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# Transport Properties of $K(NO_3)_{1-x}(ClO_3)_x$ Thick Films

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**Abstract:** ***The effect of substituting chlorate ions for nitrate ions on the transport properties of $K(NO_3)_{1-x}(ClO_3)_x$ has been investigated. The electrical resistivity, dielectric constant, loss tangent and thermal conductivity of $K(NO_3)_{1-x}(ClO_3)_x$ have been studied. The electrical resistivity-temperature curve for the x = 0.1 sample shows an anomaly on heating and on cooling which indicates a first-order phase transition. Anomalies in the dielectric constant-temperature curves, also on heating and on cooling, confirm the first-order phase transition. The introduction of chlorate ions lead to scattering which increases the phonon–phonon interaction. This results in the decrease in thermal conductivity.***

**Keywords:** resistivity, dielectric constant, dielectric loss, thermal conductivity

## 1. Introduction

A great deal of attention has been paid to ferroelectric thin films due to their device applications [1–4]. In the bulk form, potassium nitrate ($KNO_3$) has an aragonite structure at room temperature (phase II) and is rhombhohedral at 130$^o$ C (phase I). On cooling, phase I does not go directly to phase II, but changes first into a ferroelectric phase III at 120$^o$ C and then to phase II at a lower temperature around 110$^o$ C. Takeuchi [5] has investigated the dielectric properties of $K(NO_3)_{1-x}(ClO_3)_x$ solid solution grown from aqueous solution by the measurements of dielectric constant and D-E hysteresis loop. The ferroelectric phase in such a system appeared not only on cooling but also on heating in contrast to pure $KNO_3$, which shows ferroelectricity only on cooling. The temperature range of the ferroelectric phase was found to broaden drastically by the addition of $KClO_3$.

It has also been found that in the thin-film form of $KNO_3$, ferroelectric phase III exists over a wide range of temperatures down to even 0$^o$ C. The thin films of $KNO_3$ are ferroelectric at room temperature, provided they are kept dry [6–8]. Thick films of melt-quenched $K(NO_3)_{1-x}(ClO_3)_x$ have also been found to be ferroelectric at room temperature [9].

Despite the work done on the structural, phase transition and other properties of $KNO_3$ and solid solutions based on it, relatively little work has been reported on the thermal conductivity ($\kappa$). The thermal conductivity is of importance from both fundamental and applied perspectives. The thermal conductivity is a function of the mean free path of the phonons and hence is determined by both intrinsic (phonon-phonon Umklapp scattering) and extrinsic (phonon-defect scattering) factor [10, 11]. In this work, the temperature dependence of the electrical resistivity, dielectric constant, dielectric loss and thermal conductivity of thick films of melt-quenched $K(NO_3)_{1-x}(ClO_3)_x$ have been investigated.

## 2. Materials and Methods

Analytical grade powders of $KNO_3$ and $KClO_3$ were used as the starting materials. Powders with the nominal composition $K(NO_3)_{1-x}(ClO_3)_x$ ($0 < x < 0.1$) were mixed with acetone and ground in an agate mortar for about 20 min. The resultant mixture was slowly heated in an alumina crucible till it melted. The melt was stirred to ensure homogeneity. The rest of the melt was quickly poured unto a copper plate with circular groove and quenched with another copper plate. This procedure produced samples of 5 cm in diameter and 0.4 mm thick. Samples prepared this way were used for dielectric constant, loss tangent and thermal conductivity measurements. Some of the samples were cut into rectangular shapes for electrical resistivity measurements.

The electrical resistivity of the samples on the glass slides was determined on heating and on cooling using the standard four-probe technique. Constant current of 1 μA was passed through the sample. The voltage across the sample was measured with a Keithley 182 Nanovoltmeter. The sample was placed in a custom-made tube furnace. A type K thermocouple thermometer was used to monitor the temperature of the sample.

For the dielectric constant, loss tangent and electrical resistivity measurements, air-drying silver was used to make electrical contact. After the contacts were made, the samples were annealed at 150 $^o$C for about one hour to remove intrinsic stress and also to have good electrical contacts.

The dielectric constant and the loss tangent were measured using a Wayne Kerr 1EV 7330 Automatic LCR meter.

The thermal conductivity was measured using the Lee's and Charlton method [12]. The rates of cooling of the samples at selected temperatures were determined from the cooling curves and the thermal conductivity at these temperatures were calculated.

