CHAPTER VII

Electrical conductivity and SEM Studies On pure and doped TGS crystals
CHAPTER VII

7.1 INTRODUCTION

Electrical conductivity is an experimental tool to probe the structural defects and internal purity of crystalline solids. Insulators are characterized by large energy gap. Different types of defects in the crystals are responsible for the electrical conduction. The mechanism of conductivity has been explained by many researchers [1–6]. Most of the earlier investigations on alkali halides, rare earth tungstates, divalent vanadates, phosphates and oxalates and other ferroelectric materials [7–15] described the electrical conductivity in terms of electrons or holes, polarons, impurities and thereby the mechanism of ionic conductivity was established on firm footing. The electrical conductivity of ionic materials is found to be very low which may be due to the trapping of some carriers at defect sites.

EXPERIMENTAL DETAILS

7.2 ELECTRICAL CONDUCTIVITY STUDIES

The conductivity measurements were carried out on the c-cut crystal in all cases employing the conventional two-probe technique at various temperatures ranging from 300 K to 350 K. Resistance of the crystals were measured using Keithley 3322 LCZ analyzer. The dimension of the crystal used in these measurements is 1 cm x 1 cm x 1 mm. The two opposite faces of the crystals were well polished and coated with silver paste to get good ohmic contact. The samples were placed in a cell made of copper and are held between the electrodes to ensure proper contact at all temperatures. The sample cell was placed in a container in which the heater was placed thus ensuring a good thermal insulation of the cell. A thermocouple was fixed in the vicinity of the lower electrode, which was used to measure the temperature. The observations were made while cooling the sample. The dimensions of the crystals were measured using a traveling microscope with a least count of
0.001 cm. The conductivity (σ) of the crystal was calculated using the relation 7.2. The data are fitted using a least square fitting program (Appendix I).

Figure 7.1 shows the variation of conductivity for the pure TGS and FeTGS crystals and figure 7.2 shows the variation for the BaTGS, CuTGS, PbTGS and MnTGS crystals.

The conductivity values above transition temperature were fitted into the equation,
\[
\sigma = \sigma_0 \exp \left( \frac{E_g}{kT} \right) \quad \ldots \ldots \ 7.1
\]

where \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( E_g \) is the activation energy and \( \sigma_0 \) is a constant depending on the material.

Table 7.1 : Activation energy values

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pure TGS</th>
<th>BaTGS</th>
<th>CuTGS</th>
<th>PbTGS</th>
<th>FeTGS</th>
<th>MnTGS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy (eV)</td>
<td>0.41</td>
<td>0.62</td>
<td>0.56</td>
<td>0.58</td>
<td>0.46</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Table 7.2 : Conductivity values of the irradiated crystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity (×10(^{-7}) /Ωm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>unirradiated 5 kGy 10 kGy 30 kGy</td>
</tr>
<tr>
<td>Pure TGS</td>
<td>3.05820 0.9679 1.0434 1.8573</td>
</tr>
<tr>
<td>BaTGS</td>
<td>31.1020 0.8178 0.8399 0.8509</td>
</tr>
<tr>
<td>CuTGS</td>
<td>27.3047 5.4091 10.458 16.886</td>
</tr>
<tr>
<td>FeTGS</td>
<td>4.15950 3.7074 6.9879 8.1879</td>
</tr>
<tr>
<td>MnTGS</td>
<td>21.1335 5.7888 8.0372 15.467</td>
</tr>
</tbody>
</table>

The activation energy values were calculated for all the samples and the values are listed in the table 7.1.

7.2.1 Results and Discussions

The electrical conductivity of the crystalline materials is determined by the intrinsic defects in the crystal. The defects may be due to the impurities added or due to irradiation of the crystal with some radiation. In general, the conductivity of a crystal is calculated using the relation

\[
\sigma = \frac{\iota}{R \times A} \quad \ldots \ldots \ 7.2
\]
where R is the measured resistance, t is the thickness of the sample and A is the area of the face in contact with the electrode. The resistance can be measured by measuring current through a sample for a given applied potential difference using Ohm's law. However, for good accuracy, the resistance of the voltmeter used should be very high as compared to the order of magnitude of the crystal resistance at all ranges of measurement.

