

Electrical properties of carbon-doped KNO_3 thin layers

F. EL-KABBANY, S. TAHA, E. H. EL-KHAWAS

Physics Department, Faculty of Science, Cairo University, Cairo, Egypt

A series of carbon-doped KNO_3 thin layers was grown from the melt by a special technique. The changes of the dielectric constant, d.c. resistivity, energy of vacancy formation, pyroelectric current and ferroelectric hysteresis loops with carbon concentration were investigated. The present study aims to clarify the effect of doping carbon as a conducting material on the properties of the dielectric KNO_3 thin layers by extensive use of experimental data from isomorphous sets of solid solutions of carbon and KNO_3 . These systems were studied in the vicinity of the order-disorder phase transition region for various values of carbon concentration x between $x = 0$ and $x = 0.08$. For the carbon doped layers, large changes in the electrical properties were found depending on the doped carbon concentration. The dielectric constant and d.c. resistivity were reduced appreciably, while the pyroelectric current showed improved behaviour in the presence of carbon, as compared with pure KNO_3 thin layers. Anomalous ferroelectric hysteresis loops were obtained in carbon-doped layers with a reduction of the ferroelectric loop temperature region by ca. 10°C at carbon concentration $x = 0.07$. The ferroelectric loops of the carbon-doped layers could be obtained $< x = 0.07$ with little loop deformation. The results showed that the carbon doping process delayed the phase transition point by 5 to 6°C for $x = 0.06$. Also, the energy of vacancy formation showed its minimum value of 0.45 eV at $x = 0.03$ to 0.04. The marked change in the detailed character of the different electric properties of the doped layers during phase transition in the presence of carbon was interesting.

1. Introduction

KNO_3 is one of the most important monovalent nitrates and it is the least understood because its properties are sensitive to that mode of sample preparation. Under variation of temperature and pressure, seven modifications of KNO_3 were established. These have been designated [1] as phases I to VII, following the notation of Bridgeman [2]. The transformation between the three modifications I, II and III occurred between the melting point and room temperature at atmospheric pressure. At room temperature and pressure KNO_3 had an aragonite type structure [3] orthorhombic D_{2h}^{16} . The crystal structure changed from orthorhombic to trigonal at about 135°C on heating the low temperature phase II. Phase I was generally believed to have a structure closely related to the calcite structure (trigonal $D_{6d}^3 - R_{3c}$) [3, 4]. On cooling, phase I did not directly change to phase II, but to another phase named phase III (which was considered to be ordered) at about 125°C . The crystal structure of the phases I and II were nonpolar, but that of the phase III was polar and its space group was ($C_{3v}^5 - R_{3m}$) [5].

Carbon exists in two distinct crystalline modifications, diamond and graphite and in the apparently amorphous form which is very variable. The most thermodynamically stable form at atmospheric pressure [6]. Carbon atoms are arranged in coplanar

hexagonal groups of six in the crystals (Fig. 1). One particularly active area of research in recent years has been the study of the effects of addition of good conducting material to a dielectric substance. Earlier studies showed that the addition of conducting material to the dielectric thin layers caused a change in its important electrical properties. With a view to establishing a quantitative correlation between the observed variations and the basic parameters our studies covered the stable KNO_3 layer doped with carbon. Results of investigations over the accessible range of temperature and carbon content are presented. This may open up new device possibilities for pyroelectric and ferroelectric thin layers applications required in optical memory storage, display media, electromechanical transducers, high-sensitivity pyroelectric detectors and thermal imaging systems.

2. Experimental details

A series of KNO_3 and carbon mixtures were melted together in a glass vessel using very low carbon concentration compared to KNO_3 . The substrate on which the layers were grown was dipped into the melt and preferably left in the melt between 340 and 360°C for several hours. The substrate was removed from the melt by a slow motor. A thin layer of molten KNO_3 doped with carbon adhered to both sides of the

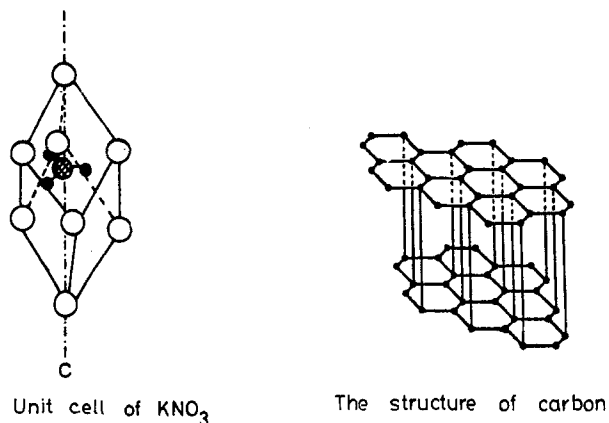


Figure 1 Structure of KNO_3 and carbon. (○) Potassium; (⊗) Nitrogen; (●) Oxygen.

substrate. It cooled above the melt and solidified a few mm above the melt along a horizontal line [7, 8].

