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Electric polarization and dielectric behaviour in dc electric fields of fused KNO_2 in phase II at room temperature

V G KHER, (Miss) V N HETE and D A DESHPANDE
Institute of Science, Nagpur 440001

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Abstract. On application of dc electric fields to a sample of KNO_2 (99·9% pure) fused between two heavily nickel plated copper plates the sample does not acquire the potential difference equal to the applied emf even though there is no external potential drop in the circuit. Also a very large capacitance of the order of 3000 μF is obtained for this sample which is attributed to interfacial polarization effect. An equivalent circuit is given to explain the dc electrical behaviour of the sample. The idea of solid state battery does not seem to be applicable in the case of fused KNO_2. The large value of the capacitance for dc fields in series with large voltage-dependent resistance is the cause of the slow discharge of the condenser.

Keywords. Potassium nitrite; dielectric behaviour.

1. Introduction

During the study of the effect of dc and ac electric fields on the conductivity and dielectric constant of fused KNO_2, a peculiar behaviour of the substance was observed. On application of a low static electric field of less than 10 V/cm for a few minutes to the dielectric, fused between two heavily nickel plated copper plates, the potential difference across the sample was retained for several days; even after shorting the plates, some residual potential difference was still retained by the sample for a few minutes.

2. Experimental

Potassium nitrite is known to undergo a number of phase transitions from monoclinic or trigonal to the cubic structure in the temperature range — 13° C to 70° C. On the basis of their DTA study, and dielectric and infrared measurements, Rao and Rao (1966) have reported that KNO_2 (purity not known) undergoes a paraelectric-ferroelectric transition at 40° C as was earlier indicated by Parry (1964). Mansingh and Smith (1971) have reported that the 40° C transition is not a paraelectric-ferroelectric transition and that the room temperature phase of KNO_2 (purity 99·5%) is not ferroelectric. We have however observed a phase transition at 64° C by DTA studies.

The nickel plated electrodes were held by two thick copper wires passing through a rubber stopper. A thermometer and two bent glass tubes also passed through the same rubber stopper. The sample was fused between the two nickel plated electrodes at melting temperature (419° C) and was quickly transferred to a thick glass tube of diameter 10 cm. During the transfer the temperature of the sample was much above 100° C. The rubber stopper was tightened to the mouth of the tube and sealed with Araldite. One bent glass tube was connected to a drying tower containing calcium chloride and the other glass tube was connected to a vacuum pump. Dry air drawn through the tower passed over the sample and was then pumped out of the system. The sample was thus cooled to room temperature under dry air flow. The pump end was then sealed off. The above process ensured that no water vapour was absorbed by the sample at any stage of its preparation and insertion in the experimental test tube. For studying the pyroelectric effect this test tube, connected to $CaCl_2$ tower, was inserted in a suitable furnace and the sample was heated slowly at a uniform rate from 25° C to about 100° C. The sample was connected to a sensitive galvanometer. As the temperature increased beyond 25° C a deflection in the galvanometer was obtained which increased with increase of temperature. When the temperature was maintained at 60° C the deflection was found to be constant for several hours. When the temperature was maintained constant at 70° C (above the transition temperature) there was a deflection in the galvanometer in the beginning which reduced to zero in about half an hour. This indicates that the sample requires some time for its transition, from monoclinic or trigonal to the cubic form, while at 60° C the sample remained in monoclinic or trigonal form. Thus, KNO_2 exhibits true pyroelectricity, *i.e.*, a potential difference is developed across the sample due to temperature alone (neither temperature gradient nor stresses are present) below the transition temperature of 64° C. This strongly indicates that the room temperature phase of KNO_2 belongs to a structural group which has a resultant vector in the crystal and is therefore of the polar class and without the center of symmetry. Hence, it is likely that the room temperature phase of KNO_2 is ferroelectric.

The charge retaining property of the fused KNO_2 sample placed between two parallel heavily nickel plated copper plates (area 9·5 cm, separation 1 mm) was studied using the circuit shown in figure 1. The sample was first charged with a low voltage low internal resistance (less than 50 ohm) source of 0·5 V and the variation of the charging current with time was measured with a sensitive galvanometer of low internal resistance (less than 50 ohm) every half minute. A discontinuous charging method was also used. In this method the sample was charged for half a minute, the source of emf disconnected and voltage across the sample measured with a VTVM (internal resistance 22 megohm). The VTVM was then disconnected and the charging source reconnected (see figure 2). This process was continued till the voltage across the sample became steady. The whole of the above procedure was repeated with the source voltage of 0·5, 1, 2, 3, 5 and 10 V.

