CHAPTER VI

ELECTRICAL CONDUCTION AND DIELECTRIC STUDIES IN THIN FILMS OF KNO$_3$ AND KNO$_3$-KI$_3$ SOLID SOLUTION

6.1 GENERAL

6.1.1 POTASSIUM NITRATE (KNO$_3$):

Ferroelectricity in potassium nitrate was discovered by Sawada et al. (1) in 1958. This undergoes certain order-disorder type molecular changes in the structure (2). The studies on the effect of high pressure on KNO$_3$ by Bridgman (3) and Rapoport et al. (4) have established that KNO$_3$ can exist in several polymorphic phases depending on its temperature.

Phase III, the ferroelectric phase, is a metastable phase at atmospheric pressure within a temperature range of 10-20°C (2,5) below ferroelectric transition temperature of 125°C. It always appears as a first-order phase transition when the crystal is cooled from above 180°C, but does not appear when the crystal is heated from phase II. Strong lattice-electric dipole interaction (2) is said to be responsible for phase transition at 125°C. It is also reported that the ferroelectric phase III appears upon heating the phase II by simultaneous application of hydrostatic pressure (3,4).

The appearances of various phases of KNO$_3$ at atmospheric pressure as a function of temperature, on
heating and cooling cycles, are schematically shown below:

\[ \text{HEATING} \rightarrow \ 130^\circ C \]

\[ \text{II or } \alpha \]

\[ \text{PARAELECTRIC PHASE} \]

\[ \text{III or } \gamma \]

\[ \text{FERROELECTRIC PHASE} \]

\[ \text{COOLING} \]

\[ \text{I or } \beta \]

\[ \text{PARAELECTRIC PHASE} \]

\[ \text{II} \]

\[ 110^\circ C \]

\[ 125^\circ C \]

The structure of Phase I, the paraelectric phase, is closely related to the calcite (trigonal) structure (6). It belongs to the space group $\text{D}_{3d}^6$. From the projected electron density map, Tahvonen suggested that the nitrate ion is oscillating along the $c$-axis with an amplitude of about $0.4 \, \text{Å}$. The structure of the ferroelectric phase is rhombohedral and is closely related to that of the paraelectric phase and belongs to the space group $\text{D}_{3v}^5$. However, in this phase the nitrate ion is known to be displaced along the $c$-axis from the centre of the unit cell by about $0.5 \, \text{Å}$ (7). Phase II has the aragonite (orthorhombic) structure and its space group is $\text{Pnma-D}_{2h}^{16}$ (8).

On the basis of the above structure analysis, Sawada et al. (5) have proposed the following model for
ferroelectricity in $\text{KNO}_3$. In the paraelectric phase the nitrate ion is oscillating along the $a$-axis. In the ferroelectric phase, there exists a potential barrier in the centre of the unit cell. This hinders the oscillation of the nitrate ion along the $a$-axis. The spontaneous polarization $P_s$ is then simply related to the displacement $\delta$ of the nitrate ion from the centre of the unit cell given by

$$P_s = Nq\delta$$

where $N$ is the number of dipoles per unit volume. Assuming $q$ to be a unit electronic charge of the nitrate ion and using the measured $\delta = 0.55 \, \text{Å}$, the resultant spontaneous polarization is $11 \, \mu\text{C/cm}^2$. This agrees well with the values $8 \, \mu\text{C/cm}^2$ and $10 \, \mu\text{C/cm}^2$, as determined by hysteresis loop and pyroelectric measurements respectively (5).

The structure of the paraelectric phase has also been interpreted as due to the disordered displacement of the nitrate ions by Shinnaka (9).

