Full Length Research Paper

Low temperature characteristics of dielectric properties for Tl$_4$S$_3$ layered single crystals

A. M. Badr*, H. A. Elshaikh and I. M. Ashraf

Physics Department, Faculty of Science, South Valley University, Aswan, Egypt.

Accepted 30 December, 2010

The current investigation was fulfilled for insight into the dielectric properties of Tl$_4$S$_3$ layered single crystals. The real part of dielectric constant $\varepsilon_r$, imaginary part of dielectric constant $\varepsilon_i$, the dissipation factor $\tan \delta$ and the alternating current conductivity $\sigma_{ac}$ were measured in an applied ac electric field of frequencies extending from 2.5 to 50 kHz. These measurements were carried out in low temperatures ranging from 77 to 300 K. In line with the dependencies of these dielectric parameters on frequency and temperature, the dielectric properties of the crystals under investigation were elucidated and analyzed. Furthermore, the ac conductivity was found to obey the power law $\sigma_{ac}(\omega) = A\omega^s$ with which the values of $s$ were evaluated to be less than unity in the range $0.77 \leq s \leq 0.69$. On increasing the conditional working temperature, the exponent $s$ was found to be linearly decreased with a temperature coefficient of about $3.69 \times 10^{-4}$. However, the resultant data showed that the temperature dependence of ac conductivity follows the Arrhenius relation. Based on this dependence, the impact of temperature on the electrical processes in an applied ac electric field was demonstrated and analyzed. In addition, the activation energy was determined for two temperature phases at all the working frequencies investigated here.

Key words: Dielectric properties of layered single crystals, charge transition in chalcogenide semiconductors, electrical conduction in an a.c electric field.

INTRODUCTION

The physical properties of layered crystals have constituted a major research area in solid-state physics. Layered crystals were largely used to test some of the most advanced techniques in modern photoemission (Clasen et al., 1983). This advantage has not been applied in large scale to chalcogenide semiconductors containing thallium (Margaritondo, 1986). The interest of these materials is stimulated not only by their fundamental properties but also by possible practical applications (Guseinov et al., 1969; Mamedov et al., 1986; Allakhverdiev et al., 1984; Henkel et al., 1982). Investigation of the electrical properties of semiconducting materials in an applied ac electric fields gives information about the nature of charge transport and the states in the forbidden gap. Such measurements allow one to determine the relative dielectric constant ($\varepsilon_r$), the loss factor ($\varepsilon'$), the dissipation factor ($\tan \delta$), and the alternating current conductivity ($\sigma_{ac}$). In order to execute the mechanism of charge transport, it is necessary to know the dependences of these parameters on frequency and temperature (Mustafaeva et al., 2007). The dielectric behavior of materials under an external ac electric field has been the focus of numerous papers, in view of its high scientific and technological importance. These measurements were made in wide frequency and temperature ranges for many types of materials (Şentürk, 2004). In line with an extensive research plan prepared for insight into the physical properties of Tl – S system, electrical and photoelectrical properties of TIS, Tl$_2$S, TlS$_2$ and Tl$_4$S$_3$ layered single crystals were elucidated in our papers (Ashraf et al., 2004a; Ashraf et al., 2004b; Elshaikh et al., 2004; Ashraf et al., 2007; Elshaikh et al., 2007; Badr et al., 2009; Badr, 2007). Thallium sulfides are unique semi-conducting compounds with complex layered structures due to their high structural anisotropy, optical and photoconductive properties. However, very little information is known about the electronic structures.
of the aforementioned materials (Youssef, 1995; Estrella et al., 2002). In addition, a special technique was designed for growing these compounds (the technique is described in Elshaikh et al. (2004)). Furthermore, the aforementioned research plan was prepared for enriching knowledge with respect to the physical properties of these semi-conducting compounds because of: i) According to the best knowledge of the authors, little information is reported in the literature with respect to the physical properties of these compounds; and ii) There are difficulties in obtaining these compounds in their single crystal forms. So, we intend to go on our research plan by the current investigation that is mainly aimed for insight into the DE properties of Tl4S3 layered single crystals.