The sample does not acquire the same potential difference as the applied emf, even though there is no external potential drop in the circuit. A current is drawn by the sample when the potential difference across it attains a steady value less than the applied emf. Thus, when the applied emf is 1 V and the steady potential difference across the sample is 0·75 V, the current through the sample is 25 μA. This current cannot be the charging current as the potential difference across the

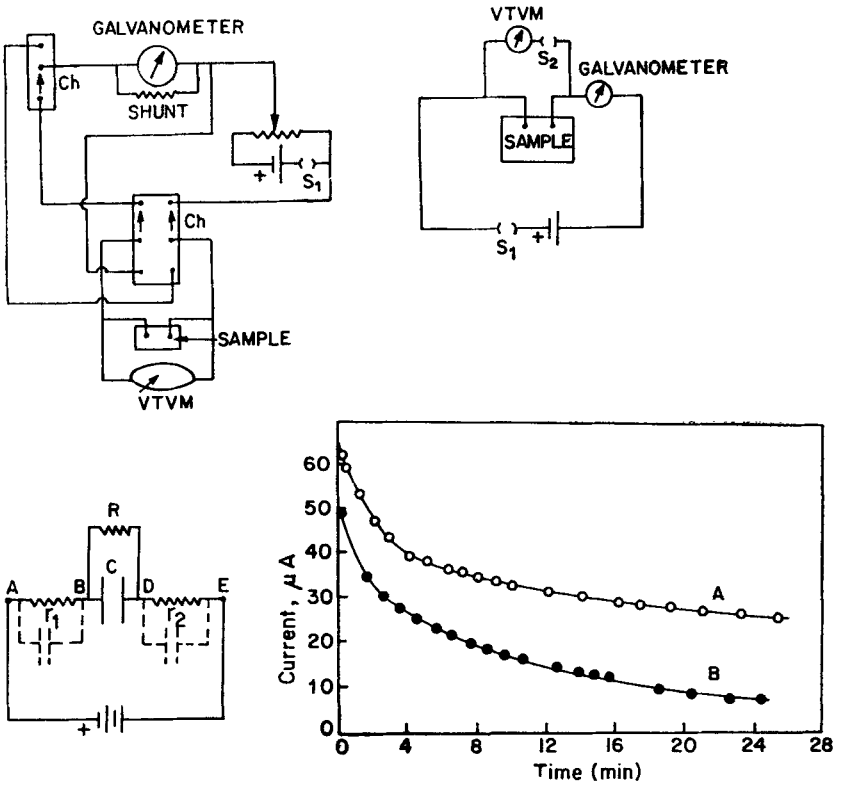

Figure 1. Circuit used for charging and discharging of a condenser (sample) 'Ch indicates position of switches for charging. (top left)

Figure 2. When S_1 and S_2 are closed, VTVM reads the source voltage 1 V. When S_1 is opened and S_2 is closed VTVM reads the voltage across the sample and this voltage is 0·75 V if the sample is charged fully by the source and the current reading with S_1 closed and S_2 open is 25 μA. (top right)

Figure 3. An electrical equivalent circuit of the sample. (bottom left)

Figure 4. Charging and discharging current versus time for fused KNO_2 (curve 'A' charging and 'B' discharging). (bottom right)

sample is constant. Also there is no resistance in the circuit external to the sample that can cause a drop of 0·25 V. Hence, the question arises as to how to account for this difference in the two voltages. The galvanometer and the cell have very low internal resistances (less than 50 ohm) and hence the potential drop across them due to 25 μA current will be negligibly small.

After charging the sample as much as possible with a particular source of emf the sample was discharged by (1) a continuous process or by (2) a discontinuous process through the galvanometer. In the discontinuous process the sample was discharged for half a minute and the galvanometer disconnected. Simultaneously a switch connects the VTVM to the sample which measures potential difference across the sample at this instant. The VTVM connection was retained for half a minute during which the potential difference indicated by it increases slightly. The VTVM was then disconnected and the discharging continued by reconnecting the galvanometer. This process was repeated for about 25 minutes.

