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Kinetics of the ferroelectrical behaviour of a thin layer of phase III KNO_3

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Abstract

The ferroelectrical behaviour and thermal properties of a thin layer of KNO_3 have been investigated mainly in its metastable phase III over the temperature range 145–90°C on cooling. The D–E hysteresis loop along the *c* axis has been observed by a modified Sawyer–Tower circuit using a 50 Hz a.c. electric field. The spontaneous polarization, coercive field and loop area of the ferroelectric hysteresis loop have been investigated as temperature dependent parameters. High accuracy differential thermal analysis (DTA) has also been used here to measure the thermodynamic and kinetic data of the phase transition phenomenon. The analysis shows that the heat of transformation is $\Delta H = 7.5$ J g^{-1} and there is a thermal hysteresis ΔT^h of 10°C. The results are discussed according to the nature of the ferroelectricity in phase III of KNO_3.

Keywords: DTA; Ferroelectrical behaviour; Heat of transformation; Potassium nitrate; Thin layer

1. Introduction

Potassium nitrate is one of the most important monovalent nitrates and its properties are sensitive to sample preparation. Phases I and II are nonpolar, but phase III is polar and its space group is (C^5_{3v}-R_{3m}) [1]. Phase I is (D^3_{6b}-R_{3c}) rhomobohedral and phase II is (D^{16}_{2h}-*phma*) orthorhombic.

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The phase transition III–I involves an order–disorder process; the entropy of the phase transition III–I is ≈ 1.81 and rather larger than the theoretical value ($R \ln 2 = 1.37$) indicating a considerable vibrational energy change, but unfortunately there is no independent assessment for this. It is, however, somewhat perplexing that the I–III transition has an entropy change of $+1.44$, which is closer to $R \ln 2$ than that for that III–I transition.

In both phases II and III cations are nearest to the anion. There are uncertainties associated with the structural arrangement and motion of the NO_3 group in the three modifications [2].

In spite of the wide spectrum of the physical data which has been obtained for KNO_3 (single crystals and polycrystalline samples), no detailed studies have been made on KNO_3 thin layers relating the kinetics of paraelectric–ferroelectric phase transition. In order to overcome such a deficiency, a programme of accurate thermal differential analysis and a step by step ferroelectric D–E hysteresis loop analysis has been carried out on thin layers of KNO_3 and the results are reported below.

2. Experimental

Thin layers of KNO_3 were prepared by slowly raising a glass substrate through molten KNO_3. The layer thickness was controlled by the speed of rise. The glass substrate on which the layer was grown was dipped into the melt and left for several hours. The substrate was pulled slowly from the melt by a motor. A thin film of molten KNO_3 adhered to both sides of the substrate. On cooling, these films solidified a few millimetres above the melt as a horizontal front. SnO_2 was the contact material because it withstood the hot KNO_3 melt, and the glass substrate coated with it. Silver paste was used as a second contact to the KNO_3 layer after solidification. The thin layer and its terminal contacts are shown in Fig. 1.

The ferroelectric D–E hysteresis loop of KNO_3 thin layer was displayed on the screen of a cathode ray oscilloscope by inserting the film samples in a modified Sawer circuit [3] at 50 Hz, Fig. 2.

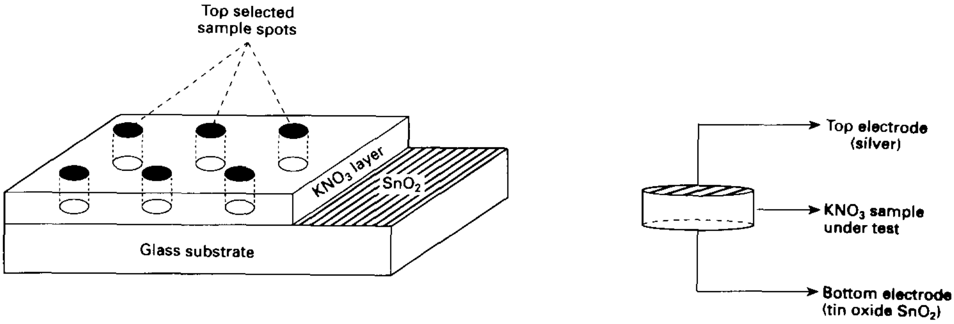

Fig. 1. Top view and cross section sketch in a selected sample over the surface of a thin layer of KNO_3.