For the measurements of their electrical properties, the layers needed to contact both sides. For this reason the substrate must be conductive so as a contact material that withstands the hot mixture melt, SnO_2 has proven useful and the glass substrate coated by it. The other contact to mixture layer applied after preparation of the layer may best be deposited by a silver electrode. The thin layer and its contact terminals are shown in Fig. 2. The dielectric constant was obtained from measurements of the sample capacitance by an RLC bridge at 1 kHz. The d.c. resistivity was measured using a conventional circuit. The pyroelectric current was also obtained here using a picoammeter. The ferroelectric hysteresis loop of carbon-doped KNO_3 thin layer was displayed on the screen of the C.R.O. by inserting it in a modified sawyer circuit [4]. In this circuit, the potential across the sample was applied on the horizontal plates of the cathode-ray oscilloscope. Thus, the quantity plotted on the x-axis was proportional to the electric field across the sample.

3. Results

According to the present different electrical measurements carried out on pure samples of KNO_3 thin layers, there were grounds for believing that the doping of carbon to the layers might add significant contributions to the process of ordering and disordering. Consequently, the various parameters previously measured could be influenced and a wide variety of information obtained. In order to find out the effect

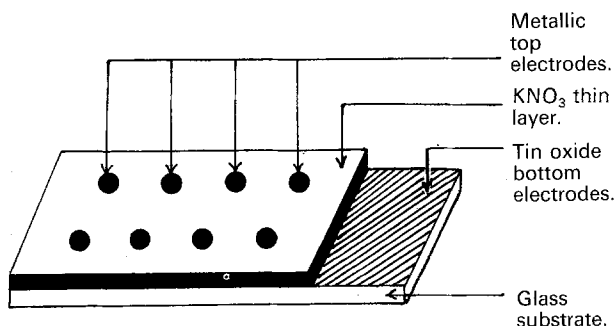


Figure 2 A sketch of KNO_3 thin layer prepared on a glass substrate provided with top and bottom electrodes.

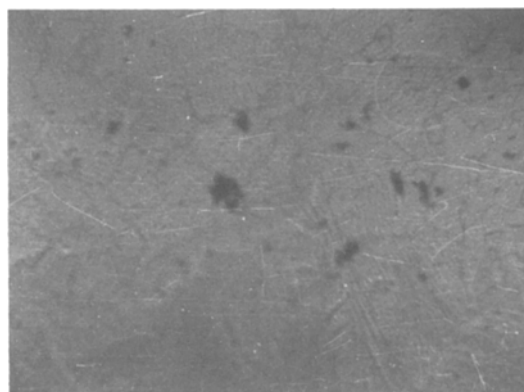


Figure 3 Optical microscope transmission photograph of the carbon-doped KNO_3 thin layer (Mag. $\times 30$).

of partial existence of carbon in the layers, a set of electrical and thermal analyses were studied to characterize the order-disorder behaviour in the mixed carbon layer system.

3.1. Effect of doped carbon on the electric, pyroelectric and ferroelectric properties

Transmission microscopic studies of carbon-grain distribution inside the thin layers under test were performed. It was found that the carbon grains were uniformly distributed inside the layers for various carbon concentrations despite the presence of different grain sizes. Sometimes a collection of grains appeared. Fig. 3 shows an example of carbon-grain distribution in KNO_3 thin layer doped with the carbon concentration $x = 0.04$ and $x = 0.07$.

The surface uniformity of the thin layer was also checked by scanning electron microscopy (SEM) after coating the KNO_3 thin layer by gold thin film. Fig. 4 shows an SEM photograph of the layer in which a very smooth surface without any cracks or holes has appeared. Checking of carbon distribution and surface tests proved to be very important and should be performed before carrying out the different electrical measurements.

3.2. Dielectric constant

Fig. 5 shows the variation of the dielectric constant of carbon-doped layers with the reciprocal of temperature ($1/T$) at different carbon concentrations. As was clear during both heating and cooling cycles, the doped carbon had no great effect on the phase

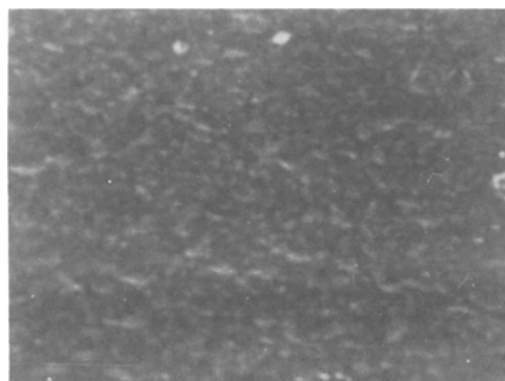


Figure 4 SEM photograph of the thin layer (Mag. $\times 600$).

