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Impedance relaxation of KH_2PO_4 at high temperatures

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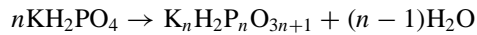
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Abstract. Measurements of complex ac impedance of KH_2PO_4 have been carried out. The dielectric constant showed a high-temperature anomaly around T_p (182 °C for the c axis and 187 °C for the a axis). An equivalent circuit model based on two parallel G – C circuits was adopted to describe the impedance relaxational behaviour observed below and above T_p . From this method we could estimate the relaxation times consisting of two components: the fast component due to proton migration and the slow component resulting from electrode–crystal interfacial polarization. The slow component relaxation time tends to increase markedly on crossing T_p , the possible origin of which is considered to be the partial decomposition of crystal on the surface of crystal.

1. Introduction

The low-temperature ferroelectric transition at -151 °C (T_c) in KH_2PO_4 crystal has been investigated for a long time by many researchers [1]. KH_2PO_4 is also known to undergo another high-temperature phase transition (HTPT) at around 180 ± 10 °C (T_p), which is not far from thermal decomposition. But T_p is scattered more widely than one would expect and there are considerable differences in the published reports concerning high-temperature behaviour. It has been reported that the phase change is indicated by an anomaly in the electrical conductivity curve [2], dielectric constant [3] and other quantities around 180 °C [4–12], or by an abrupt increase in the conductivity at 171 °C [13] or a dip in the conductivity around 150 °C [14]. In addition, there are reports which claim that there is no break below 180 °C [15] and which insist that the HTPT does exist by showing a knee in the conductivity at around 110 °C (T'_c) [16]. It has been established that protons are the main carriers of the current and in order to explain the electrical conductivity in the temperature region below and above T_p and the mechanism of HTPT, various proton transport models have been proposed [2, 13, 15, 17]. Blinc *et al.*, on the other hand, have suggested that the HTPT is associated with the onset of disordered hindered three-dimensional rotation of the H_2PO_4^- radicals around all three axes [4], although this interpretation has been questioned [18]. But, it is still inconclusive as to whether the conductivity below T_p is extrinsic or intrinsic. Moreover, the existence of the HTPT is still in controversy. Harris and Vella found a knee in the conductivity near 100 °C [17]. They pointed out that the knee temperature varies with crystal purity and that overheating and surface conduction effects are probably due to crystal decomposition involving the formation of H_2O molecules. An additional enthalpy above 100 °C was interpreted to be attributed to L defect (no hydrogen in the $\text{O}—\text{H}\cdots\text{O}$ bond) formation by incipient decomposition. Nicholson and Soest [18] pointed out from their NMR studies that the hindered rotation of H_2PO_4^- radicals and a HTPT might exist, but

the interpretation of the experimental evidence has been impeded by thermal decomposition. However, when KH_2PO_4 is heated, it tends to lose its water of constituents and various kinds of polymeric product have been identified by many investigations [19–22]. Direct heating of KH_2PO_4 above 180°C produces partial dimers [$\text{K}_2\text{H}_2\text{P}_2\text{O}_7$] and/or oligomers [$\text{K}_n\text{H}_2\text{P}_n\text{O}_{3n+1}$ ($n = 5\text{--}10$)], whereas long-chain higher polymers $\text{K}_n\text{H}_2\text{P}_n\text{O}_{3n+1}$ ($n \gg 1$) \cong $(\text{KPO}_3)_n$ are formed as a crust around the monomers [KH_2PO_4] by stepwise heating. Based upon these chemical analyses Lee proposed that the partial thermal decomposition set in around T_p , according to the equation:



and claimed that the term HTPT should be replaced by the *onset of partial polymerization at reaction sites on the surface of solids* [23]. Hence, the microscopic nature of the high-temperature phenomenon around T_p in KH_2PO_4 is still not completely understood.

In dealing with the hopping charge carrier and/or polymer-forming systems, it is often preferable to plot the complex impedance instead of the electrical conductivity or the imaginary dielectric constant. If upon heating KH_2PO_4 above T_p the decomposition begins to take place on the surface of crystals, the space charge due to the formation of a surface layer will be reflected on the impedance spectroscopy. The purpose of the present study is to obtain the complex *ac* impedance and to shed new light on the mechanism of the high-temperature behaviour of KH_2PO_4 .

