

DIELECTRIC BEHAVIOUR OF POTASSIUM ACETYLACETONATE

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The dielectric constant and the dielectric loss of potassium acetylacetonate, K(acac), are measured as a function of both temperature and frequency. A peak value is obtained at the a critical temperature $T_c = 313$ K. X-ray analysis revealed that at T_c , K(acac) undergoes phase transition from orthorhombic to triclinic structure. The Cole-Cole diagrams have been used to determine the molecular relaxation time τ . The temperature dependence of τ is expressed by thermally activated process. The impedance spectra in the frequency range from 50 Hz to 500 kHz plotted in the complex plane show semicircles. The conduction mechanism, below T_c , is predominantly operating at the surface. Above T_c , the conduction is proceeding in the bulk material with contribution from the surface.

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1. Introduction

The electrical properties of metal-acetylacetonate have attracted interest during the last few decades, because they exhibit ferroelectric behaviour. The dielectric properties of sodium acetylacetonate were studied [1]. A peak value in the dielectric constant was observed and has been ascribed to some structural irreversible change from orthorhombic phase to triclinic structure. The dielectric properties of potassium acetylacetonate K(acac) were also studied [2]. Two peaks were observed in the dielectric constant versus temperature curve at 283 and 294 K, which were explained as irreversible transition temperatures. As far as we are aware, the structure of K(acac) has not been previously reported in the literature. The determination of such a structure, below room temperature, is not available. Therefore, we carried out our investigations above room temperature. Despite a considerable effort of understanding the dielectric properties of these compounds, the problem is still far from being complete. The aim of this work is to study the dielectric properties of K(acac) as a function of both temperature and frequency.

In addition, X-ray diffraction pattern is made to give some knowledge about the structure of this compound.

2. Experimental procedure

Potassium acetylacetonate K(acac) was prepared according to standard procedures given in the literature [3]. The samples in the pellets form (diameter 10 mm; thickness 2–4 mm) were obtained by compressing the powder in a die under the pressure of 9.8×10^8 Pa. Silver paste was painted on both flat surfaces of the pellet as electrodes. The dielectric constant, dielectric loss and impedance were measured at different temperatures (293 to 343 K) and at various frequencies (50 to 500 kHz) using a Tesla BM 507 impedance meter.

3. Results and discussion

Figures 1a and 1b show the temperature dependence of the dielectric constant $\epsilon'(\nu)$ and the dielectric loss $\epsilon''(\nu)$ of K(acac), where ν is the frequency. As it can be seen from Fig. 1a, the dielectric constant shows a maximum at the critical temperature $T_c = 313$ K. The observed behaviour is similar to that obtained in

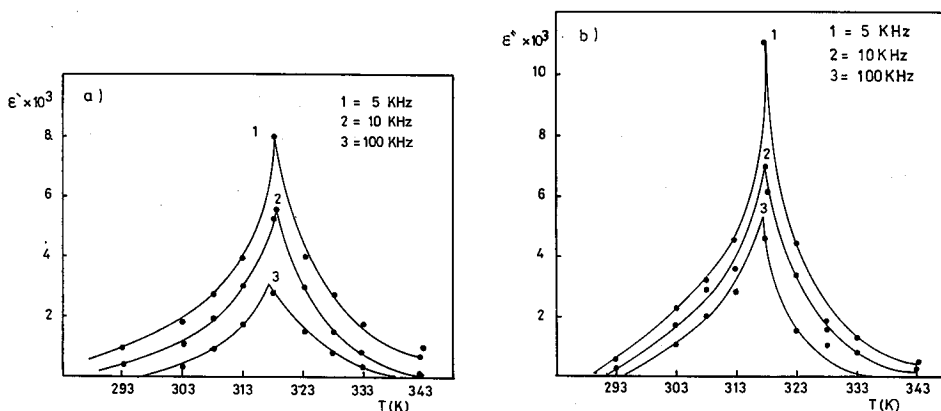


Fig. 1. (a) Dielectric constant as a function of temperature for K(acac) at different frequencies. (b) Dielectric loss as a function of temperature for K(acac) at different frequencies.

ferroelectric materials [4]. The Curie-Weiss constants evaluated from the slopes of the temperature dependence of $1/\epsilon'$ at 5 kHz were found to be $(2.6 \pm 0.1) \times 10^4$ K and $(2.0 \pm 0.1) \times 10^4$ K below and above T_c , respectively.