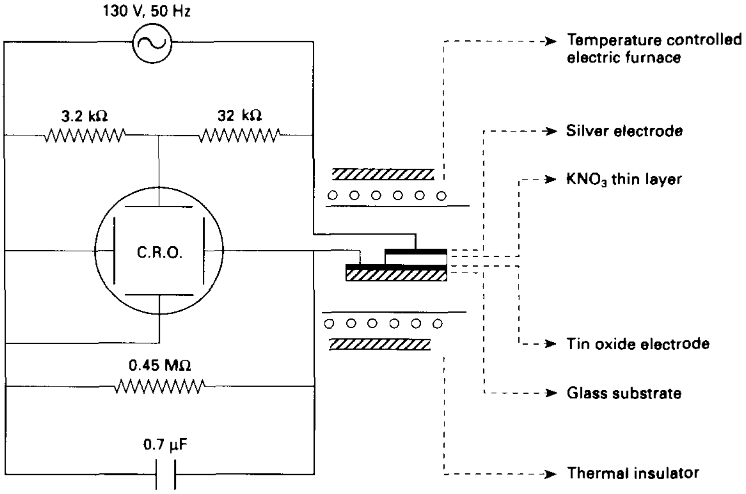

Fig. 2. Modified Sawyer circuit connected to a thin layer of KNO_3 for the observation of the D–E ferroelectric hysteresis loop.

Differential thermal analysis of the KNO_3 thin layers was carried out using a TA 500 DTA system manufactured by the Heraeus Company. It was provided with a thermal analyser temperature programmer, differential amplifier and an automatic voltage stabilizer.

3. Results

3.1. Characteristics of the D–E hysteresis loops

As is known, the ferroelectric hysteresis loop relates the change of the polarization of the thin layer to the change in its domain structure [4]. The temperature dependence of the D–E hysteresis loops at various temperature in the range 90–145°C is shown in Fig. 3. These loops were recorded during a cooling cycle as the phase transformation from the disordered phase I to the metastable phase III took place. As visualized from the series of D–E hysteresis loops, the D–E curve was found to be characteristically elliptic at 145°C, in the disordered phase I. As the layer was slowly cooled the inclination of the elliptic axis changed until the layer temperature reached 135°C. The elliptic form then transformed to the well known classical form of the ferroelectric hysteresis loop at 130°C. On further decrease of temperature, the loop area increased gradually until finally a rectangular hysteresis loop was obtained at about 115°C. When the temperature was reduced below 105°C, the characteristic hysteresis loop transformed once more to an elliptical form.

The spontaneous polarization and coercive field were also investigated as a function of temperature. Fig. 4 shows the temperature dependence of both parame-

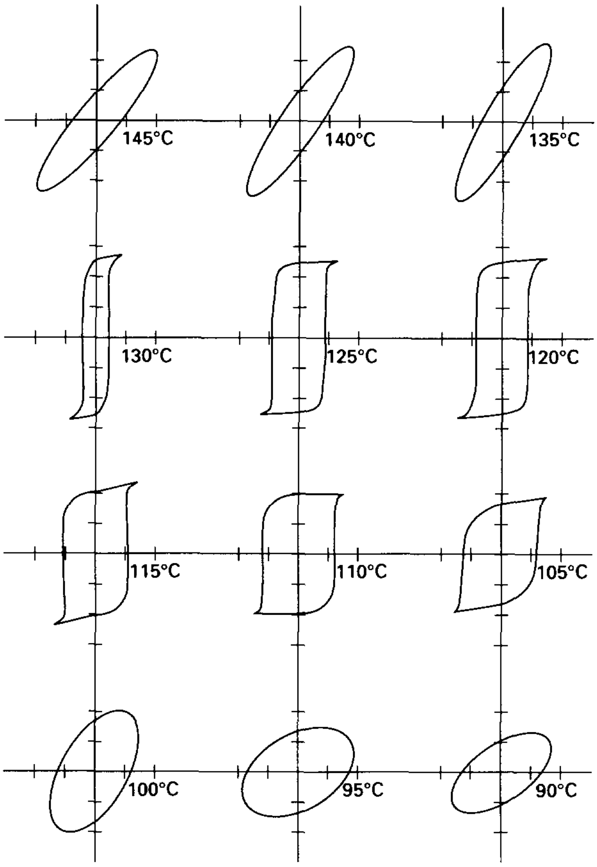

Fig. 3. Series of D–E hysteresis loops for a thin layer of KNO_3 obtained while cooling.