This material has received special attention because good quality hysteresis loop can be obtained on melt casted (10) samples. The possibility of using this material as a fast non-volatile, non-destructive readout memory element has been suggested in the literature (11). Its switching property has been studied by Dork et al. (12) and Nolta et al. (13). Hence the nature of ferroelectricity in $\text{KNO}_3$ and the underlying phenomenon for these properties, has
been extensively investigated [Nolta et al. (13), Chen et al. (2),
Teng et al. (14), Yanagi et al. (15), Gay (16)]. Dielectric
properties on crystalline KNO₃ have been investigated by many
workers [Sawada et al. (5), Yanagi (18), Mansingh et al. (19, 20)].
Lattice dynamics of ferroelectric phase has been theoretically
investigated by Krishnan et al. (22) and of \( \alpha \)-phase by Rao et
al. (23-24). Ferroelectric and other properties of thin films
of KNO₃, fused and vacuum evaporated both, have been studied
by Nolta et al. (17, 21). There are many other reports in the
literature on ferroelectric KNO₃ but here mainly the work on
films has been referred to.

6.1.2 POTASSIUM IODATE (KIO₃):

Ferroelectric behaviour in KIO₃ was first reported
by Herlach (25) in 1961 from phase transition investigations
by the NQR frequencies of halogen atoms in alkali halogenates.
However, in spite of a number of serious investigations by
Helg, Granicher (26-28) and Salje (29, 30), a clearly defined
interpretation of the contradictory data concerning the
peculiar ferroelectric behaviour and other physical properties
of KIO₃ has remained extremely difficult for correct inter-
pretation. This is explained by the fact that, due to the
difficulty in growing sufficiently large and homogeneous KIO₃
crystal, either the crystal symmetry was incorrectly determined
below the Curie point (25-30) \( (T_c = 212^\circ C) \) or was not taken
into consideration the fundamental effect of the existence of both the unusual shift in the domain structure.

Crane (31) has recently established that high temperature R3m rhombohedral phase of KIO₃ changes at 212°C to the monoclinic phase and retains this point group symmetry upto room temperature (25). According to the classification proposed by Shuvalov (32), it will belong to the 3m (3/2) AmFm space group.

According to the measurements of Shuvalov et al. (33), the KIO₃ has the following sequence of phase transitions:

-163°C → -15°C → 72°C → 212°C

The δ, γ and β phases have the same point group symmetry (class m). Thus all the three phases are ferroelectric belonging to the 3m (3/2) AmFm species. Also, the observation by Shuvalov et al. (33) of small domain structure actually taking place during δ → ε transition suggests a decrease in to the triclinic symmetry, and then the C phase should also be ferroelectric belonging to the 3m (6/2) A1F1 species (32).

The IO₃⁻ groups are rigid complex ions and their parallel alignment leads to a large permanent polarization (Ps) about 30 μC/cm² along (111) direction (27).

The ferroelectric spontaneous polarization vector
which appears at $T_c = 212^\circ C$ in one of the $\alpha$-planes of the crystal changes its orientation with temperature in this plane (33). Presently it is impossible to distinguish the non-reorientable component of ferroelectric polarization directed along polar axis $3$ of the original phase, from purely pyroelectric polarization, which will exist in the original phase and retained in the ferroelectric phase. The spontaneous polarization can be considered to have two components. The unorientable one directed along the polar axis of the original phase i.e. the pyroelectric one ($P_{sp}$) and the reorientable one, which is perpendicular to the first i.e. the ferroelectric one ($P_{sf}$) for $\text{KI}_3\text{O}_5$. The abnormality of $\text{KI}_3\text{O}_5$ is in the fact that $P_{sp} \gg P_{sf}$. $P_{sp} \approx 30 \mu \text{C/cm}^2$ whereas $P_{sf}$ is $5 \times 10^{-4} \text{C/m}^2$ in $\beta$-phase, $\sim 10^{-3} \text{C/m}^2$ in $\gamma$-phase and $\sim 8 \times 10^{-3} \text{C/m}^2$ in $\delta$-phase (27).

The $3\alpha (3/2)$ AmFm species of $\text{KI}_3\text{O}_5$ in the ferroelectric phase has three $P_s$ axes and three $P_{sf}$ axes. Because these axes are polar in the original phase, a $180^\circ$ shift of $P_s$ and $P_{sf}$ is impossible; the $P_{sf}$ axes lie at an angle of $120^\circ$ to one another, and, therefore, only a $120^\circ$ shift of $P_{sf}$ is possible. The angle between the $P_s$ axes varies with temperature depending on $P_{sf}(T)$ and $P_{sp}(T)$.

