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D.C. ELECTRICAL CONDUCTIVITY AND DIELECTRIC CONSTANT MEASUREMENTS ON CRYSTALLINE $K_2CO_3 \cdot 1.5\ H_2O$

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ABSTRACT

The d.c. electrical conductivity and dielectric constant at 100 kHz of a $K_2CO_3 \cdot 1.5\ H_2O$ crystal grown at 40 ± 1°C have been measured in the temperature range 30–620°C. It has been observed that the conductivity shows two peaks at 190 and 230°C. It also shows changes in slope at 430 and 600°C, during heating. During cooling, the conductivity shows changes in slope at 590, 420 and 260°C. The dielectric constant measurement shows two peaks at 190 and 215°C and some changes at 420 and 600°C. The peaks in electrical conductivity and dielectric constant correspond to the dehydration process. Changes of slopes at ~ 430 and ~ 600°C correspond to phase transition and extrinsic to intrinsic transition respectively. During cooling, the presence of an intermediate structure between 420 and 260°C is indicated. The peaks observed in the conductivity and dielectric constant measurements at dehydration temperatures have been explained on the basis of the release of water molecules during dehydration and subsequent dissociation of a fraction of these released water molecules into H^+ and OH^- ions. Availability of these charged particles increases the conductivity whereas the formation of space charge increases the dielectric constant.

INTRODUCTION

Several workers have studied structural changes in potassium carbonate. Huttner and Tamman [1] and Amodori [2] reported a thermal transformation at 410°C. From a DTA study of this salt under an air atmosphere Makarov and Shulgina [3] reported transitions at 250, 428 and 620°C. Jaffray and Martin [4] characterized only two transition points, one at 410° and the other at 465°C. Reismann [5] studied the influence of the nature of the surrounding atmosphere on the transition points and concluded from the DTA study that although K_2CO_3 shows transitions at 422, 367 and 253°C under an air atmosphere, under a CO_2 atmosphere it shows only one transition at 422°C. From DTA, X-ray and DSC studies, Schneider and Levin [6] showed that there is only one polymorphic transition at 416°C. In

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air, however, they found small endotherms at 100, 226, 416 and 632°C. Although Jaffray and Martin [4] have reported that there is no appreciable modification of the crystalline network between room temperature and 500°C, van Aalst et al. [7] report a reduction in symmetry of the high temperature hexagonal phase at about 422°C. At this temperature it becomes monoclinic. This monoclinic structure is not identical to the room temperature monoclinic structure. These authors have determined an intermediate structure from single crystal X-ray photographs at 310°C and found that between the monoclinic phase at room temperature and the hexagonal phase above 420°C, there exists an intermediate structure. From their X-ray study, Becht and Struikmans [8] found that a room temperature structure is formed at 250°C. From a study of transition points by electrical conductivity measurements on pellets of K_2CO_3, Cerisier and Roux [9] showed that K_2CO_3 shows only one transition at 430°C under CO_2 as well as air atmospheres. Very little information is available on the physical properties of hydrated K_2CO_3. The main reason for this neglect is probably that hydrated K_2CO_3 releases its water of crystallization during heating. This released water creates a major problem of non-repeatability of the results around the dehydration temperature, when the same crystal is used for studying several physical properties. In most of the studies, therefore, dried K_2CO_3 is used. Thus the difference, if any, in the physical properties of the crystal with and without water of crystallization is not known. The present paper describes d.c. electrical conductivity and dielectric constant measurements on a $K_2CO_3 \cdot 1.5\ H_2O$ crystal grown from the aqueous solution at 40°C.

EXPERIMENTAL

Growth of crystals

$K_2CO_3 \cdot 1.5\ H_2O$ crystals were grown by slow evaporation of its saturated solution maintained at 40 ± 1°C.

Electrical conductivity and dielectric constant measurements

The d.c. electrical conductivity of the crystal was measured by a current–voltage method in the temperature range 30–620°C. A 10 V d.c. regulated power supply was constructed and the current through the sample was measured by a Philips electronic multimeter type PM 2403. The multi-range meter can read current from 0.01 μA to 1A. The dielectric constant was measured by a VEL direct reading LC meter type VLC 2 at 100 kHz in the same temperature range. The heating rate for both the measurements was 5°C min^{-1}.