ters during cooling. Variations occurred during the transformation from the disordered phase I to the metastable phase III, and the maximum value of the spontaneous polarization P_s and minimum value of the coercive field E_c were obtained in the metastable phase. This extended over the range 135–115°C on cooling. The variation of the area of the ferroelectric hysteresis loop with temperature during very slow cooling is shown in Fig. 5.

3.2. Kinetics of the phase transition

Differential thermal analysis of KNO_3 thin layer was performed over a wide temperature range. The DTA thermograms obtained on successive heating and cooling are shown in Fig. 6. The curve clearly indicated the occurrence of an endothermic phase transition II–I at about 135°C on heating.

Sudden and sharp changes in the differential temperature ΔT accompanied the transition. The height of the peak, ΔT_{max}, was taken as a measure of the

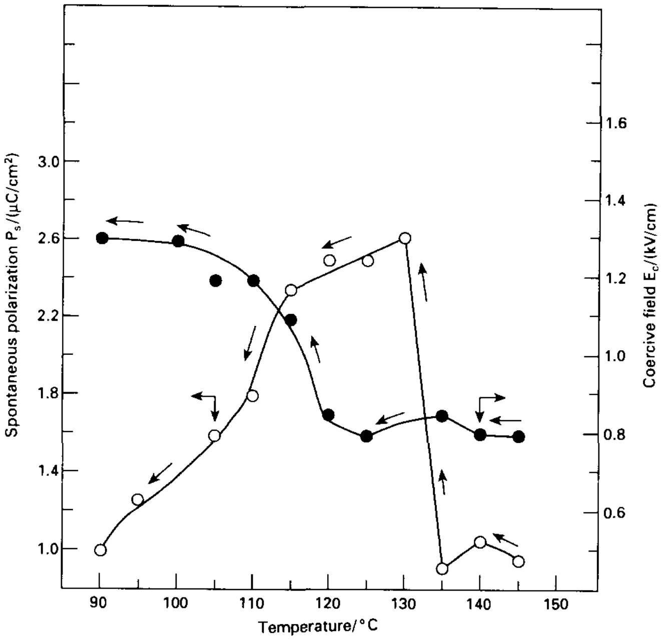

Fig. 4. Variation of the spontaneous polarization and coercive field with layer temperature.

endothermicity and exothermicity and the maximum rate of the transition. The temperature of the peak was related to the activation energy of the transition.

During cooling the reversibility of this exothermic transformation was delayed and appeared at about 125°C. It was clear that there was a pronounced thermal hysteresis recorded before the appearance of the metastable phase III [5]. This temperature hysteresis ΔT^{h} did not exceed about 10°C. The rate of cooling was very slow (1°C per 5 min).

The enthalpy ΔH of transformation was calculated from the peak area of the DTA signal [6–8]; values are listed in Table 1.

4. Discussion

Ferroelectricity is a well known phenomenon in the metastable phase III of KNO_3 single crystal. It has been extensively studied by many investigators [9]. It is nearly certain that the ferroelectricity here arises from the NO_3 group not existing exactly at the centre of the rhombohedral unit cell but being off-centre (both positive and negative positions are possible). Furthermore the NO_3 group can jump between these two equivalent positions following the reversal of the external electric field [10].

The parallel alignment of dipoles in ferroelectrics is due primarily to a relatively strong long-range interaction along the polar axis (*c* axis) and a weaker short-range