EXPERIMENTAL DETAILS AND CONDITIONS

A technique based on the Lenten Thermal Design (LTD) was used for growing the Tl4S3 compound in its single crystal form (Elshaikh et al., 2004). This technique was provided with three digital temperature controllers (Eurotherm 91e-type) that were used to control the temperature profile inside the tube furnace of this design. The aforementioned controllers were used to pinpoint a suitable fixed set inside the furnace at which a crucible containing the Tl4S3 compound was thereafter placed. The compound under study was obtained in mono-crystal form by Cooling with a rate of 3°C / h. The samples were prepared from pure (5N) elements (Aldrich) in an evacuated (10^-6 Torr) silica tube. The crystal natures of the obtained crystals were confirmed by comparing their recorded and standard X-ray diffraction patterns (Berger, 1991). The comparison showed that the resulting Tl4S3 compound is single crystal with a monoclinic symmetry, space group: P21/c and lattice parameters: a = 7.7373 Å, b = 13.0120 Å, c = 7.9499 Å and Z = 4. The resultant compound was obtained as layered single crystals from which the specimens were prepared by splitting the crystal along the cleavage plane and hence the resultant surface was mirror-like without any mechanical treatment. A piece of 1 x 2.5 mm² with a thickness of 0.5 mm is selected for the DE measurements. Thereafter, it was mounted on the cold finger inside a cryostat (Oxford DN1704-type), which was evacuated to about 10^-4 Torr. The temperature inside the cryostat was controlled by a digital temperature controller (Oxford IT601-type). The contacts between the samples and the metal electrodes were fulfilled for the two opposite flat faces of the specimen using silver paint. A High Precision LCR – 819 Meter (12 Hz – 100 kHz) was used for studying the dielectric properties of the Tl4S3 layered single crystals.

RESULTS AND DISCUSSION

The dielectric (DE) analysis is an important implement, which can be used to enrich knowledge with respect to the electrical properties of a material medium as a function of temperature and frequency. Based on the DE analysis, two fundamental electrical characteristics of a material medium could be pinpointed: i) The nature of the material as an insulating medium, which exhibits its capability to store electric charges; and ii) The nature of the material as a conductive medium, which exhibits its capability to transfer the electric charge. However, the DE analysis could be fulfilled for a material medium by executing the DE measurements. Based on the experimental data of these measurements, the DE parameters (e.g. the dielectric constant ε, dielectric loss ε', dissipation factor tanδ, and ac-C) of the material can be evaluated. In the current work, the frequency and temperature dependences of these parameters for the Tl4S3 crystalline medium were described and analyzed as following: The complex dielectric constant of the material medium is generally formulated as two parts: ε = ε' + jε'', where ε is the real part of dielectric constant (RPDEC) and ε' is the dielectric loss or the imaginary part of dielectric constant (IPDEC). Based on the relation between ε and ε', a loss tangent or the dissipation factor was defined as tanδ = ε' / ε. Dependences of the RPDEC, IPDEC, and dissipation factor (tanδ) on both temperature and frequency of the applied ac field were individually investigated for Tl4S3 layered single crystals. The DE measurements were carried out at the temperatures ranging from 77 to 300 K and frequencies ranging from 2.5 to 50 KHz.

The aforementioned dielectric DE parameters were evaluated by measuring the equivalent parallel capacitance Cp and the equivalent parallel resistance Rp of the specimen under investigation using the following equations (Amarjeet et al., 2000):

\[
\varepsilon' = \frac{C_p}{C_0} \Rightarrow \varepsilon' = \frac{C d}{\varepsilon_0 A}
\]

\[
\varepsilon'' = \frac{C_p}{\omega C_p R_p}
\]

…….(1)

where C₀ is the capacitance of the specimen medium in Farad, d is the thickness in meter, A is the area in square meter, C₀ is the geometrical capacitance of vacuum through the same dimensions as the sample, ε₀ is the absolute permittivity in the free space having a value of 8.854 x 10^-12 Fm^-1, ε is the real part of dielectric constant and ε' is the imaginary part of dielectric constant.

Investigation of the electric properties of semiconductor materials in an applied ac electric fields gives information about the nature of charge transport and states in the forbidden gap (Mustafaeva et al., 2007). So, the values of the alternating current conductivity (ac-C) for the Tl₄S₃ crystalline medium were calculated based on the measured values of the aforementioned DE parameters using the following relation (Lal et al., 2004):

\[
\sigma_{ac}(f) = 2\pi f \varepsilon_0 \varepsilon' \tan\delta
\]

…….(2)

where f is the measuring frequency of the applied ac electric field (Hz) and tan δ is the dissipation factor that describes the phase difference between the current and voltage with respect to the applied ac electric field.
Frequency and temperature dependences of RPDEC