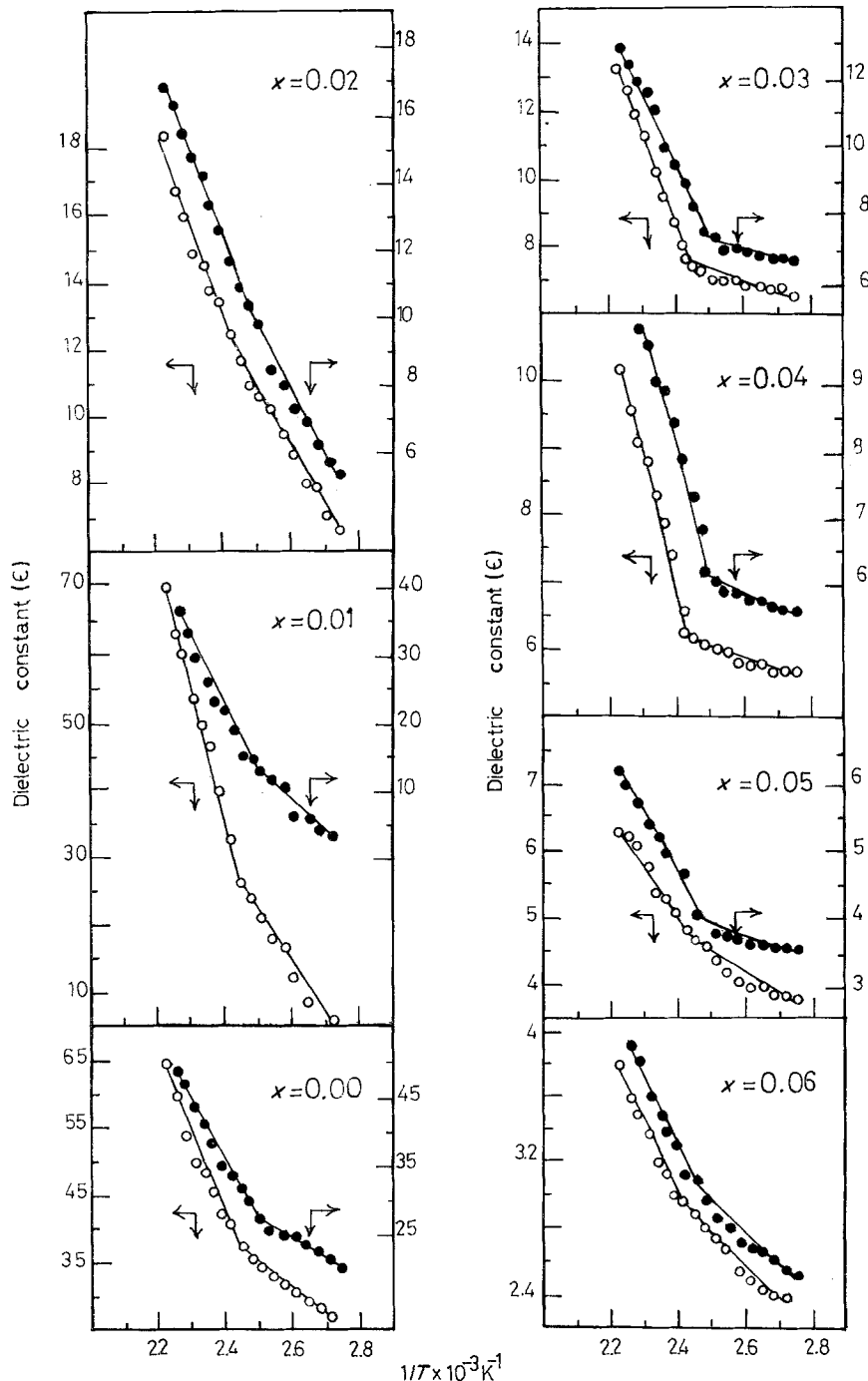


Figure 5 Effect of carbon doped in KNO_3 thin layer on the dielectric constant. (O) heating run; (●) cooling run.

transformation process, but its important effect appeared in the absolute values of the layer dielectric constant. This is clearly demonstrated in Fig. 6 in which the dielectric constant decreased with a relatively fast rate as the carbon concentration increased, which ever layer was in ordered or disordered state. The reduction in the dielectric constant became slower as the carbon concentration approached $x \sim 0.04$.

3.3. D.C. resistivity

Fig. 7 shows a set of ρ against $1/T$ relations for different carbon concentration layers between $x = 0$ up to $x = 0.06$. The general behaviour observed in the pure KNO_3 thin layer was still observed here as a linear behaviour of clear kinks at the phase transition point. However, the presence of carbon in the layers reduced the d.c. resistivity of the layer to a wide extent, depending on the carbon concentration in the thin layer Fig. 8 shows the effect of doped carbon on the

d.c. resistivity of the layer, the sudden reduction of which became slower as x approached 0.04 in both of the low-temperature ordered phase II and the high-temperature disordered phase I. For a clearer carbon effect, an estimation of the energy of vacancy formation in the presence of carbon in the layers was made by plotting the logarithm of the change in d.c. resistivity $\ln(\Delta\rho)$ against the reciprocal of temperature ($1/T$) for different layer samples of different carbon concentration. The energy of vacancy formation (E_v) for each value of carbon concentration was obtained. Fig. 9 shows the carbon concentration dependence of energy of vacancy formation. The minimum value of E_v was obtained at $x \sim 0.03$.