2. Experimental details

Platelet specimens perpendicular to the *c* and *a* axes were cut and polished from a single crystal grown by the slow evaporation of an aqueous solution. Silver was evaporated in vacuum and used as an electrode. The complex *ac* impedance, $Z^*(\omega)$, was measured between 100 and 10 MHz by using an Impedance Analyzer (HP 4194A). The experiments were performed at temperatures from 30 to 190°C in free atmosphere, and the temperature of the sample was measured using a platinum–rhodium thermocouple. After prolonged heat treatment at high temperatures, KH_2PO_4 crystal tends to lose its transparency and become milky white and opaque due to the formation of microcracks [2, 3, 6, 10, 13, 17]. So the upper temperature limit was set at 190°C due to deterioration in specimen condition. The heating rate was $0.2^\circ\text{C min}^{-1}$. The temperature of the specimen was varied stepwise, and measurements were made after the temperature was stabilized to within $\pm 0.5^\circ\text{C}$.

3. Results and discussion

Figures 1(a) and (b) show the real (ϵ'_c) and imaginary (ϵ''_c) parts of the complex dielectric constant along the *c* axis. ϵ'_c shows a broad maximum around 160°C . On further heating above 160°C , ϵ'_c and ϵ''_c reveal a high-temperature anomaly near 182°C and then increase continuously and rapidly. Figures 2(a) and (b) show the real (ϵ'_a) and imaginary (ϵ''_a) parts of the complex dielectric constant along the *a* axis. ϵ'_a shows another broad maximum over the temperature range around $100\text{--}160^\circ\text{C}$, depending on the measuring frequencies. The high-temperature anomaly of ϵ'_a and ϵ''_a appears around 187°C . According to Nakamura, the value of ϵ'_c of KH_2PO_4 in the paraelectric phase increases remarkably with increasing defect densities and ϵ'_c shows an anomalous maximum depending on the defect densities [24]. It is therefore reasonable to regard the broad maxima of ϵ'_c and ϵ'_a over the temperature range around $100\text{--}160^\circ\text{C}$ in figures 1 and 2 as being associated with the relaxation of intrinsic and/or extrinsic defects, rather than a structural phase transition. Some differences in T_p in

the c and a axes may be due to the crystal quality, which, in turn, demonstrates indirectly the topochemical nature of the high-temperature phenomenon around T_p .

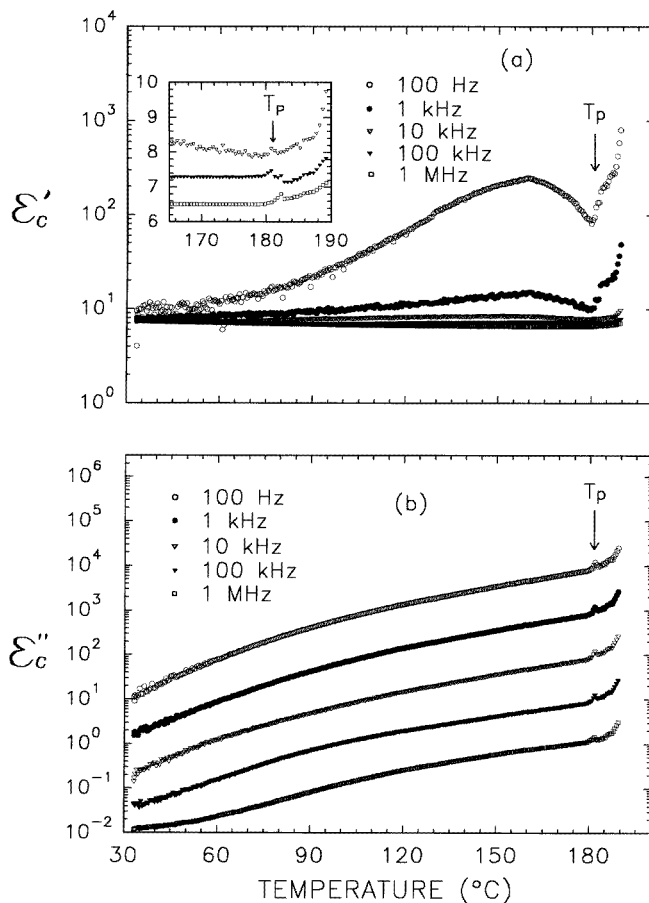


Figure 1. Temperature dependence of (a) ε'_c and (b) ε''_c of the complex dielectric constant in KH_2PO_4 at various frequencies. Inset: the region of interest on a larger scale.