The fundamental interaction mechanisms between a dielectric material medium and electromagnetic waves are strongly required to be synopsized prior the insight into the discussion and analysis of the dielectric properties of the Tl$_2$S$_3$ layered single crystals. Displacements of the charge carriers and hence the decrease of the RPDEC with increasing frequency are occurred in a dielectric material as a result of applying an ac electric field that is well known as polarization. The electrical polarization includes four categories that are well specified as electronic, ionic (or atomic), dipolar (or orientation), and space charge: i) Electronic polarization ($P_e$) that arises due to the displacement of the valence electrons relative to the positive nucleus and occurs at the frequencies up to $10^{16}$ Hz; ii) Ionic polarization ($P_i$) that arises due to the displacement of negative and positive ions with respect to each other. In this category, the ions cannot be polarized rapidly because of they are heavier than electrons leading to that the maximum frequency of the ionic polarization is approximately $10^{13}$ Hz; iii) Dipolar polarization ($P_d$) that arises due to the permanent electric dipole moments of molecules by which change orientation is governed into the direction of the applied electric field. Dipolar polarization occurs at frequencies up to about $10^{10}$ Hz; and iv) Space charge polarization ($P_s$) that arises due to the mobile charge carriers impeded by interfaces. Space charge polarization typically occurs at frequencies between 1 and $10^3$ Hz. The total polarization ($P$) of the dielectric material can be expressed as the sum of the aforementioned polarizations (Barsoum, 1997):

\[ P = P_e + P_i + P_d + P_s \]  \hspace{1cm} (3)

Figure 1 represents a schematic diagram that illustrates the frequency dependencies of the electronic, ionic, dipolar, and space charge polarization contributions to the relative dielectric constant. Depending on the bonding and structure of the dielectric material and the frequency, dielectric materials exhibit at least one of these polarization categories. The total polarization $P$ is related to the relative dielectric constant $\varepsilon$ through the following equation (Hench and West, 1990):

\[ P = \varepsilon_0 (\varepsilon - 1) E = \varepsilon_0 \chi E \]  \hspace{1cm} (4)

where $\varepsilon_0$ is the permittivity of free space, $\chi$ is the electric susceptibility, and $E$ is the applied ac electric field. Equation 4 shows the direct relation between relative dielectric constant and polarization. In line with this equation, one could predict the magnitude of the polarization in a dielectric material as the relative dielectric constant is well known for this material. The relative dielectric constant $\varepsilon$ determines the maximum energy that can be stored in the material. However, the relative loss factor $\varepsilon'$ evaluates the absorption of electrical energy by a dielectric material that is subjected to an alternating electromagnetic field. Furthermore, the dissipation factor $\tan\delta = \varepsilon' / \varepsilon$ determines how well a material can absorb the electromagnetic field (Barsoum, 1997; Hench and West, 1990). The frequency dependence of the RPDEC for the Tl$_2$S$_3$ layered single crystals was investigated in the frequency of the applied ac field ranging from 2.5 – 50 kHz at different working temperatures extending from 77 to 300 K. This variation of the RPDEC with frequency is shown in Figure 2. In line with this figure, a considerable decrease in the RPDEC commences from 2.5 kHz till the frequency of 50 kHz at the working temperatures ranging from 260 to 300 K. With respect to the values of frequencies lower than 13.5 kHz, the instrument gives inconsistent values of both the equivalent parallel capacitance $C_p$ and the equivalent parallel resistance $R_p$ that exhibit inconsistent values of the RPDEC at the working temperatures ranging from 77 to 240 K. These inconsistent values of the RPDEC were therefore not recorded in Figure 2. Because of the inconsistent values of the RPDEC, its recorded values seem with a shift toward low frequency region as the working temperature increases form 77 to 300 K. It is evident from Figure 2 that the behavior of the Tl$_2$S$_3$ crystalline medium could be interpreted with respect to the frequency intervals:

i) Behavior in the first interval is observed in the low frequency region 2.5 – 13.5 kHz in which the RPDEC sharply decreases with increasing frequency. So, the RPDEC of the Tl$_2$S$_3$ crystalline medium is therefore strongly dependent on the frequency at the low frequency region. The maximum value of the RPDEC is clearly observed at 2.5 kHz for the working temperatures ranging from 260 to 300 K. However, Figure 2 shows that the maximum value is observed at different beginning frequencies for the working temperatures ranging from 77 to 240 K. Furthermore, this maximum value was found to be extended from 186.35 to 374.11 corresponding to the working temperatures ranging from 77 to 300 K. So, the maximum value of the RPDEC at the working temperature 77 K is much less than its maximum value attained at the working temperature 300 K. Therefore, the RPDEC of the Tl$_2$S$_3$ crystalline medium is strongly dependent on the temperature at the low frequency region.

ii) Behavior in the second interval is observed in the high frequency region 13.5 – 50 KHz in which the RPDEC of the Tl$_2$S$_3$ crystalline medium starts falling slightly with the increase in frequency of the applied ac field till the value of 33.33 kHz after which it seems close to the saturation phase. In addition, the values of the RPDEC at 50 KHz were found to be 139.02 and 204.42 corresponding to the working temperatures 77 and 300 K respectively. So, the RPDEC of the Tl$_2$S$_3$ crystalline medium shows a little dependence on both frequencies and temperature at the
high frequency region. In line with Figure 2, the RPDEC of the Tl$_4$S$_3$ layered single crystals exhibits low values at the high frequency region that is of vital importance for these materials in the construction of photonic and NLO devices (Aruna et al., 2007).