X-ray diffraction patterns below and above T_c were thus made on the K(acac) sample. The recorded charts of X-ray patterns are shown in Fig. 2. Ito's method [5] was used to index the powder X-ray diffraction patterns. It was found that the unheated K(acac) compound belongs to orthorhombic system whose unit cell has the following dimensions:

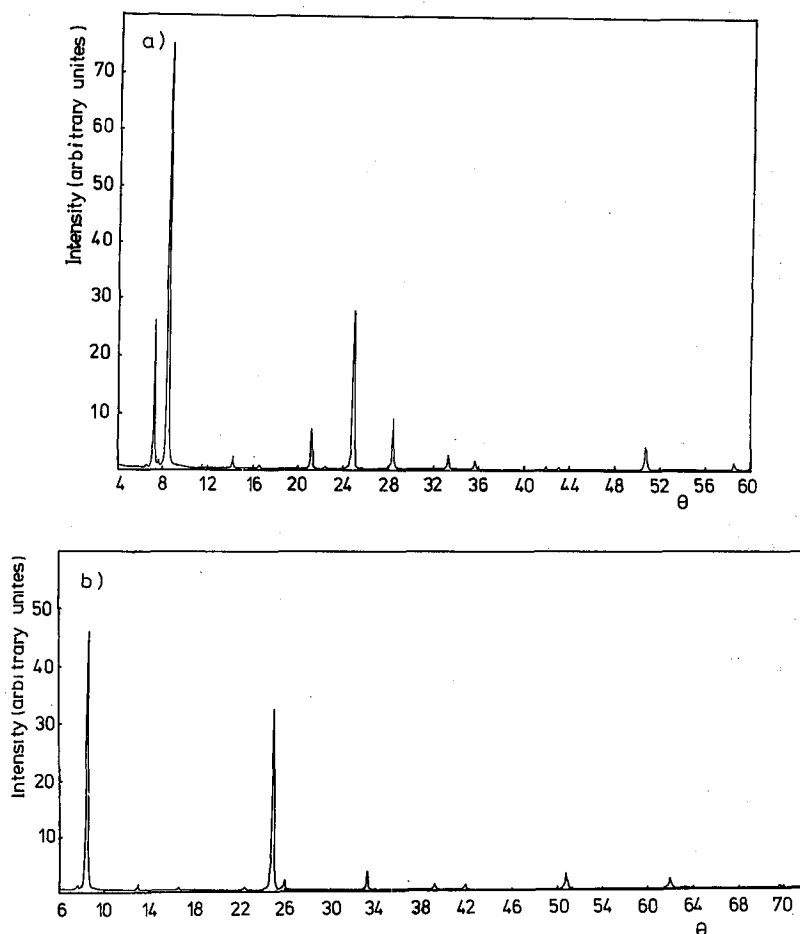


Fig. 2. X-ray diffraction pattern for K(acac): (a) below T_c ; (b) above T_c .

$$\begin{aligned}
 a &= 13.36 \text{ \AA}, & \alpha &= 90^\circ, \\
 b &= 12.60 \text{ \AA}, & \beta &= 90^\circ, \\
 c &= 11.62 \text{ \AA}, & \gamma &= 90^\circ.
 \end{aligned}$$

On the other hand, it was found that the heated compound (for $T > T_c$) belongs to triclinic system whose unit cell dimensions are

$$\begin{aligned}
 a &= 11.9 \text{ \AA}, & \alpha &= 108^\circ 52', \\
 b &= 11.2 \text{ \AA}, & \beta &= 89^\circ 12', \\
 c &= 9.36 \text{ \AA}, & \gamma &= 99^\circ 55'.
 \end{aligned}$$

Therefore, at the transition temperature T_c K(acac) transforms from orthorhombic to triclinic system.

The Cole-Cole diagrams $\epsilon''(\epsilon')$ in K(acac) are shown at several temperatures in Fig. 3. These diagrams have been used to determine the distribution parameter

α , the macroscopic relaxation time τ_0 , and the molecular relaxation time τ [6, 7]. Knowing α , one can determine τ_0 using the relation [6]

$$\frac{U}{V} = (\omega\tau_0)^{1-\alpha}, \tag{1}$$

where U is the distance on the Cole-Cole diagram between the static dielectric constant ϵ_0 and the experimental point, V is the distance between that point and the optical dielectric constant ϵ_∞ , and ω is the angular frequency, $2\pi\nu$. The symbols ϵ_0 , ϵ_∞ , α , U and V are shown in Fig. 3.