On account of low solubility it is difficult to grow crystals of $\text{KI}_3\text{O}_5$ though different techniques have been proposed. Armington et al. (34) have described the gel growth experiments to produce iodate crystals. Hamid (35) was
successful in growing single untwinned crystals of KIO\textsubscript{3} by a combination of convection and isothermal evaporation method at a relatively low temperature. Good single crystals of KIO\textsubscript{3} have been grown by a modified hydrothermal method by Helg (26).

6.2 DIELECTRIC STUDIES:

6.2.1 DIELECTRIC CONSTANT AND LOSS OF KNO\textsubscript{3}:

Dielectric constants of KNO\textsubscript{3} crystals at 100 kHz along a-, b- and c-axes measured by Sawada et al. (5) show distinct anomalies at $\sim 130^\circ$C on heating and about 125° and 115°C on cooling. The variation of dielectric constant with temperature along the c-axis is from 5 at 25°C to the peak value $\sim 65$ at 125°C. In paraelectric phase it obeys the Curie-Weiss law. Along a- and b- directions the value of dielectric constant and its variation with temperature are small i.e. about 5 at 20°C to about 14 at $\sim 124^\circ$C.

The dielectric constants and losses of solution grown KNO\textsubscript{3} along the ferroelectric c-axis in paraelectric phase have been measured at megahertz and microwave frequencies as a function of temperature (2). Unlike the molecular ferroelectric NaN\textsubscript{O}\textsubscript{2}, there is no dielectric dispersion in KNO\textsubscript{3} at these frequencies. The dielectric losses change from a positive to negative temperature dependence as the frequency is increased from 10 kHz to 18 MHz. The conduction losses due to lattice defects are predominant at low frequen-
cies, but the dielectric losses due to the permanent dipoles become more important in the megacycle region.

The dielectric constant of KNO$_3$ from 10 kHz to 18 MHz in ferroelectric phase decreases with frequency. They (2) interpret this decrease due to partial clamping of the crystal by the piezoelectric effect in this phase. The peak value of dielectric constant reaches 75 and the loss is in the range of 0.1 to 10 for various frequencies. They have also reported that the ferroelectric phase did not appear for sample which was not annealed upto 180°C.

The dielectric constant and loss of a randomly oriented single crystal at 3.6 GHz measured by Mansingh et al.(20) exhibit different phase transitions in heating and cooling cycles at about the same temperatures as reported by Sawada et al.(1,5). The peak values of ε ~ 40 and that of tan δ ~ 3.5 are very close to that at 1.043 MHz for twinned crystal reported by Sawada et al.(1).

The dielectric constant and loss of a melt-casted sample show similar behaviour and are always lower than those of single crystals. The peak value of the dielectric constant and the values in the paraelectric phase I of a melt-casted sample of KNO$_3$ were found to be lower at 3.6 GHz compared to those at 100 kHz. The measured loss at 100 kHz was also higher than that at 3.6 GHz but this is due to the contribution from the dc conductivity to the measured loss.
This indicates a dielectric dispersion in paraelectric phase I, similar to that reported by Chen et al. (2) along the ferroelectric-axis of the crystal.

The dielectric constant and loss in the paraelectric phase of melt casted films at 100 kHz to 23.5 GHz were reported by Mansingh et al. (19) in the cooling cycles. The small value of loss in paraelectric phase at 100 kHz is probably due to electrode polarization. The peak value of dielectric constant and permittivity values in paraelectric phase are reported to be lower at higher frequencies.

Measurements of permittivity from room temperature to 260°C were done on KNO₃ single crystal, fused layers and evaporated films by Nolta et al. (17, 21). From room temperature to Curie temperature the permittivity of thin films (1-2 µm thick on steel substrate) does not differ significantly from that of the single crystal or fused layers. But in the high temperature phase the permittivity tends to be much higher in the films. The permittivity of the film in phase I obeys the Curie-Weiss law but with a negative Curie constant as against the positive Curie constant in a c-cut single crystal (5). Fused layers, ~ 100 µm in thickness, show a temperature dependence intermediate to that of the evaporated films and crystals. The permittivity does not obey the Curie-Weiss law.