The electrical conductivity for ionic materials is found to be very low which may be due to the trapping of some carriers at defect sites. At any particular temperature, however, the Gibb's free energy of a crystal is minimum when a certain fraction of ions leaves the normal lattice. As the temperature rises, more and more defects are produced which, in turn, increase the conductivity [16]. In the high temperature region, the effect of impurity on electrical conduction will not change appreciably whereas in the low temperature region, the presence of impurity in the crystal increases its conductivity. The electrical conduction in dielectrics is mainly a defect controlled process in the low temperature region. The presence of impurities and vacancies mainly determines this region. The energy needed to form the defect is much larger than the energy needed for its drift [17-18].

Present study shows that the conductivity values for doped TGS crystals at all temperatures considered is higher when compared to pure TGS system. However, the activation energy is higher for the doped crystals when compared to pure TGS crystal. Further, it can be seen that, the electrical conductivity increases with the increase in temperature upto the transition temperature of the crystals and thereafter decreases. This may be due to the increase in the defect concentration with temperature. The addition of impurity further increases the electrical conduction. The conduction process in the present study seems to be connected to mobility of vacancies. The low activation energies observed suggest that oxygen vacancies may be responsible for conduction in this region.

From the figures showing the temperature dependence of dc conductivity of pure and doped TGS crystals, the following inference are drawn
• Nothing is observed to indicate the existence of a new phase transition at a temperature below the transition temperature.

• A pronounced anomaly is observed at the transition temperature both in case of pure and doped TGS crystals.

• The behaviour is mainly due to the difference in the domain configuration. A resemblance is observed between the behaviour in the variation of dielectric constant and the dc conductivity.

• 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 for the pure TGS crystal is in good agreement with the reported values [19-20].

• The value of the transition temperature for all samples is in consistence with those obtained from the measurement of the dielectric constant.

The conduction mechanism in TGS crystals is ionic in nature. This is due to the fact that TGS is 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 may be one of the reasons for the diversity in the data reported for the activation energy and the anomalous behaviour at the transition temperature. Another reason for the diversity may be due to the strength of the applied field strength [21-22].

Variation of current with applied potential for pure and doped, unirradiated TGS crystals are shown in figure 7.3. For the same doping concentration of the impurities, the electrical conductivity is higher in case of doped crystal when compared to the pure TGS (Table 7.10). So, the present study indicates that the conductivity increases with dopants. While the dopants Ba$^{2+}$, Cu$^{2+}$, Pb$^{2+}$ and Mn$^{3+}$ show a considerable increase in the value of conductivity, the addition of ferroelectric material Fe$^{3+}$ show a little increase in the conductivity. This may be due to the domain alignment of dopant and the TGS crystals in such a way that pinning of domain walls take place and thereby reduce the conduction.
Figure 7.3: I-V plot of unirradiated samples

Figure 7.4: I-V plot of irradiated pure TGS
Figure 7.5: I-V plot for irradiated BaTGS crystal

Figure 7.6: I-V plot for irradiated PbTGS crystal
Figure 7.7: I-V plot for irradiated CuTGS crystal

Figure 7.8: I-V plot for irradiated FeTGS crystal
The I-V plots of the irradiated samples are shown in figures 7.4 to 7.9. The samples are irradiated with an electron beam with doses of 5 kGy, 10 kGy and 30 kGy. The conductivity values are given in table 7.10. It can be seen that the conductivity is greatly reduced as compared to the unirradiated samples. This is due to the additional defects produced due to irradiation which is responsible for pinning the motion of the domain walls further. The conductivity is found to increase with the dose of irradiation. The effect of dopants and irradiation on the conductivity of the samples studied are in agreement with the observations on similar samples reported by several researchers [23 – 30].

7.3 SEM STUDIES

Domain mechanism and its contribution to the pyroelectric property of a number of doped TGS have already been reported [31 – 35]. Imaging ferroelectric domains with scanning electron microscopy (SEM) is challenging because all ferroelectrics are by nature dielectric materials that are highly insulating [36]. Domain pattern studies by SEM reveal that in TGS, domains occur very easily if many domains are present, but they occur with great
difficulty if a single domain exists in the crystal [37]. Hence, domain structure studies are of special interest to assess the suitability of the crystals for device applications. Polarization reversal occurs very easily in multidomain crystals compared to single domain crystals [38].

The Scanning Electron Microscopy is a type of electron microscope to study the microstructural and morphological features of a sample surface by scanning it with a high energy electron beam. The electrons are generated by a field emission gun using a high electrostatic field. They are accelerated with energies between 1 keV and 30 keV down through the column towards the specimen. While the magnetic lenses focus the electron beam to a spot with a diameter of approximately 10 nm, the scanning coils sweep the focused electron beam over the specimen surface. A material of higher atomic number produces a brighter image. To capture this information a detector is required which can either be metal, semiconductor or a scintilator / light pipe / photomultiplier.

