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ELECTRICAL CONDUCTIVITY AND DIELECTRIC CONSTANT MEASUREMENTS ON $Na_2CO_3 \cdot H_2O$ CRYSTALS

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ABSTRACT

The d.c. electrical conductivity and dielectric constant at 100 KHz of $Na_2CO_3 \cdot H_2O$ crystals grown at 40 ± 1°C have been measured in the temperature range 30–720°C. It has been observed that the conductivity shows a peak at 150°C. It also shows changes at 220, 360, 470 and 620°C. The dielectric constant measurement also shows a peak at 160°C and some changes at 190, 360, 480 and 620°C. The peaks in electrical conductivity and dielectric constant correspond to the dehydration process, the changes at 360 and 480°C to phase transformations and changes at 220 and 620°C to electrical transitions. The observed peaks in conductivity and dielectric constant measurements at the dehydration temperature have been explained on the basis of release of water molecules and the subsequent dissociation of some 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

Single crystal preparation of Na_2CO_3 by a modified Bridgman method was attempted by Midorikawa et al. [1]. From the dilatometric [1] and other measurements [2], they concluded that Na_2CO_3 is ferroelastic above 200°C and there are two crystallographic transformations at 360 and 490°C. The number of transition points of Na_2CO_3 and their nature have been studied by differential thermal analysis [4,5], dilatometry [6,7] and X-ray scattering [5,8]. The presence of thermal transformations at 360 and 490°C is detected by all the workers, but the transition between 570 and 620°C is very controversial. Cerisier and Roux [3], from electrical conductivity measurements on pellets prepared after drying the powder in vacuo at 200°C for several days, confirm that Na_2CO_3 undergoes thermal transformation at 360, 490 and 620°C. Very little information is available on the physical properties of hydrated Na_2CO_3. The main reason of the neglect is probably due to the

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fact that $Na_2CO_3 \cdot H_2O$ 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 sodium carbonate 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 discusses d.c. electrical conductivity and dielectric constant measurements on $Na_2CO_3 \cdot H_2O$ crystals grown from aqueous solution at 40°C. It is observed that, in addition to exhibiting two phase transformations shown by other forms, $Na_2CO_3 \cdot H_2O$ shows two electrical transitions.

EXPERIMENTAL

Growth of crystals

$Na_2CO_3 \cdot H_2O$ crystals have been grown by the 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 has been measured by the BPL meg-megohm meter type RM 160/3 in the temperature range of 30–720°C. For conductivity higher than 10^{-6}, a simple circuit which could measure it with the same accuracy as the meg-megohm meter has been constructed. The dielectric constant was measured by VEL direct reading LC meter type VLC2 at 100 KHz in the same temperature range. The heating rate for both the measurements was maintained at 5°C min^{-1}.

RESULTS AND DISCUSSION

The variation of $\log(\sigma T)$ vs. $1000/T$ for $Na_2CO_3H_2O$ crystals grown at 40°C is shown in Fig. 1. It is seen from the figure that, during heating, the conductivity passes through a peak at 150°C. The conductivity again starts rising from 160°C. It is also seen from Fig. 1 that on heating further there are changes in the slope at 220, 360, 470 and 620°C. On cooling, the conductivity again shows similar changes in slope at slightly different temperatures, indicating that there is a thermal hysteresis. The peak observed during heating at 150°C is completely missing during cooling.

Dynamic thermogravimetry (TG) and DTG measurements show that $Na_2CO_3 \cdot H_2O$ is completely dehydrated at 190°C [9]. The peak in the $\log(\sigma T)$ vs. $1000/T$ curve occurring at 150°C, which is lower than the final

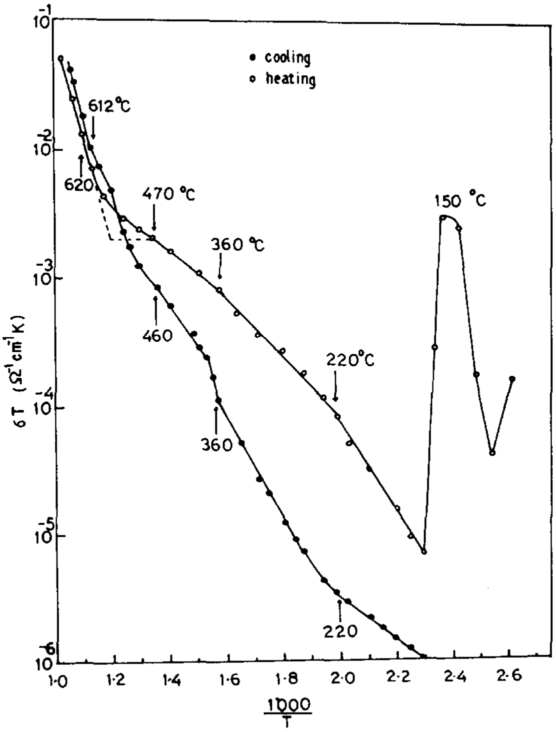

Fig. 1. Variation of d.c. electrical conductivity with temperature of $Na_2CO_3 \cdot H_2O$. ●, Cooling; ○, heating.