Figures 3(a) and (b) show the real (Z'_c) and imaginary (Z''_c) parts of the complex impedance along the c axis. It is observed that, above as well as below T_p , the Z'_c in the high-frequency region decreases slowly from 10^4 to 10^6 Hz, depending on the temperature and then continuously decreases with an increasing frequency of approximately $1/\omega$ near the relaxation frequency. The relaxational peak frequency of Z''_c moves to a high-frequency region with increasing temperature. Moreover, another relaxational behaviour appears partially in the low-frequency region ($\leq 10^3$ Hz) below and above T_p . Similar relaxational behaviour is observed for the real (Z'_a) and imaginary (Z''_a) parts of the complex impedance along the a axis, as shown in figures 4(a) and (b). The tendency of Z''_c and Z''_a reveals that the absolute value of the high-frequency slope is in fact very close to unity and seems to be independent of the measuring temperature, while the low-frequency slope has a value lower than unity and is strongly temperature dependent. The two distinct slopes and their difference in temperature dependence suggest that two dispersion mechanisms should be involved. Therefore, we assume that in KH_2PO_4 there exist two different regions, each region is

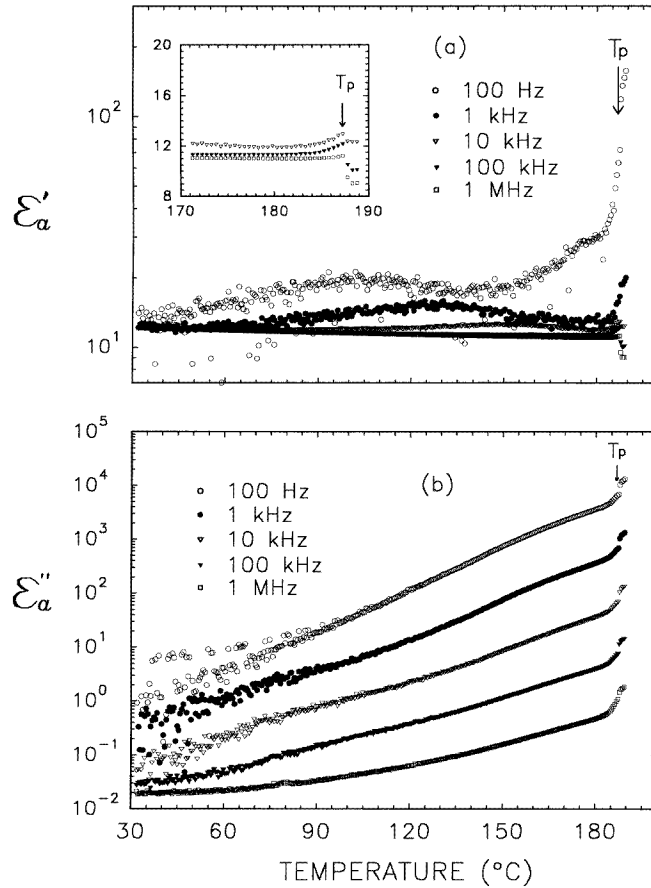


Figure 2. Temperature dependence of (a) ϵ'_a and (b) ϵ''_a of the complex dielectric constant in KH_2PO_4 at various frequencies. Inset: the region of interest on a larger scale.