The temperature dependence of the RPDEC for the Tl$_4$S$_3$ crystalline medium was investigated in the temperature range 77 – 300 K at different working frequencies of the applied ac field extending from 2.5 to 50 kHz. Behavior of the RPDEC as a function of temperature for the Tl$_4$S$_3$ crystalline medium is shown in Figure 3. However, this figure involves the behavior for selected working frequencies ranging from 4.28 to 33.33 kHz. Based on this figure, a remarkable rise of the RPDEC commences from 77 K till the temperature of 300 K at the working frequencies ranging from 4.28 to 33.33 kHz. The inconsistent values of the RPDEC at the values of temperatures lower than 200 K are not also recorded in Figure 3 leading to reduction of the recorded values as the working frequency decreases from 10 to 4.28 kHz. This exhibits a shift in behavior toward the high temperature region as the working frequency decreases from 10 to 4.28 kHz that showing different beginnings for such a working frequency. Furthermore, the maximum value of the RPDEC is obviously found to be at 300 K for all working frequencies investigated here. This maximum value of the RPDEC (at 300 K) was found to be decreased from 336.11 to 231.98 corresponding to the working frequencies ranging from 4.28 to 33.33 kHz. It is evident that the maximum value of the RPDEC at the working frequency 33.33 kHz is much less than its maximum value attained at the working frequency 4.28 kHz. Consequently, the RPDEC of the Tl$_4$S$_3$ layered single crystals is strongly dependent on the frequency of

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Dependence of i) the relative dielectric constant and ii) the relative loss factor on frequency of an alternating electric Field. Contributions of electronic, ionic, dipolar and space charge in the total polarization are determined (source of this diagram: "(Hench and West, 1990)"
Figure 2. Frequency dependence of the RPDEC for Tl$_4$S$_3$ layered single crystals.

Figure 3. Temperature dependence of the RPDEC for Tl$_4$S$_3$ layered single crystals.
the applied ac field at the high temperature region. However, Figure 3 shows an intensive rise of the RPDEC with temperature at the low working frequencies that coincides with the data described in Figure 2 leading to the RPDEC of the Tl₄S₃ layered single crystals is strongly dependent on temperature at low working frequencies. The intensive rise of the RPDEC with temperature at the low working frequencies could be attributed to space charge or interfacial polarization.

Based on this figure, the RPDEC exhibits anomalous behavior with temperature at the low working frequencies that suggests the possibility of the crystal medium to be ferroelectric (Lal et al., 2004). The higher value of the RPDEC observed at the low working frequencies in a crystal medium could be attributed to voids, dislocations and other defects (Sirdeshmukh et al., 1998). However, in the case of composites of the type reported by Mahajan et al. (2000), the large values of the RPDEC were reported to be due to the fact that ferroelectric grains are surrounded by ferrite grains that commence themselves in giving interfacial polarization (Appel, 1968).

**Frequency and temperature dependences of IPDEC**

The frequency dependence of the IPDEC for the Tl₄S₃ layered single crystals was investigated in the frequency of the applied ac field ranging from 4.28 – 50 kHz at different working temperatures extending from 77 to 300 K. The variation of the IPDEC with frequency of the applied ac field is illustrated in Figure 4. This figure shows an intensive decrease in the IPDEC with frequency commences from 4.28 kHz till the frequency of 50 kHz at the working temperatures ranging from 200 to 300 K. As a result of the inconsistent values of both the equivalent parallel capacitance $C_p$ and the equivalent parallel resistance $R_p$, there is a different beginning for such a working temperature. This shows a shift in behavior toward the low frequency region as the working temperature increases from 77 to 300 K. It is evident from Figure 4 that the behavior of the Tl₄S₃ crystalline medium
with respect to the IPDEC is similar to its behavior for RPDEC. However, behavior of the IPDEC for Tl$_3$S$_3$ crystalline medium shows the greater dependencies on both frequency and temperature, and could be interpreted according to the frequency intervals:

i) First could be observed in the low frequency region 4.28 – 20 kHz: Behavior in this region shows a pronounced decrease in the IPDEC with the increase in frequency. Hence, the IPDEC of the Tl$_3$S$_3$ crystalline medium exhibits a strong dependence on the frequency at the low frequency region. The maximum value of the IPDEC is found to be at the beginning frequency for each working temperature. Based on Figure 4, maximum value is found to be increased from 26.03 to 138.48 corresponding to the working temperatures ranging from 77 to 300 K. Therefore, the maximum value of the IPDEC at the working temperature 77 K is much less than its maximum value attained at the working temperature 300 K. So, the IPDEC of the Tl$_3$S$_3$ crystalline medium is strongly dependent on the temperature at low frequency region.