dehydration temperature, should therefore correspond to the dehydration process. The rapid rise and fall in conductivity of the crystal during heating indicates that free charge carriers are available for conduction during dehydration. Kher and coworkers [10,11], 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 the conductivity changes at the corresponding dehydration temperatures are due to dissociation of a small fraction of the water molecules that are detached from the structure into H^+ and OH^- ions. Thus, in the case of $Na_2CO_3 \cdot H_2O$ also, as dehydration starts, the water molecules are detached from the structure. It is assumed that a fraction of the detached water molecules dissociates into H^+ and OH^- ions and cause the increase in conductivity. All the water molecules released and dissociated are not able to escape from 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 the conductivity of the crystal. As the temperature reaches the dehydration points, the number of trapped ions decreases at a high rate as they are driven by the applied field and collected by the respective electrodes, while the trapped H_2O molecules can escape relatively slowly by diffusion. Hence the conductivity peak occurs earlier than the DTG peak.

The number of charged particles, n, collected during the peak of the conductivity curve can be determined experimentally by calculating the area under the current vs. time curve (curve not given in the paper) corresponding to the total charge released near the dehydration temperature and dividing this by e, the electron charge. The number of charged particles obtained in this way is 1.73×10^{16} in one of the experimental sets.

Using Maxwellian distribution and assuming the dissociation energy of H_2O to be 1.2 eV in water, the fraction, f', of water molecules dissociated after being detached at the dehydration temperature can be calculated. Let

$$f' = \frac{\text{the number of water molecules dissociated}}{\text{the total number of water molecules detached}} = \frac{n_2}{n_1}$$

where n_2 is the number of water molecules which receive thermal energy greater than $(kT + 1.2 \text{ eV})$ and n_1 is the number of water molecules which receive thermal energy greater than kT. From Maxwellian distribution

$$f' = \frac{n_2}{n_1} = \frac{\int_{kT+1.2\,eV}^{\infty} e^{-E/kT} \mathrm{d}E}{\int_{kT}^{\infty} e^{-E/kT} \mathrm{d}E}$$

Let f be the ratio of the number of water molecules dissociated, n_2, to the total number of water molecules, N, that correspond to the dehydration, i.e. $f = n_2/N$ where

$$N = \int_0^{\infty} e^{-E/kT} \, \mathrm{d}E$$

The number of water molecules dissociated, n_2, i.e. the number of free positive and negative charges produced at the dehydration temperature is equal to $f \times$ (total number of water molecules, N). N is of the same order as n_1, i.e. $N = n_1$. Hence $f = f'$. Therefore, the number of water molecules dissociated will be $N \times f$. By assuming that during dehydration one water molecule escapes, the number of charged particles produced after dissociation comes out to be 9.98×10^3, which is much lower than the experimentally observed value. This may be explained by assuming that the dissociation energy of H_2O in the crystal depends on the strength by which the H^+ and OH^- ions in the H_2O molecule are pulled in opposite directions in the crystal structure and, therefore, may be lower in solids than in liquid where these molecules are free. It is found that, if the dissociation energy of H_2O in the $Na_2CO_3 \cdot H_2O$ crystal is chosen as 0.363 eV, then the statistical calculations give the number of charge particles due to dissociation as 1.21×10^{16}, which is in close agreement with the experimental number. As pointed out above, the decrease in the dissociation energy of the H_2O molecule inside a

$Na_2CO_3 \cdot H_2O$ crystal may be due the pulling of OH^- ions by the Na^+ ions in one direction and H^+ ions by the SO_4^{2-} ions in the opposite direction.

In Na_2CO_3, two structural phase transitions have been reported in the literature [5,8]. The higher temperature α phase, belonging to the space group $P63/mmc$, transforms at 490°C to the β phase, belonging to the space group $C2/m$, and then to the γ phase at 360°C. The change in slope in the log σT vs. $1000/T$ curve at 470 and 360°C are indicative of α to β and β to γ phase transitions, respectively. All workers unanimously agree over the presence of two phase transformations, but the presence of a transition between 570 and 620°C is controversial. Cerisier and Roux [3] in their recent study suggest that the 620°C transition in Na_2CO_3 is due to the end of progressive orientational disorder which starts at 485°C. In the present study, the log σT vs. $1000/T$ curve between 470 and 620°C is non-linear and beyond 620°C it is again linear. This suggests that between 470 and 620°C 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 generation of additional charges due to orientational disorder. In the absence of such a disorder, the 620°C transition would have appeared earlier (shown by the broken line in Fig. 1). The conductivity in the γ phase and the β phase (up to 620°C) is extrinsic and is due to residual impurities and grain boundaries. Beyond 620°C, however, it is likely that the conductivity corresponds to the intrinsic region and may be due to the migration of sodium ions. This may also be inferred from the fact that the transport number, t_+, for cations in Na_2CO_3 at test temperatures varying between 550 and 680°C is 1 [3]. The activation energies in different temperature ranges are tabulated in Table 1. It is observed from the table that the activation energy in the intrinsic range is much larger than in the extrinsic range. It is also observed from the table that, during heating and cooling, the activation energy for the α-phase is nearly the same, but for other phases, the activation energies are very different. This may be due to the fact that the γ phase has no definite structure. It may be an incommensurate mixture of the two high temperature phases.

