

Dielectric Properties and Conductivity of KHCO_3

F. SALMAN, S. ABOELHSSAN, E. SHEHA, M. K. ELMANSY

Physics Department, Faculty of Science at Banha-EGYPT

Received 01.04.2003

Abstract

KHCO_3 compound was characterized in three principle realms: for its dielectric properties as a function of temperature and frequency in the ranges 300–370 K and 50 Hz to 1 MHz, respectively; bulk conductivity as a function of temperature, via impedance technique; and relaxation time as function of temperature. Variations of the bulk conductivity and relaxation time with temperature have been found to yield two segments, with two different activation energies. The activation energy for the two segments due to bulk conductivity have been found as 1.96 eV and 1.85 eV, while the activation energy due to relaxation have been found to be 1.85 eV and 1.83 eV. The phase transition which was detected by DSC at $T = 322$ K has been verified by the dielectric and conductivity measurements.

1. Introduction

Potassium hydrogen carbonate is a member of the hydrogen carbonate series of general molecular formula $M\text{HCO}_3$, where M is a monovalent element or group ($M^+ = \text{Na}^+, \text{K}^+, \text{Cs}^+, \dots$ and/or NH_4^+). This series of bicarbonate salts is a rather interesting class of compounds, for they illustrate the effect of crystal packing on the internal structure of covalently bonded molecules [1]. Potassium hydrogen carbonate KHCO_3 is one such interesting member of this series. Its hydrogen bonding system is arranged in the form of $(\text{HCO}_3)_2$ dimers instead of (HCO_3) chains [2, 3]. The dynamical transfer of hydrogen atoms in such a hydrogen bond dimer attracts wide interest. The transfer is simulated, for an example, by the motion of light atoms in asymmetric double minimum potential [4, 5]. A detailed neutron diffraction study done by Thomas et al. [6] has revealed two sites for the hydrogen atom. The result suggests that there is disorder of the (HCO_3) dimers in the room temperature phase.

KHCO_3 is also known as a proton conductor, which shows anomalous dielectric, thermal, and electric conduction properties [7]. By means of ultrasonic velocity measurement, Haussuhl [8] reported that KHCO_3 undergoes a phase transition at 318 K.

Recently, potassium hydrogen carbonate (KHCO_3) has been shown to exhibit an ferroelastic phase transition at $T_N = 318$ K [6]. The transition is of an order-disorder type. The space group of the crystal is monoclinic $C/2m$ in the high temperature disordered phase, and monoclinic but $P2_1/a$ in the low temperature phase [9]. A dielectric anomaly at 240 K from KHCO_3 crystals is observed [10]. This anomaly is described in terms of the motions of protons in the hydrogen-bonded dimer structure of KHCO_3 .

The aim of this work is to detect the phase transition at 322 K in KHCO_3 by characterizing the dielectric properties, conductivity using impedance method and thermal analysis.

2. Experimental Work

The material (KHCO_3) used in the present work was an ADWIC grade chemical. The salt was further recrystallized from doubly distilled water. After drying, the finely grounded powder was compressed under 300 kg/cm^2 pressure into discs of 1 cm diameter and 1.5 mm thickness. A sample holder with brass electrodes was specially designed to carry out the electrical measurements. Good contact was attained by painting both faces of the sample with air-drying conducting silver paste. Measurements of the sample temperature were performed using a Fluke 51 K/J digital thermometer attached to the sample. During the measurements, the temperature was changed at a rate lower than 2 K/min. Dielectric and electrical impedance measurements were measured in the frequency range 50 Hz to 1 MHz and temperature range 300–370 K with a Hioki 3532 LCR HiTESTER meter controlled via an interface to a personal computer. The double probe method without guide electrode is employed. The samples were characterized by X-ray powder diffraction. X-ray examination indicates that the KHCO_3 crystal is monoclinic, with space group P21/a at room temperature ($a = 15.1803 \text{ \AA}$, $b = 5.6302 \text{ \AA}$, $c = 3.7219 \text{ \AA}$, $\beta = 104.771^\circ$). The DSC technique was used to detect the phase transitions using a calibrated Setaram DSC 131 differential scanning calorimeter.