## 3. Results and Discussion

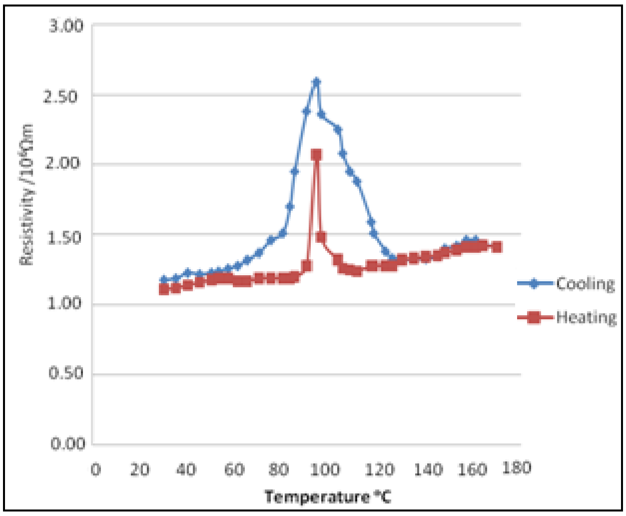


**Figure 1:** The temperature dependence of the electrical resistivity of $K(NO_3)_{0.9}(Cl_3)_{0.1}$

Fig. 1 shows the temperature dependence of the electrical resistivity of the *x* = 0.1 sample. Anomaly is observed in the resistivity-temperature curves both on heating and on cooling. The anomaly observed in the temperature range 89.7$^o$ C to 106.1$^o$C for the sample on heating and 125.7$^o$ C to 79.1$^o$ C on cooling gives indication of a ferroelectric-paraelectric transition. The transition width, ΔT, for heating is 18.5$^o$ C and the transition takes place at 95.2$^o$ C. The transition width for the cooling is 46.6$^o$ C with a transition temperature of 94.8$^o$ C. There is evidence of a hysteresis which indicates a first-order phase transition.

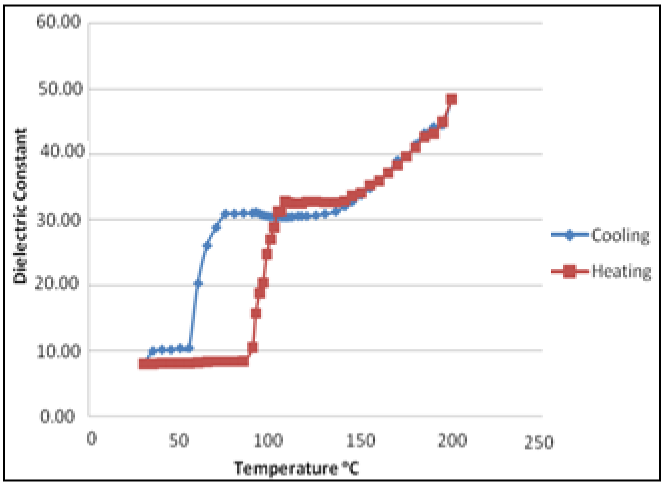


**Figure 2:** The dependence of dielectric constant of $K(NO_3)_{0.9}(ClO_3)_{0.1}$ on temperature

A hysteresis in the dielectric constant-temperature curve in Fig. 2 gives further evidence of a first-order phase transition. It is observed that the transition in the material occurs at a slightly lower temperature on cooling than on heating. The hysteresis occurs because on cooling the crystal through the transition temperature, the dipoles tend to remain in the meta-stable non-polar (paraelectric) state even below the transition temperature. Therefore, the material transforms into the ferroelectric phase at a temperature lower than the transition temperature. Conversely, on heating, the dipoles tend to transform into the non-polar phase a little above the transition temperature. The difference in the transition is ΔT = 33$^o$ C.

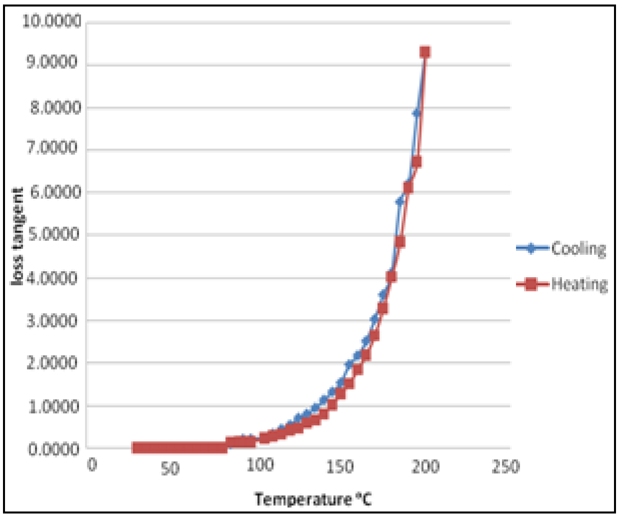


**Figure 3:** Temperature dependence of the loss tangent of $K(NO_3)_{0.9}(ClO_3)_{0.1}$ on heating and cooling.

The behaviour of the loss tangent (tan δ) as a function of temperature is illustrated in Fig. 3. It is observed that there is a sharp increase in the loss tangent around the onset of transition at about 90 $^o$C. The heating-cooling curve also shows a hysteresis.