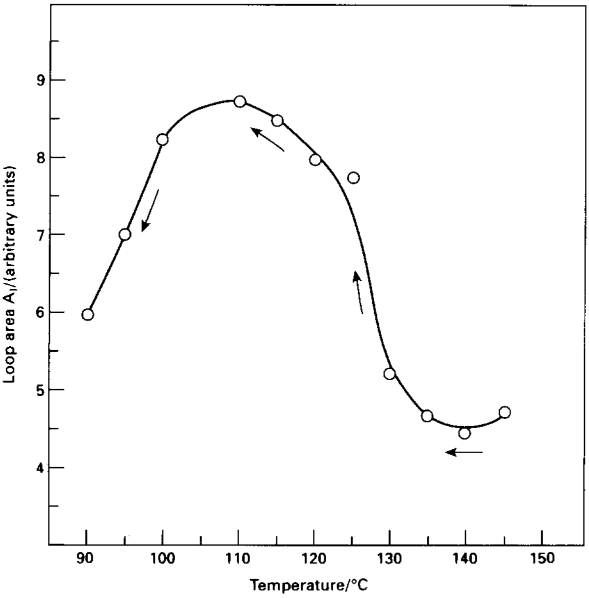

Fig. 5. Variation of the loop area with layer temperature.

interaction normal to the axis. Physically this comes about because of electric dipolar forces; the parallel alignment is energetically favourable for an isolated pair of *c* axis dipoles but not for an isolated pair of dipoles normal to the polar axis [11]. Theoretical and experimental estimates can be made of a correlation range, or

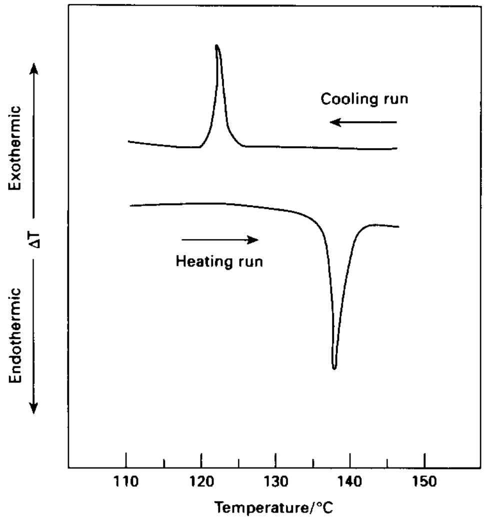

Fig. 6. DTA thermogram of a thin layer sample of KNO_3 recorded during successive heating and cooling runs.

Table 1
Data for thermal analysis of a thin layer of KNO_3

$\Delta H/(\mathrm{J\ g^{-1}})$ [a]	$T_{p}^{f}/°\mathrm{C}$ [b]	$T_{i}^{f}/°\mathrm{C}$ [c]	$T_{p}^{f}/°\mathrm{C}$ [d]	$T_{i}^{r}/°\mathrm{C}$ [e]
7.5	137	135	122	125

[a] Heat of transformation. [b] Forward peak temperature (heating). [c] Forward initiation temperature. [d] Reverse peak temperature (cooling). [e] Reverse initiation temperature of transformation.

distance over which in neighbouring cells polar displacements are strongly correlated. Although the quantitative manner in which the c axis and a axis correlation ranges L_c and L_a may vary a little, typical values for many ferroelectrics are 10–50 nm for L_c and 1–2 nm for L_a. From the above estimates the transverse correlation range L_a is of the same order as the thickness of a 180° domain wall while the polar axis L_c can amount to many tens of unit-cell lengths. Consequently as the physical dimensions of the crystal are reduced a change in the stability of ferroelectric phase (e.g. the metastable ferroelectric phase III of KNO_3) is to be expected.

A direct measure of correlation range is, in principle, possible by preparing thin ferroelectric films or layers and studying the thickness dependence of the ferroelectric properties. This procedure, however, is usually complicated by additional surface effects which arise from incomplete neutralization of depolarization fields (when the polar axis is perpendicular to the layer) and space charge fields arising from the energy band normal to the layer surface. These effects greatly influence the ferroelectric behaviour in the surface region and no unambiguous results attributed to the correlation length in thin layers have yet been obtained.

According to the present work on a thin layer of KNO_3 the discrepancies between the results for layers and single crystals must be attributed to variations in their defect structures.

The defects not only affect the ferroelectric behaviour directly but also the electrical conductivity. The thickness of the Schottky barrier layers and the magnitude of the space charge vary significantly with free-carrier concentration [4]. In the paraelectric phase both surfaces are equivalent and the expected band bending is shown in Fig. 7a. As the layer thickness D is reduced below the free carrier screening length d the depletion layer extends throughout the entire layer (Fig. 7b). It might be anticipated that the effects of the surfaces on the phase transition would be less important in very thin layers than in the layers having thicknesses comparable to the screening length.