3. Results and Discussion

The temperature dependence of the dielectric constant $\varepsilon'(T)$ and dielectric loss $\varepsilon''(T)$ for KHCO_3 compound in the temperature range 300–370 K at various constant frequencies are shown in Figs. 1a and 1b, respectively. The dielectric constant $\varepsilon'(T)$ exhibits a sharp peak at about 322 K. The height of the peak was found to decrease with increasing frequency. The temperature at which $\varepsilon'(T)$ is maximum was found to be independent of frequency. Similar behavior is exhibited by $\varepsilon''(T)$.

According to Haussul [8], the orientation of the $(\text{HCO}_3)_2$ dimers plays an important role in the phase transition. Thus one can make the following interpretation of Figure 1. At temperatures up to where the transition begins, the dimers cannot, in general, orient themselves. As the ambient temperature of the sample increases, the dimer orientations are then facilitated to align along the direction of the applied electric field, leading to an increase in the dielectric constant. As the temperature increases beyond the peak in the dielectric constant, there is greater thermal agitation of the dimers and reduction in the degree of order. Thus the value of ε' passes maximum at 322 K. Further increase of temperature in this region leads to a decrease in ε' .

Figures 2a and 2b show the frequency dependence of the dielectric constant (via $\log \varepsilon'$ vs. $\log f$) and dielectric loss (via $\log \varepsilon''$ vs. $\log f$), respectively, at various temperatures.

The obtained dielectric data can be explained by the following model. At low frequencies the dipoles can easily switch alignment with the changing field. As the frequency increases the dipoles are less able to rotate and maintain phase with the field; thus they reduce their contribution to the polarization field, and hence the observed reduction in dielectric constant ε' and dielectric loss ε'' . The larger values of dielectric constant and loss exhibited by KHCO_3 at low frequencies may also be ascribed to space-charge polarization due to crystalline defects [11].

The complex impedance method [12] was used to determine the bulk conductivity and relaxation time. The impedance $Z^* = Z' - iZ''$ measured in the frequency range 50 Hz–1 MHz was analyzed on the complex plane over the temperature range 300–370 K. Figure 3a and 3b shows the complex impedance Z' vs. Z'' at various temperatures. One may notice that $Z'(Z'')$ dependence is a locus of semicircles passing through the origin. The semicircles are equivalent to a parallel combination of bulk resistance R_b and geometrical capacitance C_g of the sample. The bulk resistance was estimated as the diameter of the semicircle. The diameter has been found to decrease with increasing temperature below the transition point; and above the transition point, the diameter increases with the temperature.

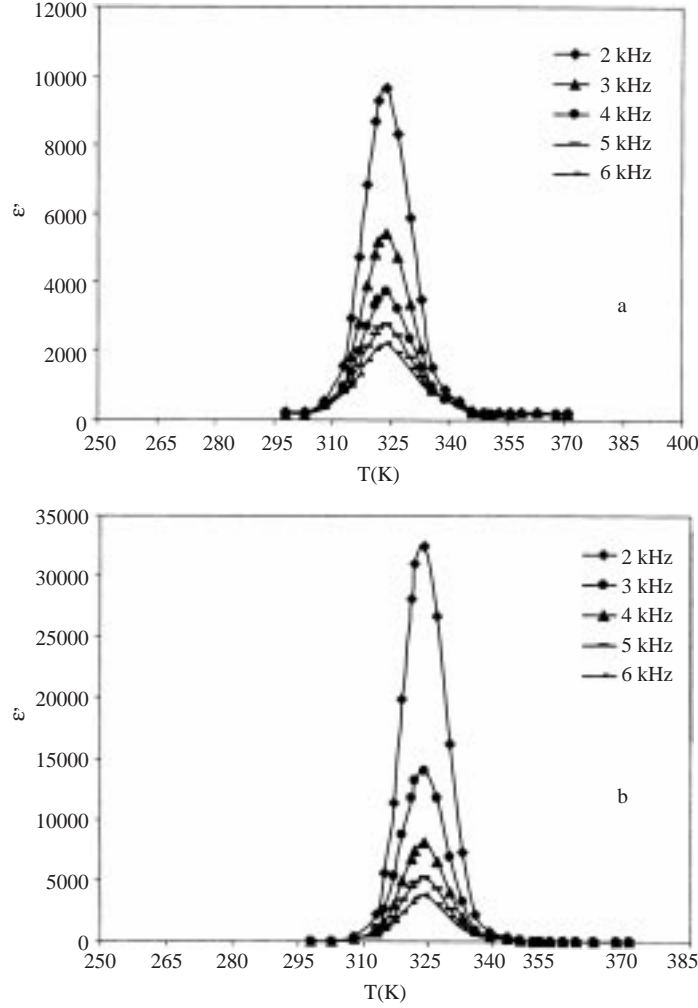


Figure 1. Temperature dependence of dielectric constant and loss for KHCO_3 at different frequencies.