RESULTS AND DISCUSSION

The variation of log σT vs. $1000/T$ for a fresh crystal of $K_2CO_3 \cdot 1.5\ H_2O$ grown at 40°C is shown in Fig. 1. It is seen from the figure that, during heating the conductivity rises and falls sharply at 190 and 230°C. The conductivity starts rising again from 240°C. It is also seen from Fig. 1 that, on heating further, the conductivity shows a sharp increase at 430°C and a change of slope at 600°C. Between 500 and 600°C, log σT vs. $1000/T$ shows a non-linear variation. On cooling the conductivity curve again shows changes in slope at 590, 420 and 260°C. The peaks in the conductivity observed during heating at 190 and 230°C are completely missing during cooling.

Dynamic thermogravimetry (TG) and differential thermogravimetry (DTG) measurements [10] show that the $K_2CO_3 \cdot 1.5\ H_2O$ crystal dehydrates

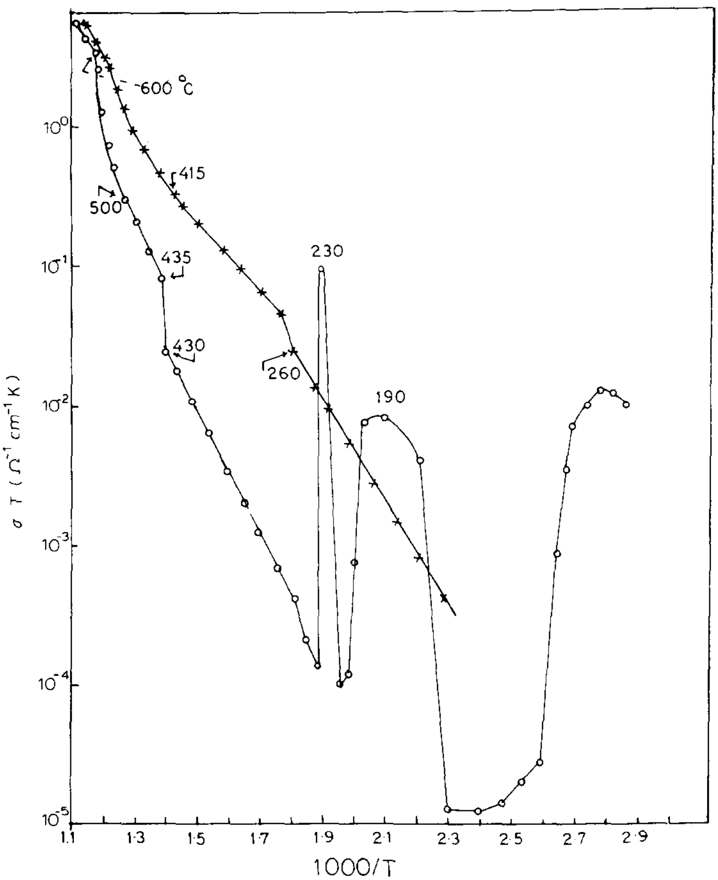

Fig. 1. Variation of d.c. electrical conductivity of $K_2CO_3 \cdot 1.5\ H_2O$ with temperature. O, Heating; ×, cooling.

in steps of 0.5 mole and 1 mole at 235 and 275°C. The peaks in the log σT vs. $1000/T$ curve at 190 and 230°C, which are lower than the dehydration temperatures, should therefore correspond to the dehydration process. The fast rise and fall in the conductivity of the crystal during heating indicate that free charge carriers are available for conduction. Kher et al. [11,12], while studying the electrical behaviour of $CuSO_4 \cdot 5\ H_2O$ and $NiSO_4 \cdot 6\ H_2O$ crystals, have shown that electrical conductivity and dehydration steps are intimately linked and conductivity changes at the corresponding dehydration temperatures are due to dissociation of a small fraction of water molecules that are detached from the structure into H^+ and OH^- ions. In the study of the $Na_2CO_3 \cdot H_2O$ crystal, we also have observed this effect [13]. Thus, in the case of $K_2CO_3 \cdot 1.5\ H_2O$, as dehydration starts the water molecule gets detached from the structure. It is assumed that the fraction of detached water molecules dissociate into H^+ and OH^- ions and cause an increase in conductivity. All the water molecules released and dissociated are not able to come out of the crystal immediately and many of them remain trapped in the interstitial space. The dissociated and trapped H^+ and OH^- ions are made mobile by the applied field contributing to the enhanced increase in conductivity of the crystal. As the temperature crosses the dehydration region the number of trapped ions increases at a high rate as they are driven by the applied field and collected by the respective electrodes, while the trapped water molecule can come out relatively slowly by a diffusion process. Hence, the conductivity peaks occur earlier than the corresponding DTG peaks.