In the case of thin films, the phase transition in
heating cycle is noticed around 130°C which is similar to that observed in single crystals. But on cooling cycle the transition from phase I to phase III is observed at a slightly lower temperature in comparison to that reported for the single crystal. Further, cooling the film does not seem to yield the phase transition from phase III to phase II which is observed in the single crystal.

From dielectric hysteresis loop studies on the films of KNO₃, the value of coercive field was found to be 30 kV/cm when spontaneous polarization is around 0.05 μC/cm² at the room temperature. It was concluded that the film form of KNO₃ was ferroelectric with high value of coercive field and low value of spontaneous polarization than those for single crystals.

6.2.2 DIELECTRIC STUDIES ON KIO₃:

The dielectric constants of KIO₃ at 10 kHz along a-, b-, c- axes and along (101) direction as functions of temperature have been measured by Helg (28) in the temperature range from -200°C to +240°C. The phase transitions of first order have been observed in these measurements. The transition from γ-phase to δ-phase is characterized by a large anomaly of dielectric constant. The temperature dependence on both sides of the transition may be described by Curie-Weiss law. Both the Curie-constant and the Curie-temperature depend on the thermal history of the sample.
Helg et al. (27) have proposed a disordering model to explain this behaviour of KIO₃.

If the dc bias field is increased slowly, the dielectric constant (≅ 75) falls suddenly to a markedly lower value (≅ 40) as the coercive field (≅ 20 kV/cm) is exceeded (27) because of three possible directions for the spontaneous polarization. The high value of dielectric constant at small field is characteristic of the polarization P along (111). If an electric field is applied perpendicular to P, the polarization P tilts into two stable positions, P₁ and P₂. The tilting angle depends on the temperature. It has been emphasized that KIO₃ is the first ferroelectric with non-invertible but tiltable polarization. This was theoretically predicted by Aizu (36). In this sense it has a peculiar ferroelectric nature.

Dielectric hysteresis loops were detected on single domain crystals of KIO₃ at 50 kHz. Measurements at temperature greater than 150°C are complicated by an increase in the conductivity of the crystals. The principal components of the dielectric constants for KIO₃ at room temperature were reported to be

\[ \varepsilon_x = 37, \quad \varepsilon_y = 81 \quad \text{and} \quad \varepsilon_z = 11.5 \quad (33). \]
6.3 ELECTRICAL CONDUCTIVITY STUDIES

6.3.1 ELECTRICAL CONDUCTIVITY OF KNO₃

The dc electrical conductivity of solution grown crystals of KNO₃ was measured at 20 V/cm field by Asoo et al.(37). The results were found to obey the conventional exponential law. The conductivity variation was between $10^{-12}$ and $10^{-7}$ ohm$^{-1}$ cm$^{-1}$ for temperatures 70 to 180°C.

The conductivity of KNO₃ along c-direction shows a steep jump on heating at the transition temperature of 129°C and with a magnitude of about hundred times. On the other hand, on cooling, a jump in the transition from phase I to the phase III is about five times and there is another jump of about two times in the transition from the phase III to the phase II. When a crystal has once been heated beyond the transition it is reported to be more conductive in phase II when compared with its initial state. The dc conductivity of KNO₃ was also measured along the a- and b- directions and a similar result as in the c-direction was obtained but any reliable determination of the anisotropy of electrical conductivity has not been made mainly due to the well known fact that around phase transition a KNO₃ single crystal develops innumerable cracks and crystallites.

The steep jump of electrical conductivity of KNO₃ at the transition temperature around 129°C is attributed to the appearance of some disordered in the position or
orientation of atoms or radicals, which is related to the
free rotation of NO$_3$ groups at high temperatures. The
successive increase in conductivity by successive heating
and cooling processes the crystal is also attributed to
microscopic disordering in the crystals.