3.4. Pyroelectric current

It was found with the carbon effect on the dielectric constant and d.c. resistivity that the two parameters were additive functions of the carbon concentration at

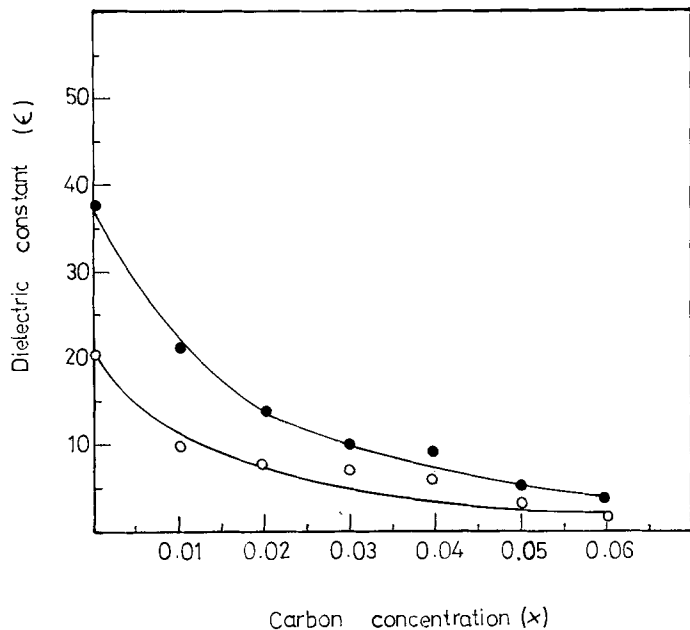


Figure 6 Variation of the dielectric constant of the carbon-doped KNO_3 thin layer with the carbon concentration. (○) Ordered phase; (●) Disordered phase.

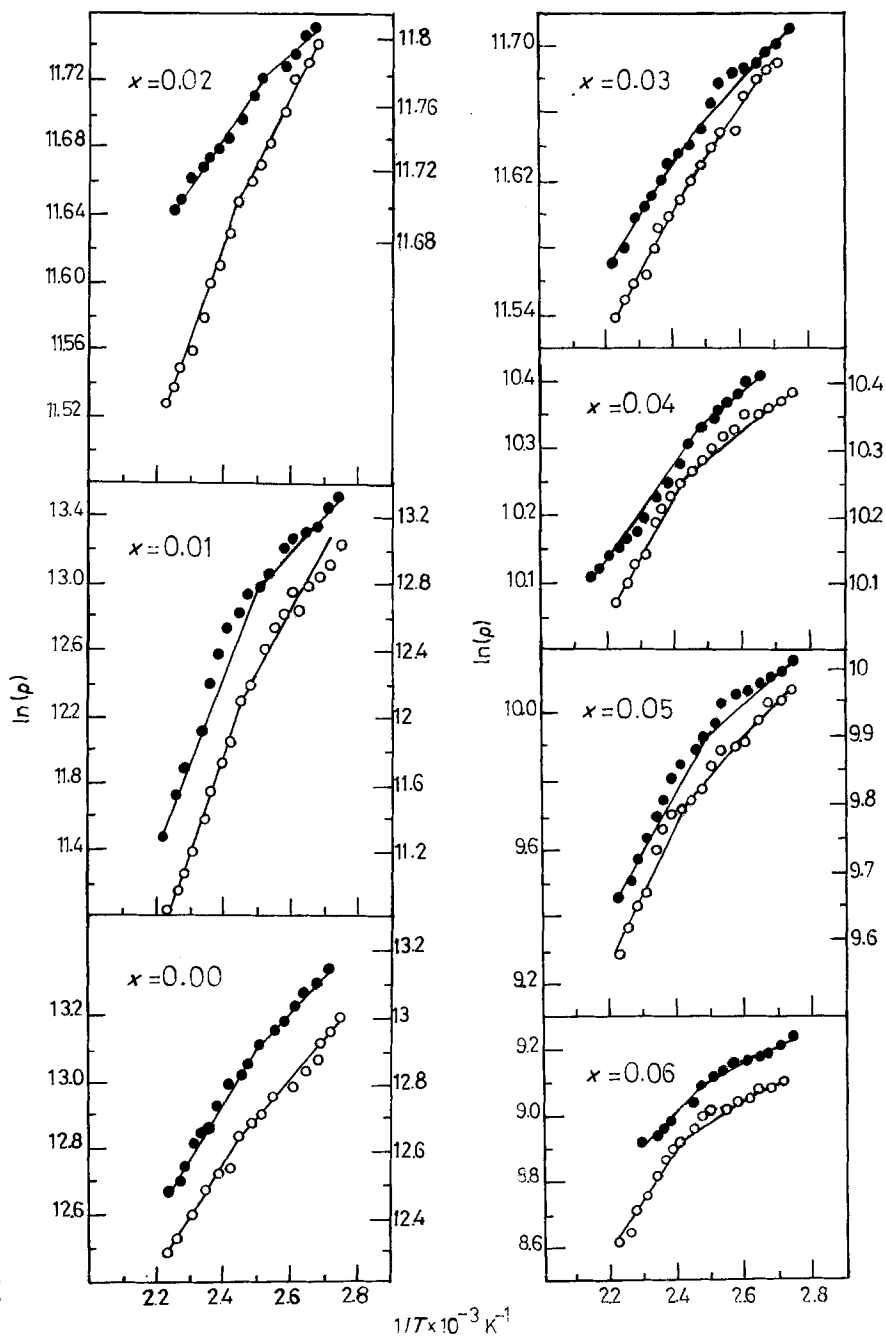


Figure 7 Effect of carbon doped in KNO_3 thin layer on the d.c. resistivity (○) heating run; (●) cooling run.