It has been observed that the electrical properties of ferroelectrics are influenced by the ordering phenomenon [13]. One of the reasons for the decrease in the carrier concentration is that, the chlorate ion, which is the doping impurity material, acts as a trapping site for the conduction electrons. In addition, the trapping of the electrons hinders the mobility of free electrons; this leads to the decrease in carrier concentration and reduction in electrical conductivity. This is evidenced in the increase in the electrical resistivity of the films with increasing chlorate ion concentration, as indicated in Fig. 4.

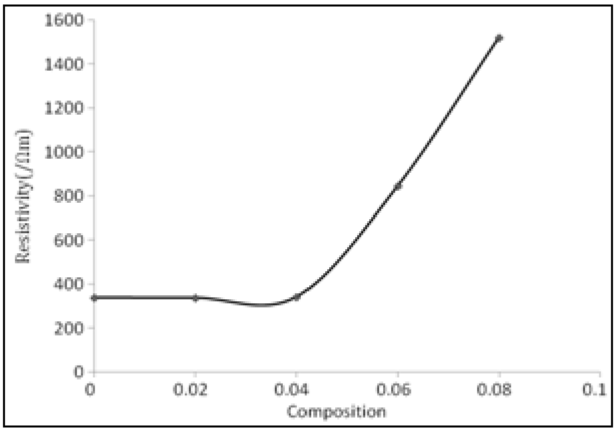


**Figure 4:** Dependence of electrical resistivity of $K(NO_3)_{1-x}(ClO_3)_x$ on the nominal chlorate concentration, x

It is possible that introduction of chlorate ions in the system leads to impurity scattering which leads to increase in the electrical resistivity [16]. It has been observed that defects do not only affect ferroelectricity directly, but also the electronic conductivity [14]. Schottky barriers could be formed at the grain boundaries by the introduction of impurities. The thickness of the Schottky barrier layers and the space charge varies significantly with free-carrier concentration.

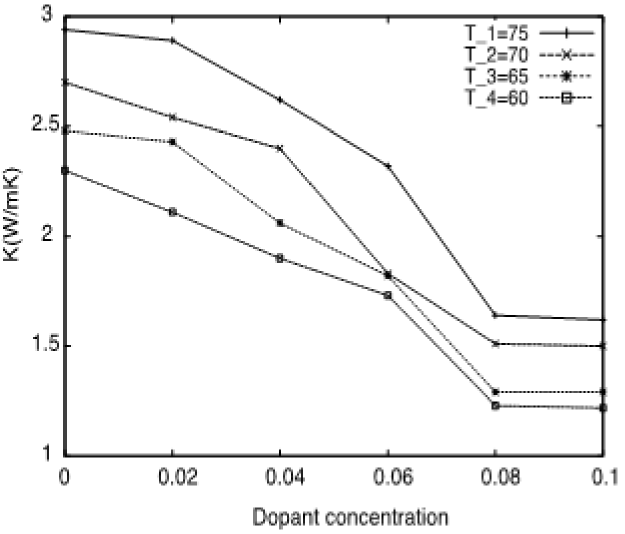


**Figure 5:** Dependence of thermal conductivity of $K(NO_3)_{1-x}(ClO_3)_x$ on the nominal chlorate concentration, x

Figure 5 shows the dependence of the thermal conductivity of the samples on the dopant concentration at various temperatures (in the ferroelectric phase). The thermal conductivity is found to decrease with increase in the dopant concentration. In non-metals heat is conducted solely by phonons. Phonon scattering on imperfections such as vacancies and stacking faults, which are introduced during film fabrication process is also important [15]. It is thought that the addition of impurities gives rise to extra scattering of phonons by electrons (holes) in the donor (acceptor) levels.

The impurities of different masses cause disruption in the periodic distribution of masses and the mean free path becomes shorter, leading to poorer thermal conductivity [16]. Similarly, polycrystalline samples are poorer thermal conductors than single crystals owing to scattering at the grain boundaries [15]. Scattering of phonons on the grain boundaries of materials have also been found to reduce thermal conductivity of films. The impurities and associated free carriers also reduce the thermal conductivity of the films. The chlorate ion is relatively larger than the nitrate ion considering the atomic radius of chlorine as 0.994 Å and that of nitrogen as 0.740 Å [17]. The introduction of the chlorate ion thus leads to scattering which increases the phonon-phonon interaction to decrease the mean free path of the phonon and hence decrease the thermal conductivity. The electrically active impurity atoms in solids can strongly reduce the thermal conductivity [18].

## 4. Conclusions

The, electrical resistivity, dielectric constant, dielectric loss and thermal conductivity of $K(NO_3)_{1-x}(ClO_3)_x$ have been studied. The electrical resistivity-temperature curve for the *x* = 0.1 sample shows an anomaly on heating and on cooling which indicates a first-order phase transition. Anomalies in the dielectric-temperature curves, also on heating and on cooling, confirm the first-order phase transition. The introduction of chlorate ions seems to lead to scattering which increases the phonon-phonon interaction. This results in the decrease in the thermal conductivity..

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