $T_C$ للعينات النقيّة ولكن في حالة الكرام ثلاثي التكافؤ تنخفض بمقدار 2.2 درجة تقريبا.

تتغير المجال الفهري $E_C$ بتعزيز درجة الحرارة بنفس الصورة التي تتغير بها الاستقطاب التلقائي مع درجة الحرارة. بالقرب من درجة حرارة الانتقال الطوري $T_C$ يختلف $E_C = \text{Const.} \cdot (T_C - T)^s$ على الصورة $T, E_C$ تختلف من حالة إلى أخرى وهي تساوي 0.77 في حالة العينات النقيّة. هذه القيمة لا تختلف كثيراً عن القيم المنشورة ولكنها تساوي نصف القيمة التي تعطيها النظريات. تصل $(s)$ إلى 1.48 في حالة العينات المطعمة بأيونات النحاس.
تمت دراسة سلوك تغير معامل البيزوكهربية بتغير درجة الحرارة ولاحظ أن معامل البيزوكهربية يختفي عند درجة حرارة الانتقال الطوروي وما بعدها في حالة العينات النقية وتلك المطعمة بالكوبلت والنيكل بينما في حالة الشوائب الثلاثة الأخرى يظل معامل البيزوكهربية موجوداً لفترة حرارية صغيرة بعد درجة حرارة الانتقال الطوروي. إضافة أيون الكوبالت ثنائي الككافؤ يزيد من قابلية المادة لتحويل الطاقة الميكانيكية إلى طاقة كهربية بينما يعمل أيون النحاس ثنائي الككافؤ على نقص هذه القابلية.

أظهرت التجارب عدم وجود دلائل تشير إلى حدوث تغير في الطور عند درجات الحرارة المنخفضة ومن وجهة نظرنا فإن تجارب طيف رامن ليست هي الأنسب في الكشف عن التغيرات الطورية في المواد الفروككهربية ولكن يكون ذلك عن طريق قياس ثابت العازل أو الاستقطاب التلقائي لهذه البلورات.