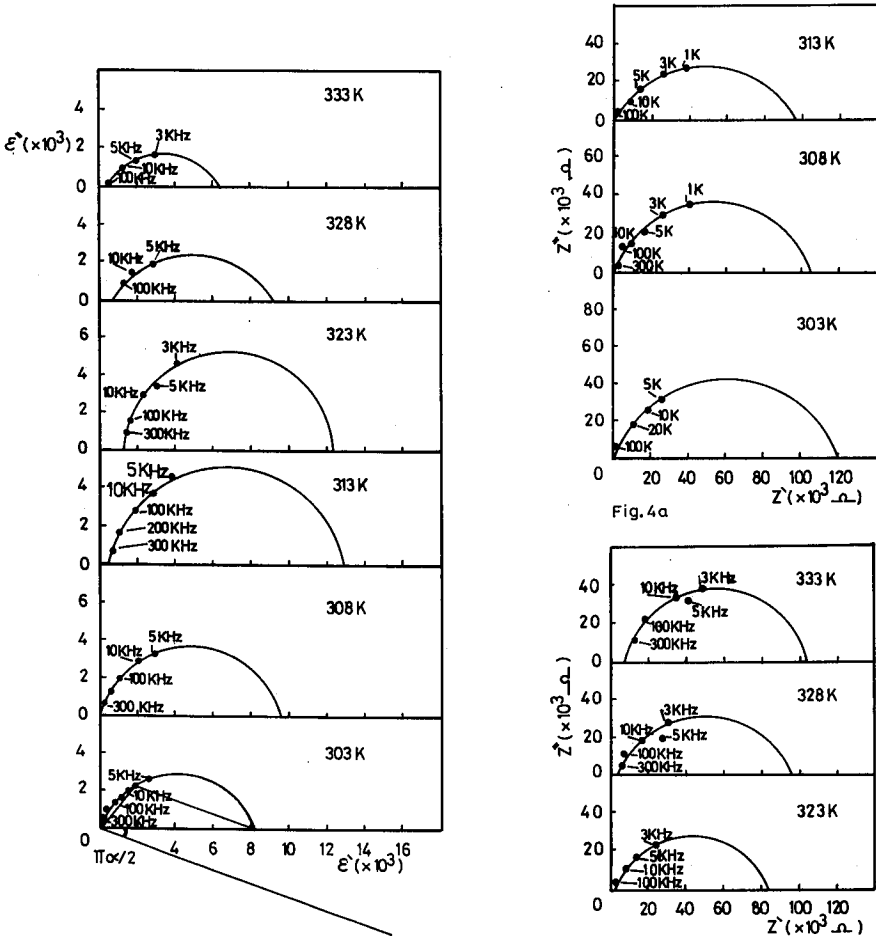


Fig. 3. The Cole-Cole diagram in K(acac) for a range of temperatures. The frequencies reported are in hertz.

Fig. 4. Complex impedance spectra of K(acac) for a range of temperatures: (a) below T_c ; (b) above T_c . The frequencies indicated are in hertz.

The molecular relaxation time τ could be evaluated from

$$\tau = \frac{2\varepsilon_0 + \varepsilon_\infty}{3\varepsilon_0} \tau_0. \quad (2)$$

The temperature dependence of τ is controlled by the following relation [8]:

$$\tau = A \exp^{-E_0/kT}, \quad (3)$$

where A is constant, k is Boltzmann's constant and E_0 is the activation energy for relaxation.

The calculated values of E_0 and A were found to be $E_0 = 0.08 \pm 0.01$ eV and $A = (4.2 \pm 0.2) \times 10^{-3}$ s below T_c and $E_0 = 0.30 \pm 0.01$ eV and $A = (8.1 \pm 0.2) \times 10^{-9}$ s above T_c , respectively.

The measured impedance $Z(\nu) = Z'(\nu) + iZ''(\nu)$ were plotted in the complex plane for various temperatures. Typical spectra related to the frequency ν of the applied sinusoidal voltage are shown in Fig. 4.

The frequency dependence of both Z' and Z'' permits separation of the sample resistance for the grain bulk R_b from the surface R_s [9]. The classical semicircular form shown in Fig. 4 leads to an equivalent circuit for K(acac) comprising R_b in series with parallel R_s - C_s combination; this leads to the established relations

$$Z' = R_b + R_s/[1 + (\omega C_s R_s)^2], \quad (4)$$

$$Z'' = i\omega C_s R_s^2/[1 + (\omega C_s R_s)^2]. \quad (5)$$

It is clear that Z' varies throughout the applied frequency and is equal to $(R_b + R_s)$ at zero frequency (DC) and only R_b at higher frequency. Therefore, the complex semicircle $Z''(Z')$ impedance diagram would reflect R_b at higher frequencies whereas contribution of R_s increases upon shifting to the zero frequency (DC). It can be seen from Fig. 4 that below T_c the intersection of the real axis with zero frequency extrapolation of the semicircle gives R_s , the surface resistance of the sample. The activation energy of the surface conduction was found to be 0.17 ± 0.01 eV. Therefore, it is believed that the conduction is of ionic character predominantly operating at the surface. Above T_c , the semicircle $Z''(Z')$ dependence would suggest conduction via ionic mechanism proceeding in the bulk material with contribution from the surface. The activation energies for the bulk and surface conduction were found to be 0.78 ± 0.01 eV and 0.17 ± 0.01 eV, respectively.

4. Conclusion

Dielectric measurements reported for K(acac) reveal the following items:

1. The anomalous behaviour in the dielectric properties of K(acac) is attributed to the structural phase transition from orthorhombic to triclinic system.
2. The molecular relaxation time τ , determined from the Cole-Cole diagrams, reveals its activated character.
3. Ionic conduction operating at the surface is exhibited below T_c , above which the conduction is via ionic mechanism proceeding in the bulk material with contribution from the surface.

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