ii) The second could be observed in the high frequency region 20 – 50 KHz: Behavior in this region exhibits slightly falling in the IPDEC of the Tl$_3$S$_3$ crystalline medium with the increase in frequency of the applied ac field starting from the frequency of 20 kHz till the value of 33.33 kHz. Thereafter, the value of the IPDEC seems close to the saturation phase for all working temperatures. So, the IPDEC of the Tl$_3$S$_3$ crystalline medium shows a little dependence on frequency at the high frequency region. Furthermore, the values of the IPDEC at frequency 50 kHz were found to be 10.56 and 54.08 corresponding to the working temperatures 77 and 300 K respectively. Hence, the IPDEC of the Tl$_3$S$_3$ crystalline medium shows a remarkable dependence on temperature at the high frequency region.

The temperature dependence of the IPDEC for the Tl$_3$S$_3$ layered single crystals was investigated in the temperature range 77 – 300 K at different working frequencies of the applied ac field extending from 2.5 to 50 kHz. The variation of the IPDEC with temperature is depicted in Figure 5. However, this figure involves the behavior for selected working frequencies ranging from 4.28 to 40 kHz. This figure shows a considerable rise of 300 K at the working frequencies ranging from 12 to 40 kHz. With respect to the values of IPDEC at temperatures lower than 200 K, the instrument gives inconsistent values of both the equivalent parallel capacitance $C_p$ and the equivalent parallel resistance $R_p$ at the working frequencies ranging from 4.28 to 10 kHz. The resultant inconsistent values of the RPDEC are not recorded in Figure 5 exhibiting a shift in behavior toward the high temperature region as the working frequency decreases from 10 to 4.28 kHz that shows a different beginning for such a working frequency. Based on this figure, the behavior of the Tl$_3$S$_3$ crystalline medium could be also illustrated with respect to the temperature intervals:

i) First interval involves the variation of the IPDEC with temperature in the low temperature region 77 – 200 K: In this region, the IPDEC of the Tl$_3$S$_3$ crystalline medium commences slightly rise at 77 K with the increase in temperature till reaching the temperature of 200 K for the working frequencies ranging from 12 to 40 kHz. The same behavior was observed for the working frequencies retained, but with different starting points due to the inconsistent values of both the equivalent parallel capacitance $C_p$ and the equivalent parallel resistance $R_p$.

Figure 5 shows a little dependence of the IPDEC on temperature in the low temperature region. However, the value of the IPDEC at the beginnings of this interval was found to be 76.22 and 16.78 corresponding to the working frequencies 4.28 and 40 kHz respectively. So, the IPDEC of the Tl$_3$S$_3$ crystalline medium shows a little dependence on frequency in the low temperature region.

ii) Second interval involves the variation of the IPDEC with temperature in the high temperature region: 200 – 300 K: This region exhibits an intensive rise in the IPDEC with increasing temperature. So, the IPDEC of the Tl$_3$S$_3$ crystalline medium is strongly dependent on temperature at the high temperature region. It is observed in this interval that the maximum value of the IPDEC is found to be at 300 K for all working frequencies investigated here. This maximum value of the IPDEC (at 300 K) extends from 138.48 to 70.13 corresponding to the working frequencies ranging from 4.28 to 40 kHz. The maximum value of the IPDEC at the working frequency 40 kHz seems much less than its maximum value attained at the working frequency 4.28 kHz. Therefore, the IPDEC of the Tl$_3$S$_3$ layered single crystals is strongly dependent on the temperature at the high temperature region.

**Frequency and temperature dependencies of dissipation factor**

The variation of the dissipation factor with frequency for the Tl$_3$S$_3$ crystalline medium was measured in the frequency range 7.5 – 50 kHz at different working temperatures extending from 77 to 300 K. Figure 6 shows the dissipation factor as a function of frequency. In line with this figure, the dissipation factor slightly decreases with the increase in frequency showing a little dependence on frequency at all working temperatures investigated here. Based on Figure 6, the beginning and ending values of the dissipation factor at the working temperature of 77 K were calculated to be 0.139 and 0.076 respectively. These values were calculated at the working temperature of 300 K to be 0.392 and 0.264 respectively. The difference between the beginning values at the working temperature 77 K and that at the working temperature 300 K and the same difference with
Figure 5. Temperature dependence of the IPDEC for Tl$_4$S$_3$ layered single crystals.