Following the method suggested by Kher et al. [11,12] the dissociation energy was calculated. It was found that the dissociation energy of H_2O in the $K_2CO_3 \cdot 1.5\ H_2O$ crystal for the two dehydration steps are 0.265 eV and 0.308 eV, respectively. This energy of dissociation is less than that in free water. The decrease in the dissociation energy of an H_2O molecule inside the $K_2CO_3 \cdot 1.5\ H_2O$ crystal may be due to the pulling of the OH^- ion by the potassium ion in one direction and the H^+ ion by the CO_3^{2-} ion in the opposite direction.

All the workers unanimously agree over the presence of a phase transformation at ~ 420°C, but there are reports of transitions at other temperatures. In K_2CO_3, the high temperature hexagonal α-phase, belonging to the space group $P6_3/mmc$, undergoes a transition at 420°C to the monoclinic β-phase, belonging to space group C2/C. From an X-ray study, van Aalst et al. [7] reported that after the 422°C transition, the monoclinic structure is not identical to that of the room temperature monoclinic structure. The intermediate structure was determined by these authors. From an X-ray study, Becht and Struikman [8] found that the room temperature γ-phase monoclinic P2/C structure is formed at 250°C. The change in slope of the log σT vs. $1000/T$ curve at 430°C in the present study is indicative of a γ to β-phase transition during heating. While cooling, this transition occurs at

420°C indicating the presence of thermal hysteresis. The change of slope observed at 260°C during cooling may be indicative of the transformation of an intermediate structure (monoclinic β-phase) to the room temperature (monoclinic γ-phase) structure. The activation energy in different temperature ranges during heating and cooling is tabulated in Table 1. It is seen from the table that activation energies for the γ-phase during heating up to 430°C and below 260°C during cooling are nearly the same. The α-phase values above 430°C during heating and up to 420°C during cooling are also not very different; but the activation energy between 420 and 260°C during cooling is quite different from other values. The difference in the activation energy values also indicates the presence of an intermediate structure during this temperature interval. The crystal grown at 40°C shows only one phase transformation during heating and two phase transformations during cooling. This indicates that the intermediate structure is formed only when the crystal is heated above 422°C and then cooled. During heating, the log σT vs. $1000/T$ curve between 500 and 600°C is non-linear and beyond 600°C, it is again linear. This suggests that during this temperature interval some additional factor contributes to the conductivity. It is assumed that the non-linear nature of conductivity may be the consequence of impurity saturation and the generation of additional charges due to a progressive orientational disorder which starts at 500°C. The conductivity is extrinsic up to 500°C and is due to residual impurities and grain boundaries. Beyond 600°C, however, it is likely that the conductivity corresponds to the intrinsic region. While heating and cooling the activation energy in the intrinsic range has almost the same value.

In a DTA study Reismann [5] found that K_2CO_3 under an air atmosphere shows transitions at 422, 360 and 253°C, while under a CO_2 atmosphere it shows only one transition at 422°C. To explain the presence of the three transitions in air he assumed that the 360°C transition is the carbonate-rich eutectic in the system K_2O–K_2CO_3, and the 250°C transition corresponds to a phase change in K_2O. To check the validity of Reismann's assumption, we studied the loss in mass of the K_2CO_3 crystal up to 620°C. For this purpose

