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Phase transitions in $CaHPO_4$ and $BaHPO_4$ above room temperature

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ABSTRACT. Phase stability of $MHPO_4$ ($M = Ca, Ba$) in the solid state was studied by means of differential scanning calorimetry, high-resolution ac-calorimetry and ion-mobility analysis above room temperature. Both salts showed a sequence of phase transitions that were very dependent on mechanical and thermal treatments of the samples. Since similar observations have been previously reported for many alkali-metal hydrogen double salts, it seems then plausible the involment of hydrogen bonds in the structural disorder that marks the onset of the fast-ion state in all these salts at higher temperatures.

RESUMEN. Se estudió la estabilidad de las fases sólidas de $MHPO_4$ ($M = Ca, Ba$) por encima de la temperatura ambiente, por medio de la calorimetría diferencial de barrido, la calorimetría ac de alta resolución y el análisis de la movilidad iónica. Ambas sales mostraron una serie de transiciones de fase que dependieron mucho de los tratamientos mecánicos y térmicos de las muestras. Puesto que se han tenido previamente observaciones similares en muchas otras sales dobles hidrogenadas de metales alcalinos, parece entonces factible que los enlaces de hidrógeno intervienen en el desorden estructural que marca el inicio del estado de ion rápido en todas estas sales a altas temperaturas.

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1. INTRODUCTION

During the last few years it has become apparent that hydrogen-bonded compounds, such as the acid salts, show anomalous phase behavior above room temperature due to the appearance of structural disorder that gives rise to the fast-ion state in these ionic systems [1-5]. Many of these salts exhibit a ferroelectric ordering at low temperatures, such as the well-known KDP (KH_2PO_4) ferroelectric family, in which the hydrogen bonds play an important role in the ferro-paraelectric transition [6]. The KDP family also shows at high temperatures (far below melting) a fast-ion mobility that has been claimed by many authors to be mostly protonic [1,2].

The activities in the field, mainly concerning transport properties and conduction mechanism in protonic conductors, have been reviewed many times [7–13]. There is a considerable uncertainty in the literature data about some phases and phase transitions of the salts with hydrogen bonds. This is very much the case for salts of the type $MHAO_4$ and $MH_2A'O_4$, with $M = K$, Rb, Cs or NH_4; $A = S$ or Se; $A' = P$ or As; and H either hydrogen or deuterium [14,15]. Thus, while some phase transitions are well-established, others are difficult to reproduce. The reason is either that the transitions are too sluggish, or that they are "irreversible", which means that there is a strong tendency for some phases to become metastable at lower temperatures.

The purpose of the present investigation is to look for similar thermal effects in compounds of related composition and structure, in which hydrogen bonds are of importance. Thus, this report concerns the phase behavior of two hydrogen phosphates of alkaline-earth metals, calcium and barium, by the use of combined differential scanning calorimetry (DSC), high-resolution ac calorimetry and ionic conduction analysis.

2. EXPERIMENTAL TECHNIQUES

The experiments were performed on polycrystalline samples of $CaHPO_4$ (CHP) and $BaHPO_4$ (BHP) that were prepared from aqueous solutions, by mixing stoichiometric amounts of H_3PO_4 and the corresponding alkaline-earth hydroxide. The solutions were kept at a controlled temperature near 60°C and in a dry atmosphere. For BHP, Aldrich reagent grade $BaHPO_4$ powder was also used as starting material. The samples were neither annealed nor submitted to any thermal treatments above 100°C before the measurements.

The DSC thermograms were recorded with a Perkin-Elmer DSC-7 analyser, at a scanning rate of 5-10 K/min and in a nitrogen atmosphere.

An ac calorimeter apparatus for high temperature thermal analysis of solid samples in a dry atmosphere, which has been described elsewhere [16,17], was used to determine the temperature-dependent heat capacity of the samples. The calibration constant of the apparatus, K, according to the basic equation of the ac calorimetry method, $C_P = K/|T_{ac}|$, was not obtained, so the reported data correspond to $1/|T_{ac}|$ on a scale of arbitrary units.

The samples were further characterized by electrical resistivity measurements, which were performed by the conventional ac two-probe method applied to slab-shape samples with silver electrodes. The samples were ground and pressed into pellets with applied pressure in the range 1.0–10.0 ton/cm^2.