The phase transition in a thin layer of KNO_3 is of the order–disorder type. The role played by disorder in the behaviour of ferroelectrics has received considerable attention [12–17]. Ferroelectrics have received considerable attention and impurities are of special interest. For these later materials measurements of Raman scattering cross-section [14], dielectric constant [15] and refractive index [16] have been carried out. For such disordered systems the measured parameters were particularly characteristic showing a gradual change between the high and the low temperature phases rather than the sharp change found in pure ferroelectrics and this led several authors to characterize such materials as "dirty" ferroelectric [13–15] or ferroelec-

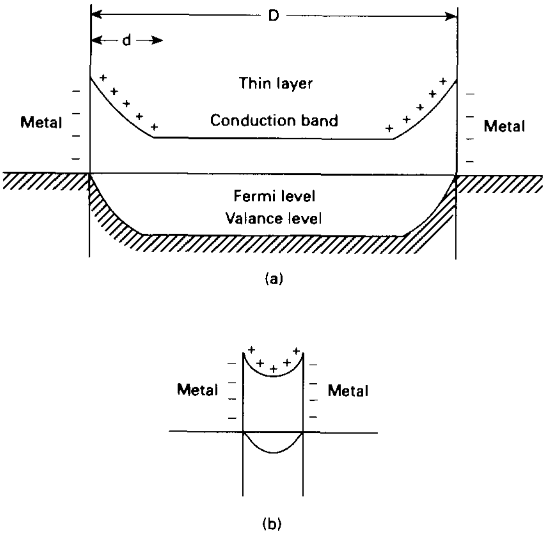

Fig. 7. (a) Schottky barriers at both interfaces when the layer thickness D is greater than the depletion layer of width d and (b) small band bending when $D < d$.

trics having a "diffuse" phase transition [13]. It was shown that the crystallography disorder and non-stoichiometry could lead to anomalous behaviour in dielectric properties, e.g. dielectric constant, d.c. resistivity, and pyroelectric current. If care was taken to produce homogeneous and well crystallized KNO_3 a thin layer polarization reversal effect closely similar to those characteristic of the bulk ferroelectric could be obtained. In particular the crystalline anisotropy of polarization and optical properties of thin layers of KNO_3 closely followed that observed in single crystals.

References

[1] B. Read, D. Weinreich and H.F. Matare, Phys. Rev., 113 (1959) 454.

[2] F. El-Kabbany, W. Badaway, N.H. Tahr and E.H. El-Khwas, Ferroelectrics, 76 (1987) 209.

[3] H. Diament, K. Dreuch and R. Pepinaky, Rev. Sci. Instrum., 28 (1957) 30.

[4] M.E. Lines and A.M. Clase, Principle and Applications of Ferroelectrics and Related Materials, Clarendon Press, Oxford, 1979.

[5] F. El-Kabbany, G. Said, S. Mahrous and S. Taha, Phys. Status Solidi A, 95 (1986) 495.

[6] H.J. Borehard, J. Chem. Educ., 33 (1956) 213.

[7] J.A. Pask, Univ. Calif. Inst. Publ. Ser. 18, ISSN, 3 (1952).

[8] R.L.N. Sastry, S.R. Yayanaarasin, Han. F.M. Mehratra and C.N.R. Rao, J. Inorg. Nucl. Chem., 28 (1966) 1165.

[9] T. Mitsui, I. Tatsugaki and E. Nakamura, Ferroelectricity and Related Phenomena, Vol. 1, Gordon and Breach, New York, 1976.

[10] S. Sawade, S. Nomura and Y. Asao, J. Phys. Soc. Jpn., 16 (1961) 2486.

[11] S.H. Wemple, Phys. Rev. B, 2 (1970) 2679.

[12] T. Chuis, Phys, Rev. B, 11 (1975) 3457.
[13] G.A. Smolesuky, J. Phys. Soc. Jpn. Suppl., 28 (1973) 26.
[14] G. Burns and B.A. Scott, Solid State Commun., 13 (1973) 417.
[15] G. Burns and B.A. Scott, Solid State Commun., 13 (1973) 423.
[16] G. Burns and E. Burstein, Ferroelectrics, 7 (1974) 297.
[17] Y. Yacoby and S. Just, Solid State Commun., 15 (1974) 715.