Midorikawa et al. [2] from the microscopic observations of domains above room temperature on the melt-grown Na_2CO_3 crystals showed that, above 200°C, the domain boundaries could be moved easily by applying stress. Thus, in these crystals above 200°C, ferroelasticity was established. In the present investigation, a change of slope in the log σT vs. $1000/T$ curve at 220°C has been observed, which may be indicative of the onset of ferroelasticity.

Figure 2 shows the variation of dielectric constant, ϵ', with temperature of $Na_2CO \cdot H_2O$ crystals in the temperature range 30–720°C during heating and cooling. It is seen from the figure that ϵ' remains fairly constant up to 150°C. Beyond this temperature, ϵ' increases rapidly and shows a peak at 160°C, the temperature corresponding to dehydration of the $Na_2CO_3 \cdot H_2O$

TABLE 1

Values of activation energies for different phases during heating and cooling

Temperature range (°C)	Phase	Activation energy (eV)	
		Heating	Cooling
160–220	γ	0.71	0.69
220–360	γ	0.45	1.50
360–470	β	0.22	1.20
> 620	α	2.67	2.62

crystal. The large increase in ϵ' at 160°C is due to the orientation of permanent dipoles of the water molecules released from the crystal structure but trapped within the material and also to the space charge polarization produced by the trapped positive and negative charges generated after dissociation of water molecules. As the number of free detached water molecules and dissociated water molecules decreases, ϵ' also decreases at a fast rate beyond 160°C.

The dielectric constant again shows a sudden increase at 190°C followed by a slow increase with some changes at 360 and 480°C. Beyond 480°C,

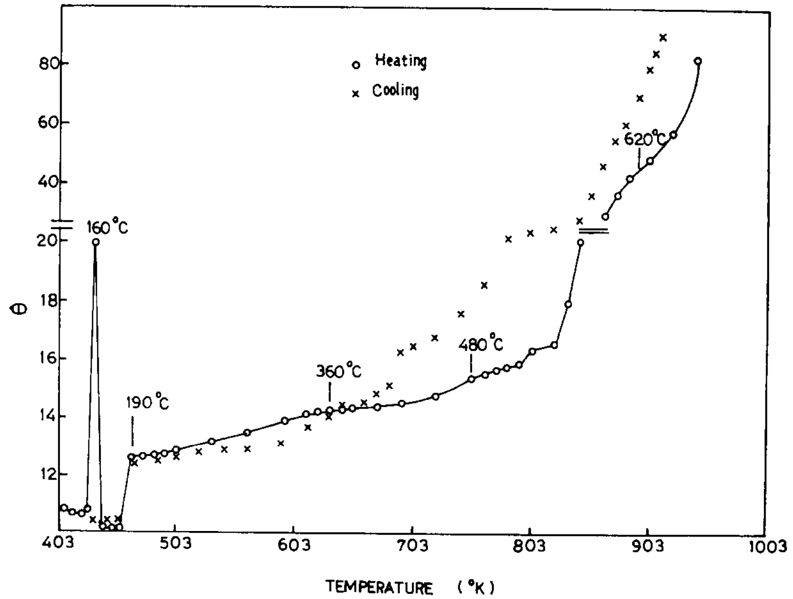

Fig. 2. Variation of dielectric constant with temperature of $Na_2CO_3 \cdot H_2O$ (frequency 100 KHz). O, Heating; ×, cooling.

however, ϵ' increases at a very fast rate. This rapid increase beyond 480°C may be due to the onset of orientational disorder. Such an increase in ϵ' has been reported in many solids (e.g. KNO_3) [12].

The weak dielectric anomaly observed at 190°C and the onset of ferroelasticity near this temperature indicate that both may be coupled through strain to the soft optic modes. Thus ϵ' measurement shows changes at 190, 360, 480 and 620°C which have also been shown by the conductivity measurement at these tempertures. The assumption that the onset of orientational disorder at 480°C and the 620°C transition is an intrinsic point transition seems to be valid.

CONCLUSION

It is concluded from the study that the $Na_2CO_3 \cdot H_2O$ crystal exhibits both the phase transitions shown by its other forms. In addition to the two phase transitions, it shows two electric transitions, one connected with the onset of ferroelasticity and the other with the intrinsic point transition. The study also suggests that there is an onset of orientational disorder near 480°C.

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