characterized by a relatively conducting volume of the sample and a highly capacitive but weakly conducting barrier. The descriptions ‘volume’ (high frequency) and ‘barrier’ (low frequency) denote a physically plausible assignment of the two regions if $C_1 \ll C_2$ and $G_1 \gg G_2$, in which case the two regions may be presumed to be physically connected in series [25]; see the equivalent circuit shown in figure 5. The complex impedance may be written in the superposition of the two Cole–Cole expression:

$$Z^*(\omega) = \frac{1/G_1}{1 + (i\omega\tau_1)^{1-m}} + \frac{1/G_2}{1 + (i\omega\tau_2)^{1-n}} \quad (1)$$

$$\tau_1 = 1/\omega_{p1} = C_1/G_1 \quad \tau_2 = 1/\omega_{p2} = C_2/G_2$$

where ω_{p1} and ω_{p2} are the first and second characteristic angular frequencies, corresponding to the fast (in higher frequency region) and slow (in lower frequency region) relaxational mechanisms, respectively. The full curves in figures 3 and 4 are the theoretical curves obtained by using equation (1). Only the data relative to the imaginary part were used in the fitting. The six parameters obtained, G_1 , G_2 , τ_1 , τ_2 , m and n were then introduced into the real part of the formula to check whether the calculated values are also in agreement with

the measured values of Z'_c and Z'_a . The agreement between experimental and calculated values for both real and imaginary parts of the impedance confirms that the model proposed here is pertinent for the description of the high-temperature behaviour of KH_2PO_4 .

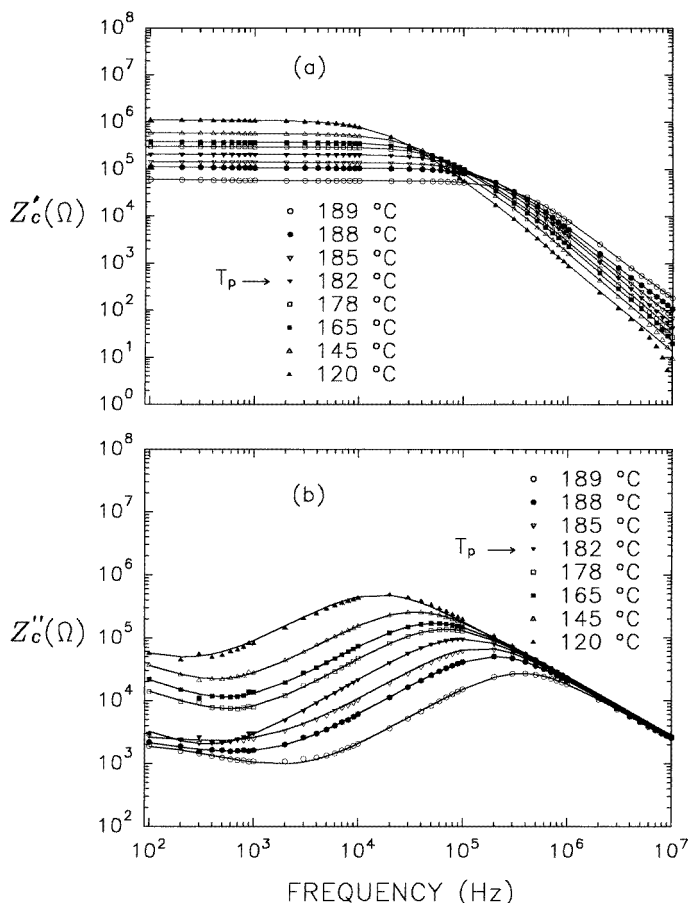


Figure 3. Impedance spectra of (a) Z'_c and (b) Z''_c of KH_2PO_4 . The solid line represents a fit to equation (1).

In the temperature range 20–190 °C, the temperature dependences of exponents m and n are shown in figure 6. The parameters m and n take values over the entire range $0 \leq m, n \leq 1$ and may be functions of the temperature. The fitting of equation (1) in the case of the c axis always leads to a value of m close to about 0.95 and weakly dependent on the temperature, but shows a very strong variation in the value of the exponent n . Otherwise, the exponents m and n increase toward unity near the high-temperature anomaly, but we have not found the limiting value for $m, n = 1$ measuring temperature range. The behaviours $m(T), n(T)$ in the case of the a axis are similar to the case for the c axis.