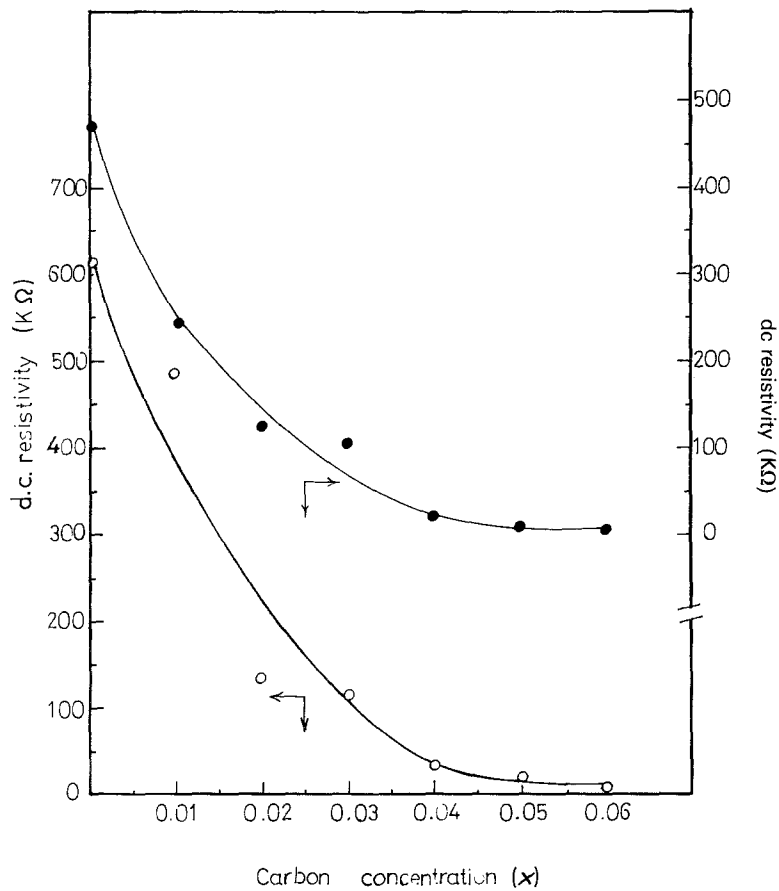


Figure 8 Variation of d.c. resistivity of carbon-doped KNO_3 thin layer with carbon concentration. (O) Ordered phase; (●) Disordered phase.

any layer thickness and the layer state (ordered or disordered). The pyroelectric current measurements of carbon-doped KNO_3 thin layers showed no departure from the systematic additivity rule. Fig. 10 shows a set of the pyroelectric current data as a function of the reciprocal of temperature for different carbon-doped concentration at fixed layer thickness. The same trend of ϵ and q appeared in the pyroelectric current which strongly supported the accepted action of carbon. As

the carbon concentration increased in the layer, the pyroelectric current of the layer also increased for both of the two phases I and II. Fig. 11 clearly illustrates this conclusion.

3.5. Ferroelectric properties

Fig. 12 shows the effect of doped carbon on the ferroelectric hysteresis loops. The KNO_3 phase III-type loop was observed clearly when the concentration of

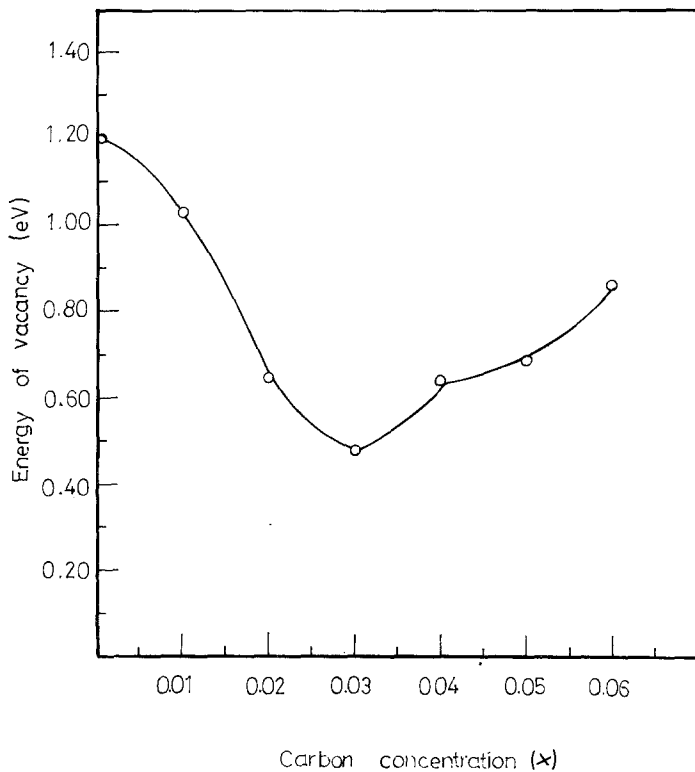


Figure 9 Variation of the energy of vacancy with carbon concentration doped in KNO_3 thin layer.