The bulk conductivity σ_b of the sample was estimated from the resistance R_b . In Figure 4a the temperature dependence of the conductivity σ_b is shown over the temperature range, extended from room temperature up to 373 K, including the phase transition at about 322 K. Over this range, a linear relationship exists between $\ln\sigma$ and T^{-1} in two segments, according to the well-known relationship

$$\sigma = \sigma_0 e^{\pm E_a/kT},$$

where E_a is the activation energy and σ_0 is a pre-exponent that encompasses several constants, including the vibrational frequency of the potentially-mobile charge carriers. Plotting $\ln\sigma$ and T^{-1} , as is done in Figure 4a, one can calculate the activation energy associated with each segment. The calculated values are: $E_1 = 1.96$ eV, $E_2 = 1.85$ eV and $\Delta E = 0.11$ eV. The change in the values of the activation energy is taken as an evidence of the existence of a phase transition. It is interesting to note that the two straight lines intersect at 322 K, the value identified as the transition temperature.

In the case of the complex impedance, the relaxation time of the process can be calculated from the relation [13]:

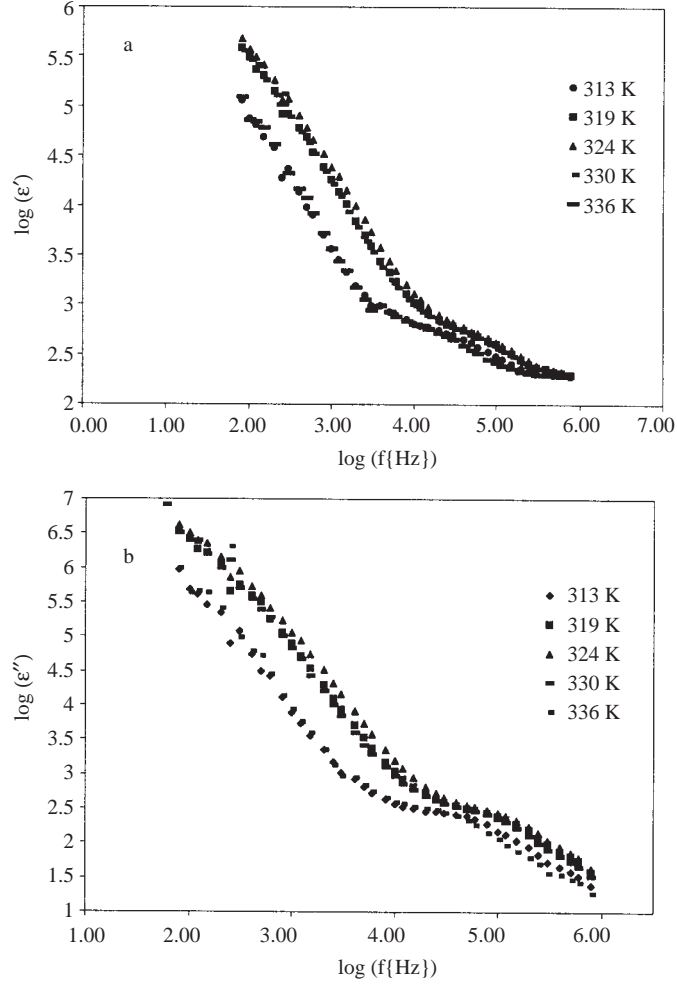


Figure 2. Frequency dependence of dielectric constant and loss for KHCO₃ at different temperatures.

$$\frac{v}{u} = (\omega\tau)^{1-h}$$

where v denotes the distance on the impedance plot between (O, R) and an experimental point, u is the distance between the experimental point and (0, 0) and $h = 2\alpha/\pi$, where α is the depressed angle from the z' -axis.

Figure 4b shows the variation of the relaxation time τ versus ambient temperature in the temperature range 298–370 K, in the form of a $\ln \tau$ vs. inverse temperature. As one can observe from the graph, the relaxation time decreases with increasing ambient temperature, to a point corresponding to a minimum relaxation time at a maximum temperature of $T \sim 322$ K. Above this temperature, the relaxation time can be observed to increase with a character very similar to the decrease.