Figure 6. Frequency dependence of the dissipation factor for Tl$_4$S$_3$ layered single crystals.
respect to the ending values show that the dissipation factor is strongly dependent on temperature at the whole investigated range of frequencies.

The variation of the dissipation factor with temperature for the Tl₄S₃ crystalline medium was measured in the temperature range 77 – 300 K at different working frequencies of the applied ac field extending from 2.5 to 50 kHz. However, Figure 7 shows the dissipation factor as a function of temperature with respect to selected working frequencies ranging from 10 to 33.33 kHz. Based on this figure, the dissipation factor shows a similar rise with increasing temperature at all working frequencies investigated. In addition, the figure indicates a sharp increase in the dissipation factor as the temperature increases at all working frequencies. A little dependence of the dissipation factor on frequency is observed with the aids of Figure 7 that coincides with the data described in Figure 6. The dissipation factor of the Tl₄S₃ layered single crystals exhibits low values suggesting that the grown crystals possess good optical quality. However, this DE parameter is of vital importance for nonlinear optical materials in their applications (Balarew and Duhlew, 1984).

Based on Figures 4 – 7, the IPDEC and dissipation factor of the Tl₄S₃ crystalline medium exhibit similar dependences on temperature and frequency of the applied ac electric field. Similarity in behavior has been observed for many materials like lanthanum heptamolybdate (Bhat et al., 1995a), neodymium heptamolybdate (Bhat et al., 1995b) and La–Nd heptamolybdate (Bhat et al., 1995c). Otherwise, the intensive increase in the dissipation factor with temperature (see Figure 7) and the large value of the RPDEC at low frequency (see Figures 2, 3) may be due to the presence of space charge polarization near the grain boundary interfaces which depends on the purity and perfection of the sample (Smyth, 1965). The contribution from space charge towards polarization depends on purity and perfection of crystals as the impurities and/or defects create potential barriers that limit the transport of charge carriers. So, the space charge (or diffusing) contribution involves a limited transport of charge carriers until they are stopped at a potential barrier, possibly a grain boundary or phase boundary (Lal et al., 2004). However, space charge and dipolar polarizations are relaxation processes and are
strongly temperature dependent (Moulson and Herbert, 1990).

**Frequency and temperature dependences of the ac-C**

Figure 8 illustrates the frequency dependence of the ac-C in the frequency range 2.5 – 50 kHz at the working temperatures extending from 77 to 300 K. For all working temperatures investigated here, this figure shows a typical dependence of the ac-C on frequency. Based on the aforementioned figure, a pronounced rise in the ac-C of the Tl₄S₃ layered single crystals is observed for all working temperatures. However, the behavior for such a working temperature commences a peak starting at the frequency of 33.33 kHz. Before the starting point of the beak frequency, Figure 8 shows strong dependence of the ac-C on frequency at all working temperatures. Furthermore, the figure exhibits little dependence of the ac-C for the Tl₄S₃ layered single crystals on temperature in the low frequency region, thereafter the ac-C rises gradually to be strongly dependent on temperature in the high frequency region. It is also clear from this figure that before the starting point of the beak frequency, the ac-C increases linearly with increasing frequency for all working temperatures investigated here. This coincides with what is reported in Jonscher (1977) that the ac-C increases linearly with increasing frequency for most semiconductors.

In line with this figure, the dependence of the measured ac-C with frequency of the applied ac field at all working temperatures investigated here could be formulated as (Chen et al., 2000):

\[ \sigma (\omega) = \sigma (0) + A \omega^s \]

where \( \sigma (0) \) is the dc conductivity, \( A \) is the pre-exponential factor and \( s \) is the exponent. The aforementioned equation is referred as the universal dynamic pattern of ac electrical behavior of conducting solids and liquids as proposed by Jonscher (1978) based on the exponent \( s \) lies in the range 0 < \( s \) < 1. It has been used mostly to characterize the electrical conduction in disorder ionic glasses, amorphous semiconductors, ionic conductors and some crystals (Ingram, 1987; Angell, 1990; Long, 1982; Elliott, 1987; Pollak and Geballe, 1961; Bruce et al., 1982; Lee et al., 1991). This power
law is related to the dynamics of hopping transport between states in the forbidden gap. The exponent $s$ is the measure of the degree of interaction with the environment. Experimental evidence of this behavior is a power law of the ac conductivity $\sigma_{ac}(\omega) = A\omega^s$ observed over many decades of frequency (Murowski and Barczynski, 1995). The interpretation usually involves analysis of the temperature dependence of $s$ ($T$) which makes it possible to find the relevance of the hopping mechanism in terms of pair approximation (Elliott, 1987).