Mansingh et al. (20) have observed the different
phase transitions on heating and cooling runs through their
dc conductivity studies of polycrystalline melt samples and
solution grown randomly oriented single crystals of KNO$_3$.
The observed dc conductivity in the melt sample was larger
due to grain boundary effect (38) than that observed in a
single crystal. This may also account for higher activation
energies observed in the melt sample. The conductivity
variation was between $10^{-11}$ and $10^{-3}$ ohm$^{-1}$ cm$^{-1}$ in the
temperature range 80 to 160°C.

Specific electrical conductivity at 1 kHz for pure
KNO$_3$ melt in the temperature range 340-500°C has also been
reported to increase from 0.6 to 1.2 ohm$^{-1}$ cm$^{-1}$ by Gaur et
al. (39). The conductivity follows the equation $k = a + bt + ct^2$
where a, b and c are empirical constants and t is the
temperature in °C.

The ac conductivity at 1 kHz versus temperature
characteristics of KNO$_3$ did not show any significant
difference with thickness among the three types of specimens
i.e. single crystal, fused layer and vacuum evaporated thin
films of KNO$_3$ (17, 21). The usual transition temperature on
heating was observed for the phase I $\rightarrow$ phase III transition at slightly lower temperature and phase III $\rightarrow$ phase II transition was not detected in the case of evaporated films of KNO$_3$.

6.3.2 **ELECTRICAL CONDUCTIVITY OF KIO$_3$**

The dc electrical conductivity of ferroelectric cut pure KIO$_3$ single crystal has been reported to vary between $10^{-15}$ ohm$^{-1}$ cm$^{-1}$ and $10^{-10}$ ohm$^{-1}$ cm$^{-1}$ from room temperature to 230°C (40). The conductivity was measured in dry air at $E = 1.2$ kV/cm. The conductivity study revealed the phase transition at 220°C.

Dc electrical conductivity of polycrystalline pellets of KIO$_3$ pressed at 2.5 and 3.5 tonnes of pressure from room temperature to 240°C has been reported by Sarbhai (44). High temperature phase transition from $\beta$ to $\alpha$ phase has been observed between 212 and 215°C and variation of conductivity is between $10^{-12}$ to $10^{-3}$ ohm$^{-1}$ cm$^{-1}$. Anomalous behaviour at 212°C is ascribed to the mobility and reorientation of pyramidal IO$_3$ anions.

AC conductivity measurements of KIO$_3$-2HIO$_3$ at 300 kHz in different crystallographic axes by Baranov et al. (41) show a marked anisotropic ionic conductivity. Anisotropy in activation energy (0.49 eV) has not been observed. The maximum value of $\sigma$ lies in the direction close to (100) and at room temperature $\sigma$ must reach values $\approx 10^{-5}$ ohm$^{-1}$ cm$^{-1}$. 
6.4 **EXPERIMENTAL**

6.4.1 **PREPARATION OF SAMPLE FILMS**

Transparent good quality crystals of KNO₃ were first grown for further enhancing the purity of AR grade KNO₃. The grown single crystals were then dissolved in the distilled water to get saturated solution of KNO₃. The solution temperature was maintained at about 45°C. Polycrystalline thin films of KNO₃ were prepared from this solution by spinning disc technique at about 85°C at a speed of ~ 4000 rpm. The details of preparation of Al-KNO₃ film – Al sandwich cells, measurement of film thickness and lamellar crystallite size on the film have been described earlier in Chapter II. Good quality film selected for measurements was about 2 μm thick with lamellar crystallite size ~ 50 μm, as examined for the film quality through the polarizing microscope (photograph No. 6.1).