The variation of the relaxation time on both sides of the transition temperature was found to obey the Arrhenius relation [14]

$$\tau = \tau_0 e^{\pm \Delta E_r / kT}$$

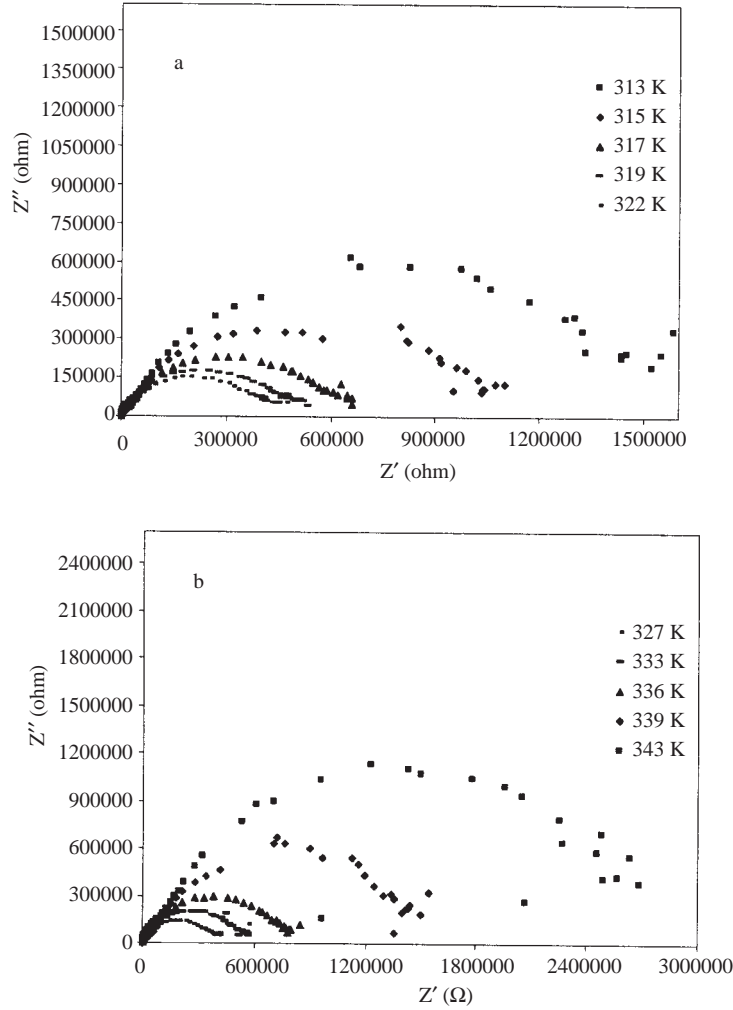


Figure 3. Complex Cole-Cole plot of impedance for KHCO_3 at various temperatures. (a) before phase transition; (b) after phase transition.

where ΔE_r is the activation energy of relaxation and τ_0 is a factor which is the inverse of the dipole (or charge) oscillation frequency in its potential well. The variation of $\ln\tau$ against $1/T$ yields two arms with two different slopes at the temperature ranges 298–322 and 322–370 K (see Fig. 4b). The activation energy of relaxation associated with each slope in the two ranges of temperature has been calculated by means of the least squares method. They have been found as 1.85 eV and 1.83 eV for the two temperature ranges, respectively.

The phase transition at about 322 K, detected by dielectric and electric measurements (Figures 1 and 4), was verified by measuring via differential scanning calorimetry (DSC) at a heating rate of 8 K/min. The DSC scan is shown in Figure 5, where one can observe an endothermic peak at around 320 K. This peak can be related to the phase transition mentioned above.