The loss peak frequencies, ω_{p1} and ω_{p2} , are obtained by fitting the imaginary impedance data to equation (1) and the variation of relaxation times of $\tau_1 = 1/\omega_{p1}$ and $\tau_2 = 1/\omega_{p2}$ as a function of reciprocal temperature are shown in figures 7(a) and (b). With the exception of the anomalous behaviour in the vicinity of T_p , both τ_1 and τ_2 decrease upon heating to around 170 °C. These results then can be described by an Arrhenius behaviour as given

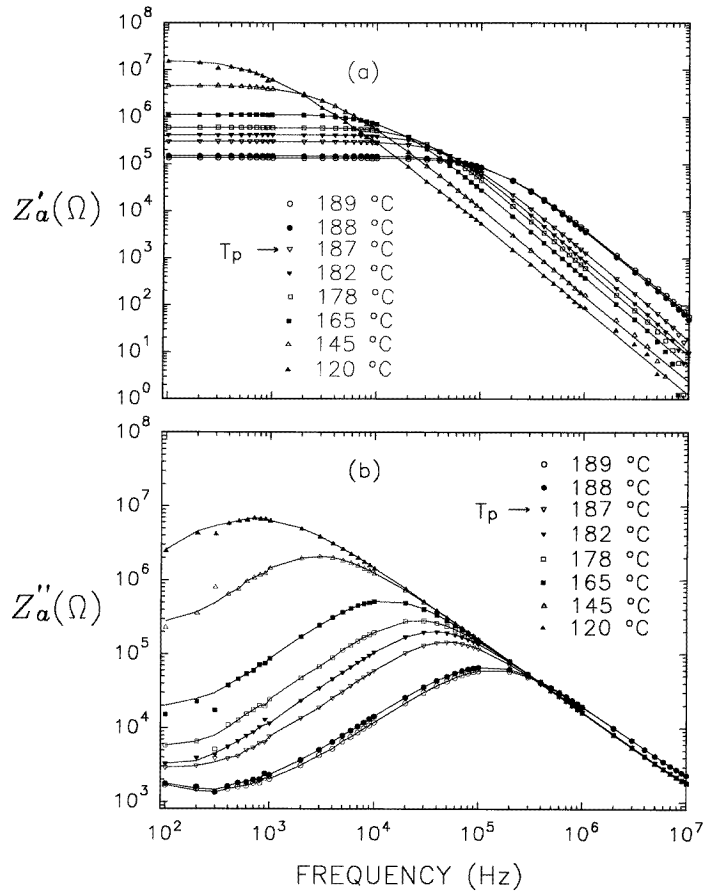


Figure 4. Impedance spectra of (a) Z'_a and (b) Z''_a of KH_2PO_4 . The solid line represents a fit to equation (1).

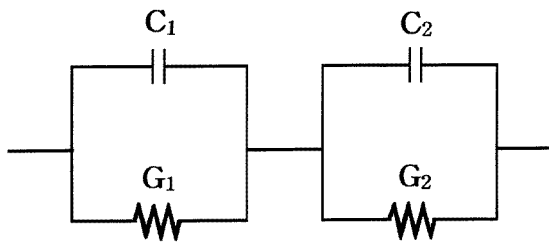


Figure 5. Equivalent circuit proposed for description of high-temperature behaviour of KH_2PO_4 .

below

$$\omega_p(T) = \frac{1}{\tau(T)} = \frac{1}{\tau_0} \exp\left(-\frac{\Phi}{k_b T}\right) \quad (2)$$

with the natural relaxation time τ_0 and the activation energy Φ . The activation energies estimated are 0.21 eV for τ_{c1} , 0.11 eV for τ_{c2} , 0.41 eV for τ_{a1} , and 0.24 eV for τ_{a2} below

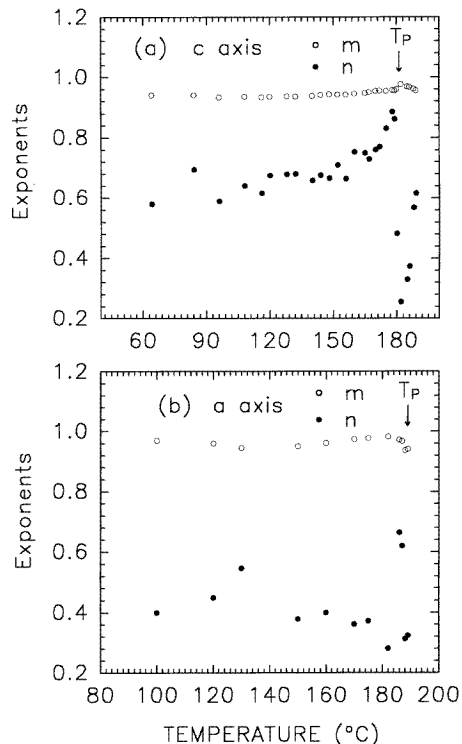


Figure 6. Temperature dependence of the exponents m and n in KH_2PO_4 : (a) c axis, (b) a axis.