Based on the aforementioned power law, the quantity $\ln \sigma_{ac}$ was plotted as a function of $\ln \omega$ that is depicted in Figure 9. In line with this figure, the values of the exponent $s$ for all working temperatures were evaluated by calculating the slopes of resultant straight lines. In the current work, the estimated values of the exponent $s$ were found to be less than unity in the range $0.77 \geq s \geq 0.69$. The exponent $s$ was plotted as a function of temperature for all frequency investigated here to describe the temperature impact on it and determining its temperature coefficient. However, the exponent $s$ was observed to be frequency dependent and it decreases linearly with increasing working temperature (Inset of Figure 9) with temperature coefficient of about $3.69 \times 10^{-4}$.

The ac-$C$ of the Tl$_4$S$_3$ layered single crystals was evaluated by substituting the values of $\varepsilon$ and $\tan \delta$ in Equation 2. Figure 10 shows the temperature dependence of the ac-$C$ in the temperature range $77 – 300$ K at the working frequencies ranging from 2.5 to 50 kHz. However, Figure 10 shows the ac-$C$ as a function of temperature with respect to selected working frequencies ranging from 12 to 40 kHz. Based on this figure, a typical dependence of the ac-$C$ on temperature is observed at all working frequencies investigated here. In addition, the ac-$C$ is noted to be slightly increased with increasing temperature in the low temperature region at all investigated working frequencies. However, the ac-$C$ fulfills an intensive rise with increasing temperature in high temperature region at all investigated working frequencies. In line with this region, the ac-$C$ of the Tl$_4$S$_3$ layered single crystals shows strong dependence on temperature at all investigated working frequencies.

It is obvious from Figures 2 – 7, 8 and 10 that The Tl$_4$S$_3$ layered single crystals exhibit an intensive dependence of RPDEC, IPDEC, dissipation factor and ac-$C$ on temperature and frequency of the applied ac field (Table 1). So, the functional dependence of these DE parameters

![Figure 9. Plot of the quantity ln($\sigma_{ac}$) as a function of ln($\omega$) for Tl$_4$S$_3$ layered single crystals.](image-url)
on temperature and frequency forms an important characteristic of these materials and is strongly required to be investigated. However, strong dependencies of these DE parameters on temperature and frequency of the applied ac field have been applicable for a large number of materials (Lal et al., 2004; Bhat et al., 1995a, b, c).

Figure 11 depict a plot of the quantity \(\ln \sigma\) as a function of \(1000 / T\) in the temperature range 77 – 300 K at selected working frequencies extending from 12 to 33.33 kHz. This graph was plotted based on an Arrhenius plot using the following relation (Verwey and Heilmann, 1947):

\[
\sigma = \sigma_0 \exp \left( -\frac{E_a}{kT} \right) \quad \text{……(6)}
\]

where \(\sigma\) is the conductivity at temperature \(T\), \(E_a\) the activation energy for the ac electrical process, and \(k\) the Boltzmann’s constant. In line with Figure 11, the inversely dependence of the quantity \(\ln \sigma\) exhibits two straight lines with different slopes at such a working frequency. So, the activation energy of the electrical processes could be evaluated with respect to the temperature intervals. In the low temperature region, the activation energy of the ac electrical processes for the Tl\(_4\)S\(_3\) layered single crystals was calculated with respect to the working frequencies investigated here to be found in the range 0.084 eV \(\leq \Delta E_{ac} \leq 0.073\) eV, however it is estimated in the high temperature region to be found in the range 0.3 eV \(\geq \Delta E_{ac} \geq 0.26\) eV. The complete data concerning the activation energy of the ac electrical processes for the Tl\(_4\)S\(_3\) layered single crystals is reported in Table 2.

**Conclusion**

The DE measurements of the Tl\(_4\)S\(_3\) layered single crystals show that in the low frequency region, the
RPDEC is strongly dependent on both the frequency and temperature. However, it seems with a little dependent on frequency and temperature at the low frequency region. It is also observed that the RPDEC is strongly dependent on the frequency of the applied ac field at the high temperature region. The RPDEC of the Tl₄S₃ layered single crystals exhibits low values at the high frequency region that is of vital importance for these materials in the construction of photonic and NLO devices. The intensive rise of the RPDEC with temperature at the low working frequencies could be attributed to space charge or interfacial polarization. The RPDEC exhibits anomalous

Figure 11. Inversely dependence of the quantity \( \ln (ac-C) \) on temperature for the layered Tl₄S₃ single crystals.