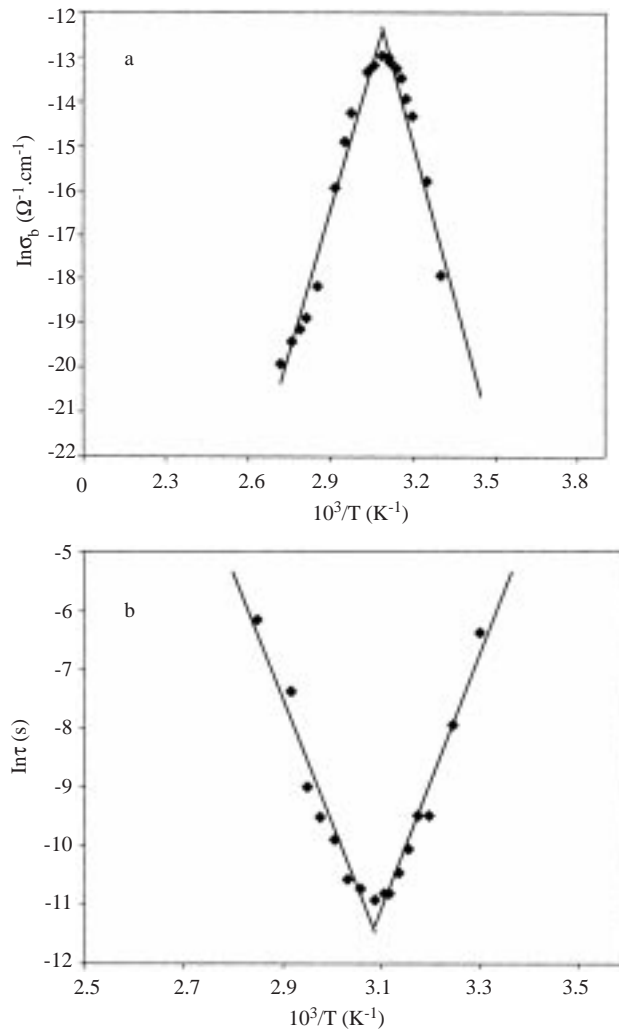


Figure 4. Temperature dependence of conductivity and relaxation time for KHCO_3 .

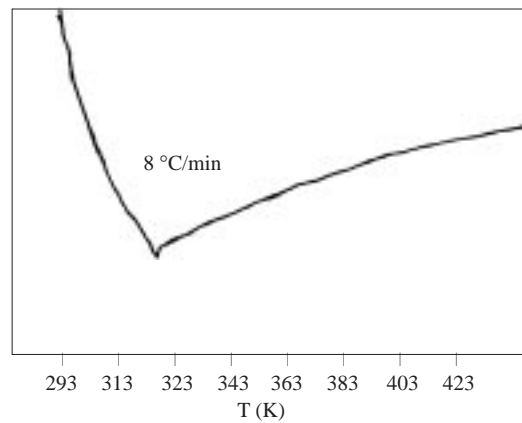


Figure 5. Degree of difference scanning calorimetry of KHCO_3 between 300 and 400 K.

4. Conclusion

KHCO₃ compound has been observed from dielectric and conductivity measurements to have a transition at 322 K, an observation that is confirmed by differential scanning calorimetry. The anomalous dielectric results may be explained by the disordering effects of dipoles originating from (HCO₃) dimmers.

References

- [1] R.L. Sass and R.F. Scheuerman, *Acta cryst.*, **15**, (1962), 77.
- [2] I. Nitta, Y. Tomile and C.H. Koo, *Acta cryst.*, **5**, (1952), 292.
- [3] J.O. Thomas, R. Tellgren and I. Olovsson, *Acta cryst.*, **30**, (1974), 1155.
- [4] R. Meyer and R.R. Ernst, *J. Chem. Phys.*, **86**, (1987), 784.
- [5] P. Postorino, *J. Chem. Phys.*, **94**, (1991), 4411.
- [6] G. Eckol and H. Grimm, *Physica B*, **180**, (1992), 336.
- [7] M.M. Abdel-Kader, M. Fadly, M. Abu Taleb, K. Eldehamy and A.I. Ali, *Phys. Stat. Sol.*, **142**, (1994), 69.
- [8] S. Haussuhl, *Solid State Commun.*, **17**, (1986), 643.
- [9] S. Kashida and T. Yagi, *J. Korean Phys. Soc.*, **32**, (1998), 5176.
- [10] A.I. Ali, B. Kim and I. Yu, *J. Korean Physical Soc.*, **35**, (1999), 1419.
- [11] K.V. Rao and A. Smakula, *J. Appl. Phys.*, **36**, (1965), 2031.
- [12] J.E. Bauerle, *J. Phys. Chem. Solids*, **30**, (1969), 2657.
- [13] K.K. Srivastava, A. Kumar, O.S. Panwar and K.N. Lakshminarayan, *Journal of Non-Crystalline Solids*, **33**, (1979) 205.
- [14] V.B. Kapustlanik. *Phys. Stat. Sol. (a)*, **168**, (1998), 109.