T_p . These values are roughly in accord with those reported in conductivity measurements [2, 13, 15, 17]. So, impedance relaxation can be interpreted as consisting of two parts: a fast component in the higher frequency region due to the bulk conductivity, and a slow component in the lower frequency region characterized due to a surface layer or electrode/crystal interfacial polarization. A remarkable increase in the slow component of the relaxation time of τ_{c2} and τ_{a2} , i.e. a slowing-down around T_p was obtained, indicating the progressive formation of large clusters on approaching T_p . This may be associated macroscopically with the nucleation and growth of polymerized products [$\text{K}_n\text{H}_2\text{P}_n\text{O}_{3n+1}$] and may be caused microscopically by the partial break-up of hydrogen bonds, the rotation of PO_4 and the formation of H_2O molecules on or near the crystal surface.

4. Conclusions

In summary, the high-temperature phenomenon observed on heating above room temperature in KH_2PO_4 can be explained as follows. The dielectric constant shows a broad maximum over the temperature range 100–160 °C and a high-temperature anomaly near T_p : 182 °C for the c axis and 187 °C for the a axis. The appearance of a broad maximum seems to be associated with the relaxation of proton defects produced by residual impurities or thermal excitation, rather than structural phase transition. In the high-temperature dielectric anomaly, there is a difference in value of T_p between the c and a axes. The reason may be due to the onset of polymerization at different temperatures in the specimens with different

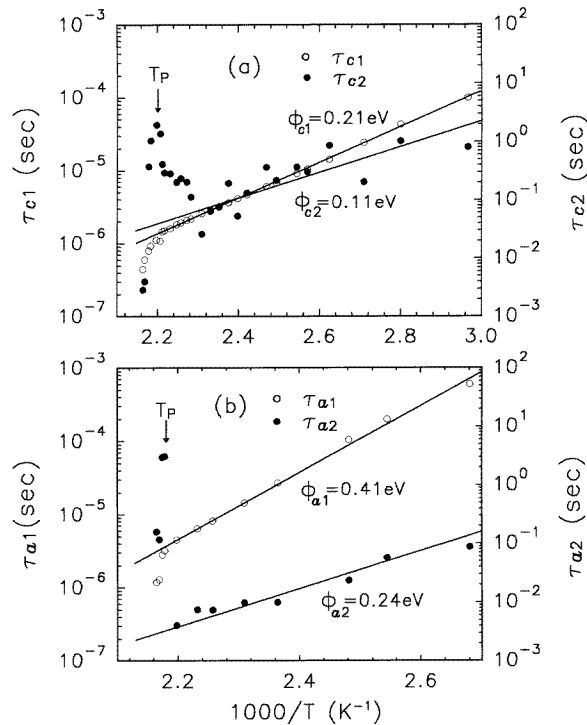
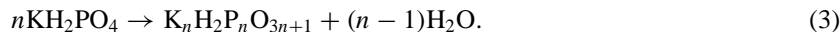


Figure 7. Temperature dependence of the relaxation time τ_1 and τ_2 on $1/T$ in KH_2PO_4 : (a) c axis, (b) a axis.

defect concentration inside the bulk and/or on the surface. The impedance behaviour of KH_2PO_4 has been described by using an equivalent circuit model based on two parallel G - C circuits. A good fitting between experimental data and theoretical calculations was obtained. The results show evidence for two relaxation mechanisms: a fast component is attributed to proton defect migration, while a slow component is associated with the electrode interfacial polarization. The slow component relaxation time tends to increase considerably around T_p , suggesting the formation of large clusters. This extraction supports that around T_p thermal condensation commences on the surface, according to the equation



Acknowledgments

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