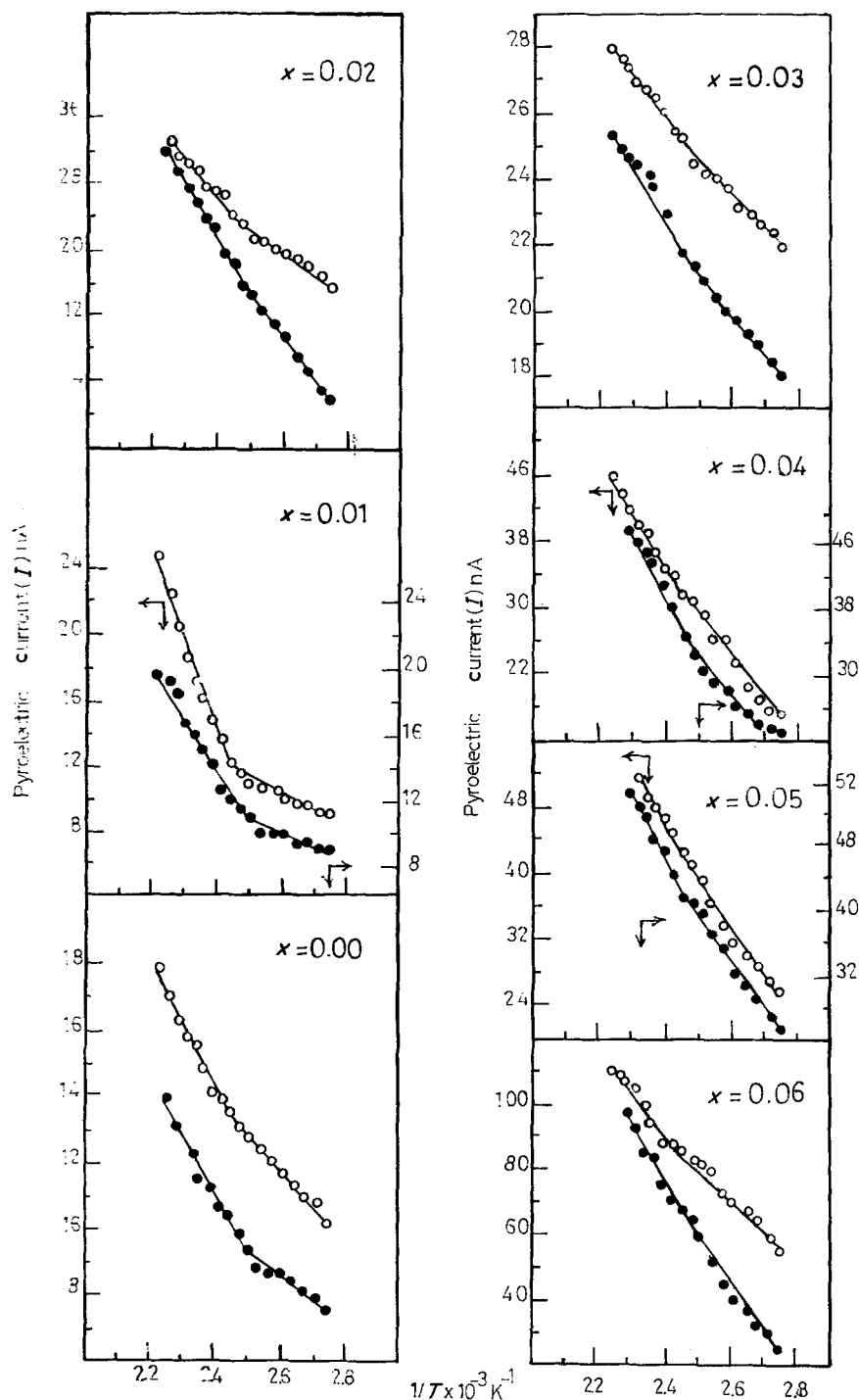


Figure 10 Effect of carbon doped in KNO_3 thin layer on the pyroelectric current. (○) Heating run; (●) Cooling run.

the doped carbon x was small and disfigured when x was large. The ferroelectric hysteresis loop was seen up to the mixing limit $x = 0.07$. With increasing x , the temperature region itself, in which the ferroelectricity existed, reduced monotonically and its width narrowed, e.g. the ferroelectric loops lay at ca. 125 and 105°C at $x = 0$, but lay at ca. 125 and 115°C at $x = 0.08$. This meant that mixed carbon KNO_3 thin layers were also ferroelectric in phase III on cooling, up to the size of the unit cell volume and ionic radius of the partners in the mixture, but, as a detailed mechanism, it has not been consistently explained.

4. Discussion

4.1. Phase transformation in carbon doped layers

The addition of carbon to the KNO_3 compound did not produce a new phase, but formed a relatively

homogeneous solid solution of the two materials. This solid solution could be either a substitutional solid solution, where the solute atoms (carbon) replaced those of the solvent (KNO_3), or an interstitial solid solution where the solute atoms fitted into spaces between those of the solvent. In the latter, the solute atoms were much smaller than the solvent atoms and the most important solute atoms in the interstitial solid solution were potassium, carbon, nitrogen and oxygen. The general properties of these primary solid solutions could be summarized as: random arrangement of the different types of atoms was found in cases where no heat treatment was applied and for the same crystal structure as the solute content increased, minor changes occurred in the dimensions of the unit cell.