In the present work scanning electron microscopy is carried out with Stereoscan 440 which is discussed in chapter II.

7.3.1 Results and discussion

In this investigation, pure and doped crystal plates were cleaved into (010) platelets. These were etched using hydrochloric acid and rinsed with double distilled water to reveal the domain morphology. The etchant is capable of producing a high contrast between the positive and the negative domains with clear domain boundaries on the cleaved planes of the crystal. The domains were clearly visible with a magnification of 500x. The observation has revealed a variation in the domain morphology in different crystals. The scanning electron beam reverses the polarization [39]. In all the cases lenticular domains were observed as shown in figures 7.10 (a) – (f). The domains were found to be aligned perpendicular to the c-axis as reported earlier for pure and doped TGS crystals [40, 41]. The brighter regions, where the surface potential is lower than...
the surroundings are negative domains and relatively darkened are positive domains.

There are several possible explanations for the domain contrast. One is based on electrostatic interaction. When the sample is irradiated by the primary electron beam, secondary electrons are emitted from a certain depth below the surface. At the positive end of the dipole, some primary electrons are captured. Hence, there is a stronger secondary emission and therefore a brighter contrast from the negative end [42]. Another possible explanation lies in the converse piezoelectric effect. The sample contracts or expands depending on the domain orientation because of the electric field generated by the electrons deposited at the surface [43]. Also, the pyroelectric effect may play a role, because of the heating of the sample by the electron beam and this too has been proposed to explain domain contrast. Finally, an asymmetry of elementary electron processes in noncentrosymmetric crystals was suggested [44]. Although the domain-contrast mechanism in SEM imaging is still under discussion, the method can non-destructively visualize domain patterns with submicron resolution [45].

The shape and size of domains for undoped TGS crystal are in agreement with earlier observations [46]. In the case of doped crystals, presence of elongated domains is prominent and is a common feature which has been previously reported by other researchers [47]. The elongation in the shape of the domains may be attributed to the linear and volume defects introduced in the crystal due to doping [48]. In comparison to pure TGS, the doped crystals have exhibited a wide variation in the domain sizes and also show a higher domain density which is in agreement with the already reported earlier observations by other researchers [49].
Figure 7.10 (a): SEM of pure TGS

Figure 7.10 (b): SEM of Ba\(^{2+}\) doped TGS
Figure 7.10 (c) : SEM of Cu$^{2+}$ doped TGS

Figure 7.10 (d) : SEM of Pb$^{2+}$ doped TGS
Figure 7.10 (e): SEM of Fe$^{3+}$ doped TGS

Figure 7.10 (f): SEM of Mn$^{3+}$ doped TGS
7.4 CONCLUSIONS

For the same doping concentration of the impurities, the electrical conductivity is higher in case of doped crystal when compared to the pure TGS. Present study on the electrical conductivity indicates that the conductivity increases with the addition of different dopants. With the dopants $\text{Ba}^{2+}$, $\text{Cu}^{2+}$, $\text{Pb}^{2+}$ and $\text{Mn}^{3+}$, there is a considerable increase in the value of conductivity while the addition of ferroelectric material $\text{Fe}^{3+}$ show a little increase in the conductivity. The samples are irradiated with an electron beam with doses of 5 kGy, 10 kGy and 30 kGy to find the effect of irradiation on the electrical conductivity of doped TGS crystal. The conductivity values obtained for the electron irradiated samples show that the conductivity is greatly reduced as compared to the unirradiated samples and the conductivity increases with the dose of irradiation.

Study of temperature dependence of the conductivity shows that at all temperatures considered the doped TGS crystals have higher conductivity when compared to pure TGS system. However, the activation energy is higher for the doped crystals when compared to pure TGS crystal. Further, it can be seen that, the electrical conductivity increases with the increase in temperature upto the transition temperature of the crystals and thereafter decreases. The addition of impurity also found to increase the electrical conduction.

The SEM observations have revealed a variation in the domain morphology in different crystals. In all the cases lenticular domains have been observed. The domains were found to be aligned perpendicular to the c-axis as reported earlier for pure and doped TGS crystals. In the case of doped crystals, the presence of elongated domains is prominent which is found to be a common feature. The elongation in the shape of the domains is attributed to the linear and volume defects introduced in the crystal due to doping. In comparison to pure TGS, the doped crystals have exhibited a wide variation in the domain sizes and also show a higher domain density.
REFERENCES