3. Discussion

Ishibashi *et al* (1969) have studied the electrical field effect on fused KNO_3. They observed an emf of about 1 V between two electrodes stuck into the sample after a dc electric field of about 1 kV/cm was once applied to the crystal at high temperatures and then taken off. The magnitude of this emf was found to be temperature dependent. It disappears at low temperatures but recovers when the samples are heated again. Drastic change in emf at about 130° C seems to correspond to the phase transition of KNO_3 crystals. The emf decays with time but decay constant is quite large. Even after the electrodes are shortcircuited the emf gradually recovers almost to the same voltage as expected without any short circuiting. The phenomenon may appear similar to that reported here. However, the two phenomena are different for the following reasons:

(1) Very low fields (less than 10 V/cm) are enough for charging the sample as against 1 kV/cm used by Ishibashi *et al.*

(2) High temperatures (greater than 120° C) are needed for the phenomenon to occur in KNO_3.

This temperature is connected with the phase transition temperature of KNO_3. The KNO_2 effect is observed at low temperatures much below its transition temperature. Ishibashi has attempted to explain the effect as due to some chemical reaction taking place by the application of dc field and leading to the formation of a solid state battery. It is difficult to imagine the decomposition of KNO_3 into K^+, NO_2^-, and O^{2-} ions by mere application of dc field. In the case of KNO_2 it will be still more difficult to imagine the decomposition as the dc fields involved are very small. Hence, the idea of solid state battery being formed in case of KNO_2 is not valid.

3.1. *An electrical equivalent circuit for the sample.*

The observed variation of the current through the sample and the voltage across it with time can be understood by an electrical equivalent circuit of the sample shown in figure 3. The equivalent circuit consists of a capacity ' BD ' of the order of 3000 μF in series with the resistances r_1 and r_2 ($r_1 + r_2 = 10$ kohm) while an equivalent resistance $R = 30$ kohm is in parallel with the capacity. The large capacity 'BD' has to be charged or discharged through the resistances r_1 and r_2 as its electrodes are not directly connected to the source of emf. ' R ' represents an equivalent parallel resistance of this capacity. Using this equivalent circuit it is possible to account for the 0·25 V potential difference between the applied emf (1 V) and the maximum potential difference across the sample (0·75 V) when a current of 25 μA is passing through it. At this stage the condenser ' BD ', inside the sample, is charged to the potential which appears across it. As the entire 1 V emf is not appearing across it, a fraction of this (0·25 V) appears across r_1 and r_2. Hence, the charging current at this stage is zero. The 25 μA current is passing through r_1, r_2 and R.

At the beginning of the charging process (when applied emf is 1 V) the current recorded by the galvanometer is mostly the charging current as the discharging current is small as ' R ' itself is large for smaller values of potential difference across ' BD '. A curve is plotted (see figure 4) between the charging current and time

and from this $\int i dt = Q$, the total charge needed to charge the inside condenser to 0·75 V is calculated. Using this value of Q, C the capacity is calculated and is found to be of the order of 3000 μF. The value of $\int i dt = Q'$ corresponding to the discharge of condenser is found to be less than $\int i dt = Q$ for charging. The large value of the capacity for dc electric fields is responsible for the slow decay of the voltage once the sample is charged. For ac fields only the orientation mechanism is effective in polarizing the dielectric and hence at 50 Hz it is observed that the value of the capacity is of the order of 0·002 μF while its parallel resistance is of the order of 30 kohm.

4. Conclusion

The observed phenomenon can be understood with the help of an equivalent circuit consisting of a very large capacitance in series with large voltage dependent resistances. The interfacial or the space charge polarization effect may be responsible for the observed high value of capacity of the order of 3000 μF for dc fields. The idea of solid state battery does not seem to be applicable in this case due to the following reasons:

(1) $\int i dt$ for charging is greater than that of $\int i dt$ for discharging.

(2) It does not seem possible that KNO_2 will dissociate into K^+ and NO_2^- ions by the application of low dc fields (less than 10 V/cm) for the formation of a solid state battery.

A large value of the capacity for dc fields in series with large voltage-dependent resistance is the cause of slow decay of the condenser.

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