For preparing solid solution, the fine powder of pure KNO₃ crystal was thoroughly mixed with the fine powder of AR grade KIO₃ in 60/40 ratio. A small amount of this mixture was sprinkled on a clean glass slide already having a deposited strip of 4 mm wide transparent conducting electrode on it. It was placed on a horizontal hot plate and slowly heated. The KNO₃ powder initially melts at its melting point and then it starts dissolving the KIO₃ powder.
Photograph No. 6.1

Polycrystalline Thin Film of $\ce{KNO_3}$ (Solution Grown)
at a temperature lower than the melting point of \( \text{KIO}_3 \). Thus a clear transparent molten viscous liquid is obtained on the slide. Using mica spacers of 40 \( \mu \text{m} \) at the four corners of the slide outside the conducting electrode and by sliding and pressing another similarly electroded slide above the melt of substrate slide the thin films of \( \text{KNO}_3-\text{KIO}_3 \) system is obtained. Small air bubbles, if any, were removed. Similarly a 70 \( \mu \text{m} \) thick film of \( \text{KNO}_3 \) was also prepared for comparative study. The thickness of the film is the thickness of the mica spacers. The crystalline form of melt-casted \( \text{KNO}_3 \) film is shown in microscopic photograph No. 2 and that of melt-casted \( \text{KNO}_3-\text{KIO}_3 \) film in photograph No. 3.

6.4.2: CHARACTERISATION:

To characterise the film of \( \text{KNO}_3-\text{KIO}_3 \) solid solution, a small quantity of the film material was removed from the substrate and powdered. The fine powder was then thoroughly mixed in Nujol and its IR spectrum was recorded by Perkin–Elmer Spectrophotometer. The IR spectrum is shown in Fig. 6.1.

The appearance of absorption peaks at 750 cm\(^{-1}\) (strong) and at 840 cm\(^{-1}\) (sharp and weak) in Fig. 6.1 confirm the presence of \( \text{IO}_3^- \) ions. The absorption peaks at 1380 cm\(^{-1}\) and 1450 cm\(^{-1}\) (strong); and at 1760 cm\(^{-1}\) (sharp and weak) represent the presence of \( \text{NO}_3^- \) ions in the
Photograph No. 6.2
Polycrystalline Thin Film of $\text{KNO}_3$ (Melt-Casted)

Photograph No. 6.3
Polycrystalline Thin Film of $\text{KNO}_3$-$\text{KIO}_3$
Solid Solution (Melt-Casted)
FIG. 6.1 IR SPECTRUM OF KNO₃-KIO₃ SOLID SOLUTION.
film. Thus, the film of KNO₃-KIO₃ solid solution contains both the ions without reduction and establishes that KIO₃ is dissolved in molten KNO₃. This is to emphasise here that in our maiden attempt to dissolve KIO₃ in KNO₃ melt matrix has been successful and it is its first report.

6.4.3: MEASUREMENTS:

Capacitance and ac conductance of the sample films were simultaneously measured by Wayne Kerr Autobalance Bridge B642 at 1591.5 Hz. Dc electrical conductivity was measured by Keithley Digital Multimeter. The temperature of the samples was measured by a precalibrated chromel-alumel thermocouple in conjunction with OSAW Vernier Potentiometer and Spot Galvanometer with a precision of 0.25°C. The samples were duly annealed prior to any measurements. The experiments were carried out in heating as well as cooling cycles.

6.5: RESULTS AND DISCUSSIONS:

Fig. 6.2 shows the temperature dependence of the dielectric constant (ε) and dielectric loss (tanδ) of the film of KNO₃ (about 2 µm thick) prepared by spinning disc technique. During heating cycle the dielectric constant of virgin film increases slowly up to 115°C and suddenly rises to peak value of about 280 at about 117°C showing the phase II → phase I transition [Curve (a)]
Fig 5.2: Dielectric constant and loss vs. temperature of KNO₃ film.
marked I]. In paraelectric phase (phase I), the dielectric constant increases sharply and follows Curie-Weiss law with negative Curie constant. This result is in good agreement with the result of Nolta et al. (17, 21) on vacuum evaporated films of KNO₃. Upon cooling the film from 130°C, ferroelectric phase (phase III) appears at ~102°C with $\varepsilon_{\text{max}} = 260$ and does not disappear till room temperature and thus the phase II is not observed. Subsequent repetition of the dielectric measurements hindered the appearance of the ferroelectric phase III on cooling while phase II $\rightarrow$ phase I transition took place as usual on heating cycle and the dielectric constant is now increased. The disappearance of ferroelectric phase III on subsequently repeating the experiment is attributed to the microcracks developed in the film during reconstruction transformation transition from phase III to phase II (2). The increase in dielectric constant can be explained by assuming the formation of space-charge polarization (43) near the electrodes. The material KNO₃ slowly reacts with the aluminium electrode and forms a low conducting thin layer near the electrode which collects the charges of impurity ions and produces space-charge polarization. Thus, the dielectric constant is apparently increased. Lowering of transition temperatures can be explained on the basis of high internal bias in films.