Complete miscibility of the two compounds in the solid state could favourably occur if the crystal structures of the two substances were essentially the same.

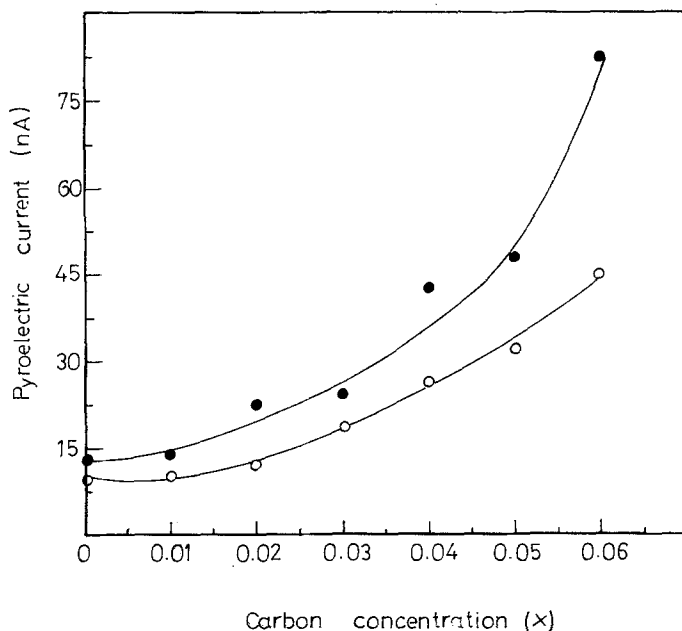


Figure 11 Variation of the pyroelectric current of carbon-doped KNO_3 thin layer with carbon concentration. (○) Ordered phase; (●) Disordered phase.

Even considerable differences in the axial ratios might not prevent the formation of a continuous series of solid solutions, provided that the atomic volumes of the two substances were similar [9]. Consequently, it was suggested that when the atomic diameters of the solvent and the solute differed by $> \text{ca. } 15\%$ of that of the solvent, the size factor was unfavourable and the solid solution was rather restricted, whilst, when the atomic diameters were within this limit, the size factor was favourable and considerable solid solution would be formed. The size factor indicated which elements were likely to form considerable solutions. Other factors might prevent the formation of solid solution

even though the size factor was favourable, e.g. the tendency to form stable intermediate compounds at the expense of the primary solid solution.

Considering these points and the properties measured, one might conclude that, the formed mixtures were most probably of the solid solution type. This conclusion might be supported by the values of the atomic radii values given in Table I for K, N, O and C atoms, respectively.

The partial doping of carbon into KNO_3 layers caused a change in the interatomic forces. The interatomic force played an important role in phase transition. The change in the interatomic forces came from the variations in the interatomic distance, which in turn increased with temperature in the stability range of a given state of aggregation. It was found that the transition to a higher temperature state of aggregation always involved reduction in some of the interatomic distances [10–13]. The energy of thermal vibrations increased with temperature and the interatomic distance increased, whilst the bond strengths decreased, especially in relation to the increasing energy of the thermal vibrations. However, bond breakage seemed to be replaced by the substitution of shorter stronger bonds, which could exist at the given temperature. As

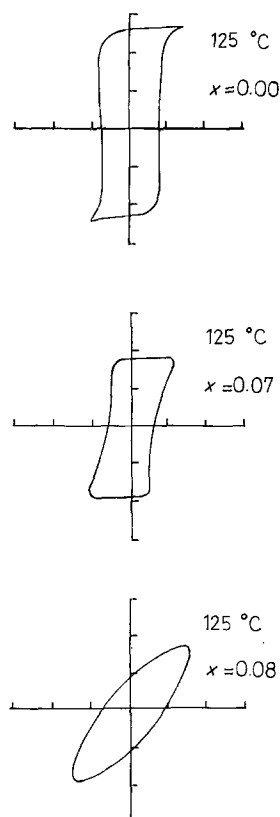


Figure 12 Effect of doped carbon on the ferroelectric hysteresis loop of KNO_3 thin layer.

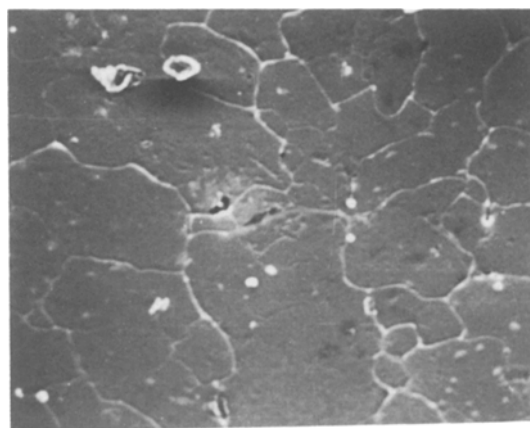


Figure 13 SEM photograph for KNO_3 thin layer in which microcracks have clearly appeared (Mag. $\times 200$).