Table 1. A resultant data showing the variation of RPDEC, IPDEC and the dissipation factor with frequency and temperature.

<table>
<thead>
<tr>
<th>Measuring frequency (kHz)</th>
<th>Real part of dielectric constant at ( T = 77 ) K</th>
<th>Imaginary part of dielectric constant at ( T = 77 ) K</th>
<th>Dissipation factor at ( T = 77 ) K</th>
<th>Real part of dielectric constant at ( T = 300 ) K</th>
<th>Imaginary part of dielectric constant at ( T = 300 ) K</th>
<th>Dissipation factor at ( T = 300 ) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>186.35</td>
<td>280.09</td>
<td>0.139</td>
<td>0.76</td>
<td>0.376</td>
<td></td>
</tr>
<tr>
<td>13.5</td>
<td>185.22</td>
<td>274.23</td>
<td>0.135</td>
<td>0.368</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>185.19</td>
<td>268.35</td>
<td>0.132</td>
<td>0.367</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.67</td>
<td>183.39</td>
<td>264.74</td>
<td>0.128</td>
<td>1.347</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18.18</td>
<td>182.24</td>
<td>262.48</td>
<td>0.128</td>
<td>0.344</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>179.05</td>
<td>257.96</td>
<td>0.130</td>
<td>0.339</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.22</td>
<td>175.21</td>
<td>253.67</td>
<td>0.129</td>
<td>0.337</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>173.86</td>
<td>249.15</td>
<td>0.128</td>
<td>0.328</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28.57</td>
<td>168.79</td>
<td>241.92</td>
<td>0.129</td>
<td>0.319</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33.33</td>
<td>161.53</td>
<td>231.98</td>
<td>0.123</td>
<td>0.313</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
behavior with temperature at the low working frequencies that suggests the possibility of the crystal medium to be ferroelectric. The higher value of the RPDEC observed at the low working frequencies in a crystal medium could be attributed to voids, dislocations and other defects. Furthermore, the in the low frequency region, the IPDEC of the Tl₃S₃ crystalline medium exhibits a strong dependence on both temperature and frequency of the applied ac electric field. But in the high frequency region, it shows a little dependence on frequency and a remarkable dependence on temperature. In the same way, the IPDEC shows a little dependence on temperature and frequency in the low temperature region, whereas it exhibits strong dependence on temperature at the high temperature region. The dissipation factor of the Tl₃S₃ layered single crystals is observed to be slightly decreased with the increase in frequency showing a little dependence on frequency at all working temperatures investigated here, however it is strongly dependent on temperature at the whole investigated frequencies of the applied ac electric field. The dissipation factor of the Tl₃S₃ layered single crystals exhibits low values suggesting that the grown crystals possess good optical quality. However, this DE parameter is of vital importance for nonlinear optical materials in their applications. The intensive increase in the dissipation factor with temperature and the large value of the RPDEC at low frequency may be due to the presence of space charge polarization near the grain boundary interfaces which depends on the purity and perfection of the sample. In line with the electrical processes in the applied ac electric field, it is noted that the ac-C for the Tl₃S₃ layered single crystals exhibits a little dependence on temperature in the low frequency region, thereafter it rises gradually to be strongly dependent on temperature in the high frequency region. The ac-C of the crystals under investigated undergoes a little dependence on temperature at all conditional working frequencies. However, it fulfills an intensive rise with increasing temperature in high temperature region at all investigated working frequencies. The ac-C of the Tl₃S₃ layered single crystals is observed to be linearly increased with increasing temperature that coincides with the data reported for most semiconductors. It is found to be obey the power law \( \sigma_{ac}(\omega) = A \omega^s \) with which the values of s are evaluated to be less than unity in the range 0.77 \( \leq s \leq 0.69 \). On increasing the conditional working temperature, the exponent s is found to be linearly decreased with a temperature coefficient of about 3.69 \( \times 10^{-4} \). In addition, the resultant data showed that the temperature dependence of ac conductivity follows the Arrhenius relation. Based on this dependence, the activation energy is determined for two temperature phases. The Tl₃S₃ layered single crystals exhibit an intensive dependence of RPDEC, IPDEC, dissipation factor and ac-C on temperature and frequency of the applied ac field. So, the functional dependence of these DE parameters on temperature and frequency forms an important characteristic of these materials and is required to be investigated, where strong dependencies of these DE parameters on temperature and frequency of the applied ac field have been applicable for a large number of materials.

### REFERENCES