In Fig. 5.2 (b), the dependence of dielectric loss on temperature shows the presence of phase III on cooling.
On repeating the experiment the ferroelectric phase is not seen and the loss is decreased. The decrease in loss supports the formation of space-charge polarization (Fig. 6.2 (b) curve marked II). In paraelectric phase, the loss increases with temperature. This may be attributed to the increased conduction of the film due to defects in addition to host ions.

The results on the measurements on the thin films of \( \text{KNO}_3 \), solution grown as well as fused and of \( \text{KNO}_3-\text{KIO}_3 \) (fused) are summarised in Table 6.1.

Fig. 6.3 shows the variation of dielectric constant with temperature from \( 40^\circ \) to \( 220^\circ \)C of melt casted films of \( \text{KNO}_3 \) (dotted curve) and of \( \text{KNO}_3-\text{KIO}_3 \) (60/40) (solid line curve) in heating as well as cooling runs. Sharp phase II \( \rightarrow \) I transitions around \( 115^\circ \)C are observed. The dielectric constant of \( \text{KNO}_3-\text{KIO}_3 \) system is slightly higher at low temperatures (i.e. \( \varepsilon \sim 15 \) from \( 40^\circ \) to \( 100^\circ \)C) but lower than that of the film of \( \text{KNO}_3 \) at high temperatures. Phase transitions at \( 58^\circ \)C and around \( 197^\circ \)C are not pronounced in the mixed system. Thus the behaviour of the mixed system is intermediate to the behaviour of \( \text{KNO}_3 \) (17) and \( \text{KIO}_3 \) (25). The decrease in transition temperatures may be ascribed to the high internal bias fields due to stressed condition of the films between the two glass substrates, due to mismatch of thermal expansions of the film and the substrate. Other features of the films properties are very similar to those of the bulk materials.
<table>
<thead>
<tr>
<th>Phase</th>
<th>Dielectric constant at low loss</th>
<th>Dielectric constant at high loss</th>
<th>Transition temperature (°C)</th>
<th>Activation energy (eV)</th>
<th>Activation frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film</td>
<td>111 1.2 × 10⁻⁷ 1.4 × 10⁻⁷ 1.7 × 10⁻⁷</td>
<td>114 1.2 × 10⁻⁷ 1.4 × 10⁻⁷ 1.7 × 10⁻⁷</td>
<td>117 1.2 × 10⁻⁷ 1.4 × 10⁻⁷ 1.7 × 10⁻⁷</td>
<td>117 1.2 × 10⁻⁷ 1.4 × 10⁻⁷ 1.7 × 10⁻⁷</td>
<td>117 1.2 × 10⁻⁷ 1.4 × 10⁻⁷ 1.7 × 10⁻⁷</td>
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Table 6.1: Properties of thin films of KNO₃ and KNO₃-KIO₃ solid solution
FIG. 63: DIELECTRIC CONSTANT vs TEMPERATURE OF KN03 AND KN03-KI03 FILMS.
Fig. 6.4 shows the variation of loss tangent \((\tan \delta)\) of the melt casted films of KNO\(_3\) and KNO\(_3\)-KIO\(_3\) (60/40) system from room temperature to \(220^\circ\)C in heating and cooling cycles. The loss of the mixed system at low temperature is about one order of magnitude higher than that of the KNO\(_3\) film. This shows that I\(_{3}^-\) ions are more free than NO\(_3^-\) ions to contribute towards electrical conduction and, therefore, the loss is high in mixed system. However, at high temperatures the losses are comparable to each other for the two films. The phase transitions are judged from the change in slopes appearing around the reported transition temperature of the bulk material.