TABLE I Atomic radii of the elements of the solid solution

Element	Atomic radius (Å°)
Potassium	2.23
Nitrogen	0.71
Oxygen	0.60
Carbon	0.77

a consequence, the coordination number of near bonds increased, i.e. the number of nearest bonds decreased. Strengthened compact atomic groups were created and the kinks between these groups were weakened or completely broken (melting and evaporation).

The phase transition caused by temperature change could be considered as a two-stage process involving, on one hand, the approach between atoms in groups, and on the other the weakening of the kinks between groups. As a result, the overall volume change in phase transition could have either a sign or be zero. The high-temperature phase nucleated via a process of approach between the atoms to form doublets and triplets occurred readily. The converse processes, involving moving a part of these closer groups, was more complex and the nucleation probability was small in the low-temperature phases. The structure changes arising from the approach between atoms is thought to be the direct cause of the phase transition [14–16]. To elucidate the initial stage of phase formation, we needed to consider the layer growth incorporating the atom approach. The amplitude of the thermal vibration in the surface of the layer was much greater than those inside the layer [17]. The thermal approach between systems should occur at lower temperatures; consequently, the surface might have a layer of high temperature or a metastable layer at any temperature.

4.2. The effect of carbon on the electric process

The conduction process in KNO_3 was evidently ionic [18] and could therefore occur either via vacancy jumps and or through interstitial jumps of K^+ ions. During the heating run of carbon-doped layers, the conductivities were large compared with those of undoped KNO_3 layers. This meant that the additional charge carriers contributed to the conductivity in carbon-doped KNO_3 thin layers. Thus, in the carbon-doped layers the role of carbon impurities towards the increase in electrical conduction was quite evident. The additional charge carriers (extrinsic conduction) responsible for the conduction process in these layers were the potassium ion vacancies which moved through the lattice with K^+ ion jumps. The appreciably large values of conduction in heating runs of carbon-doped samples compared to the corresponding cooling-run values might be explained if it was

assumed that the carbon impurities embedded in the crystal were oxidized and thus precipitated during the heating process. The oxygen for such process might come from the nitrate ions with simultaneous creation of NO^- . This liberation of NO^- also seemed to establish that the precipitation of impurities in this system was irreversible. The layer was found turbid after measurements and it appeared that this turbidity was due to microcracks created within the layer as a consequence of the escaping gas. These are shown in an SEM (Fig. 13). They did not cause any detachment of electrodes, because this would have resulted in decreased conductivity even in the intrinsic region, contrary to our observation. The precipitation of impurity ions envisaged would cause the depletion of associated potassium ion vacancies from the crystal and thus resulted in a decrease in conduction while cooling followed by heating. This phenomenon could also be explained on the basis of expulsion of impurities from the interior to the surface similar to what was previously reported by Tacaman *et al.* [18] in alkali halide crystals doped with divalent impurities.

References

1. E. RAPOPORT and G. C. KENNEDY, *J. Phys. Chem. Solids* **26** (1965) 1995.
2. P. W. BRIDGEMAN, *Proc. Amer. Acad. Arts. Sci.* **51** (1916) 582.
3. A. KODYASHI, Z. ODA, S. KAWAJI, H. ARATA and K. SUGUJAMA, *J. Phys. Chem. Solids* **14** (1960) 37.
4. C. S. HUNG and J. R. GLIESMAN, *Phys. Rev.* **99** (1955) 406.
5. B. READ, D. WEINREICH and H. F. MATARE, *Phys. Rev.* **113** (1959) 454.
6. A. HAMPEL, "The Encyclopedia of the Chemical Elements" (Reinhold Book Corporation, New York, 1968).
7. T. HAMMAD, F. EL-KABBANY and Y. BADR, *Phys. Stat. Solidi(a)* **94** (1986) 121.
8. F. EL-KABBANY, W. BADAWAY, N. H. TAHR and E. H. EL-KHWAS, *Ferroelectrics* under publication, 1987.
9. C. V. RAYNOR, "Structure of metals and Alloys", (The Institute of Metals, London, 1954).
10. K. MEYER, *Metallurgiya*, **196** (1972) 38.
11. E. A. MOELWYN-HUGHES, *I. Izd. Inost. Lit* **1** (1962) 492.
12. B. V. NEKRASOV, *Izd. Khimiya* **3** (1970) 26.
13. W. L. BUCK and L. W. STOCK, *Am. Mineral* **40** (1955) 192.
14. T. BAARS and J. BRAND, *J. Phys. Chem. Solids* **34** (1973) 5.
15. S. K. FILATOV, *Uch. Zap. LGU, Ser. Geol. Nauk*, **14** (1973).
16. A. MARADUDIN and A. BERANDER, *J. Phys. Radium* **24** (1963) 89.
17. M. L. KITE and O. F. TUTTLE, *Izd. Inost. Lit* (1954) 215.
18. M. J. YACAMAN and A. G. BASSETT, *Thin Solid Films* (1976) 35.

Received 7 December 1987
and accepted 29 April 1988