TABLE 1

Activation energy values for different phases during heating and cooling

Temperature range (°C)	Phase	E_g, heating (eV)	E_g, cooling (eV)
< 400, heating 260, cooling	γ	0.861	0.765
430–500, heating 500–415, cooling	α	0.854	0.696
600–620, heating and cooling	α	0.789	0.800
420–260, cooling	β		0.449

a crystal of mass 0.511 g was chosen. This mass of crystal was equal to the mass of crystal used for studying conductivity. The crystal was heated at a rate of 5°C min^{-1} which was also the rate used in conductivity measurements. Between room temperature and 300°C this crystal lost 0.085 g mass which was equal to the mass of 1.5 H_2O molecules; but between 300 and 620°C and from 620°C to room temperature no loss in mass was observed. Since the sensitivity of the thermobalance is 0.1 mg, even 1% conversion of K_2CO_3 to K_2O could have been detected. The study shows that the decomposition of K_2CO_3 to K_2O must be negligible in this temperature range. Therefore, the transition points observed in air by Reismann must be due to some other effects. As has been pointed out earlier there is an intermediate structure between 420 and 250°C. The transition points might correspond to this phase change.

Figure 2 shows the variation of dielectric constant ϵ' with the temperature of the $K_2CO_3 \cdot 1.5\ H_2O$ crystal in the temperature range 30–620°C during heating and cooling. It is seen from the figure that the ϵ' curve passes through a peak value at 215°C with a shoulder at 190°C. These temperatures correspond to the two dehydration steps of the $K_2CO_3 \cdot 1.5\ H_2O$ crystal. The large increase in ϵ' at 215°C is due to orientation of permanent dipoles of the water molecules released from the crystal structure, but trapped within the material and also due to the space-charge polarization produced by the trapped +ve and −ve charges generated after dissociation of water molecules. As the number of free detached molecules and dissociated water molecules decreases, the ϵ' value also decreases beyond 215°C.

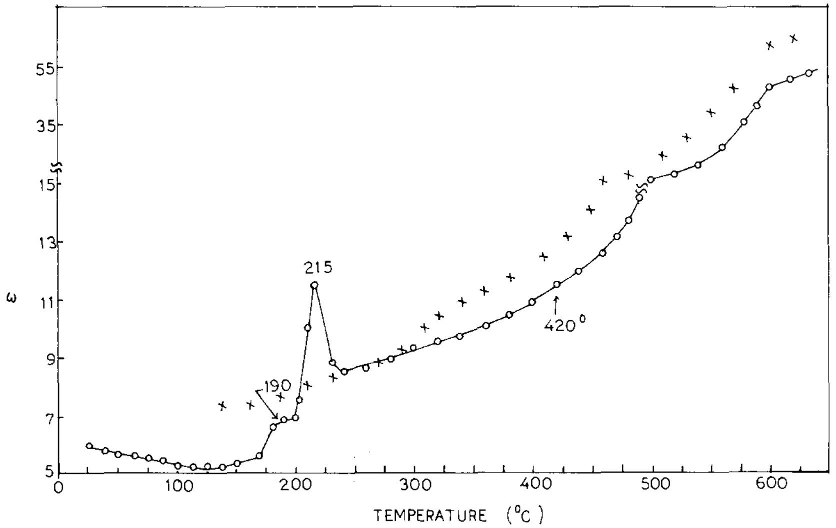

Fig. 2. Variation of dielectric constant of $K_2CO_3 \cdot 1.5\ H_2O$ with temperature. ○, Heating; ×, cooling.

The dielectric constant again shows a gradual increase from 240°C onwards. There is a sudden increase at 420°C. Between 500 and 600°C, ϵ' increases at a very fast rate beyond which this rate again decreases. This fast increase between 500 and 600°C may be due to the onset of an orientational disorder in this temperature range. Such an increase in ϵ' has also been observed in the $Na_2CO_3 \cdot H_2O$ crystal [13].

CONCLUSION

It is concluded that during heating, the $K_2CO_3 \cdot 1.5\ H_2O$ crystal shows a phase transition at ~ 420°C and an extrinsic to intrinsic transition at ~ 600°C. While cooling, however, it shows an additional transition at ~ 260°C. Between 420 and 260°C an intermediate structure is present. This study also suggests that there is an onset of orientational disorder at about 500°C which probably ends at ~ 600°C.

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