The semi-logarithmic plots of ac- and dc electrical conductivities vs \(10^3/T\) of the film of KNO\(_3\) prepared by spinning disc technique are shown in Fig. 6.5 in both heating and cooling cycles. Conductivity measurements do not show the appearance of phase III on cooling the film as explicitly as reported by Mansingh et al.\((20)\) for single crystals of KNO\(_3\). However, phase II \(\rightarrow\) I occurs between 113\(^\circ\)C and 120\(^\circ\)C in log \(\sigma_{ac}\) vs 1/T plots and between 112\(^\circ\)C and 118\(^\circ\)C in log \(\sigma_{dc}\) vs 1/T plots. DC conductivity is slightly lower than that of the single crystal \((20)\). It again supports the formation of space-charge polarization near the electrodes \((43)\). The ac-conductivity of the film is about 3-4 orders of magnitude higher than the dc value. This shows that the motions of defects and host ions (NO\(_3^-\) and K\(^+\)) are not impeded much by the space-charge
FIG. 64 DIELECTRIC LOSS (tan δ) vs TEMPERATURE OF KNO₃ AND KNO₃-KIO₃ FILMS.
FIG. 65 AC AND DC CONDUCTIVITIES VS TEMPERATURE OF KNO₃ FILM.
polarization in ac field. In cooling cycles the magnitude of the conductivities near room temperature is reduced by about one order of magnitude than the corresponding value in heating cycles. This suggests that the defects contributing to the conduction mechanism during heating cycles are collected by the electrodes at high temperatures. Therefore, on cooling cycles the number of charge carriers is reduced and hence low conductivity results.

Fig. 6.6 shows the variation of dc electrical conductivity of fused film of KNO$_3$ and KNO$_3$–KIO$_3$ with temperature in both heating and cooling cycles. The values are about one order of magnitude higher in KNO$_3$ film than those of the single crystal of KNO$_3$ (37). But the conductivity of the mixed system is about 3–4 orders of magnitude less than that of single crystals of KIO$_3$ (40). This shows that some of NO$_3^-$ ions of KNO$_3$ are replaced by IO$_3^-$ ions of KIO$_3$ and solution of KNO$_3$ and KIO$_3$ is formed and, therefore, the conductivity of KNO$_3$–KIO$_3$ solid solution film has increased due to free motion of IO$_3^-$ ions. The conductivity of the films reduces by about one order of magnitude near room temperatures during cooling cycles. This needs the same explanation as mentioned in preceding paragraph.

Fig. 6.7 shows the variation of ac conductivities of the fused films of KNO$_3$ and KNO$_3$–KIO$_3$ system with temperature. The behaviour is similar to the dc conductivity
Figure 6: log $\sigma$ vs. $10^3 / T$ of KNO$_3$ and KNO$_3$-KI$_3$ films.
\[ \log \sigma \text{ vs } 10^3 / T \text{ of } \text{KNO}_3 \text{ and KNO}_3-\text{KIO}_3 \text{ films.} \]
variation of the respective films. But the values are about 2-3 orders of magnitude higher than the corresponding dc values. The conductivity variation is between $10^{-10}$ ohm$^{-1}$ cm$^{-1}$ and $10^{-6}$ ohm$^{-1}$ cm$^{-1}$ from room temperature to 220°C.

In all the measurements of film of KNO$_3$-KIO$_3$ system, the transition temperatures depend on the history of the sample.

To conclude, our initial effort to prepare films of KNO$_3$-KIO$_3$ system has been successful. The intermediate film property of this system in comparison to the original members can provide means to obtain system in which their individual desirable property of polarization, conduction or transition is to be affected keeping in view certain device potential.
REFERENCES