3. RESULTS AND DISCUSSION

3.1. DSC measurements

Figure 1 represents an example of the first DSC heating curve of a fresh CHP sample. Two endothermic regions due to phase transformations in the solid state of the sample were recorded. The first one in the 440–470 K range with onset temperature at about 453 K and a small change of enthalpy, $\Delta H = 0.14$ kJ/mol. The second one in the 680-760 K range with onset temperature at 693 K and a large change of enthalpy, $\Delta H = 46.7$ kJ/mol. The higher temperature anomaly is a combination of two consecutive broad peaks at 718 K and 746 K, respectively, that emerges into only one peak at 711 K (onset = 693 K, as before) on subsequent heating runs of the sample. However, no DSC peak was recorded during the subsequent cooling of the sample. For materials that were treated mechanically by applying one-dimensional pressure, the transition at 693 K was accompanied by only one

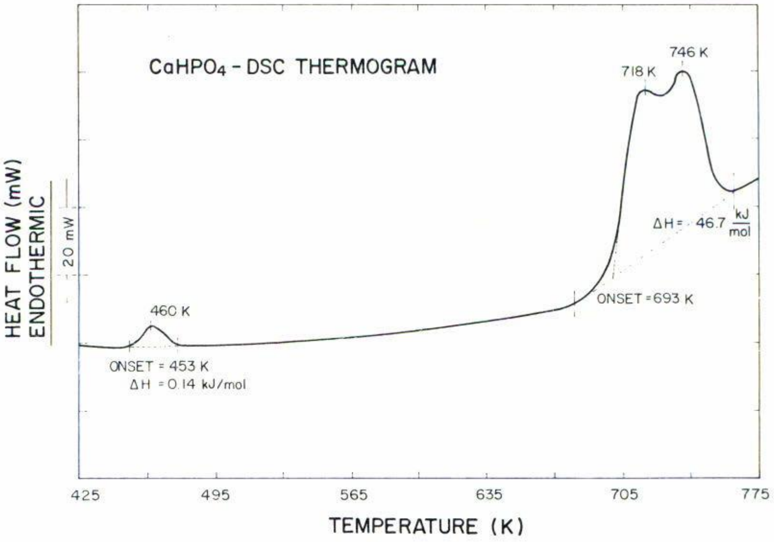

FIGURE 1. DSC heating curve for a freshly prepared $CaHPO_4$ sample. The transition points are 453 K and 693 K, respectively. The heating rate is 10 K/min.

peak but with a higher change of enthalpy ($\Delta H = 136$ kJ/mol). It should be emphasized that CHP decomposed above 970 K.

Concerning BHP (melting point 686 K), only one DSC peak was recorded on a first heating of the samples, but none during the subsequent cooling run, indicating the irreversible character of the transition. The transition occurred around 498 K (onset temperature) with a change of enthalpy approximately equal to 1.42 kJ/mol.

3.2. AC-calorimetry measurements

Typical $1/|T_{\text{ac}}|$ plots, which are proportional to the heat capacity at normal pressure, $C_P(T)$, resulting from the ac-calorimetric analysis on pressed pellets samples of CHP and BHP, are shown in Figs. 2 and 3. For all samples, the low temperature region of the $C_P(T)$ curves were essentially of the same shape, showing that the heat capacity increases slowly with increasing temperature between room temperature and near the first transition at T_1, namely 460 K and 410 K for CHP and BDP, respectively. Above T_1, a steeper variation of $C_P(T)$ with increasing temperature was observed, indicating the appearance of a more disordered process in the ionic system of both salts above this transition point.

On an amplified scale, Fig. 2 is a plot of the $C_P(T)$ data in the 400–530 K temperature range for a CHP sample on a first heating run, showing the $T_1 = 460$ K anomaly where a small latent heat was developed, in close agreement with the DSC results that showed an endothermic peak near this transition temperature (see Fig. 1).

On the other hand, the first $C_P(T)$ anomaly of BHP recorded at $T_1 = 410$ K (see Fig. 3), was not detectable by means of DSC. This is probably due to either a small enthalpy change or a continuous phase transition that occurs in BHP when is heated through this point.

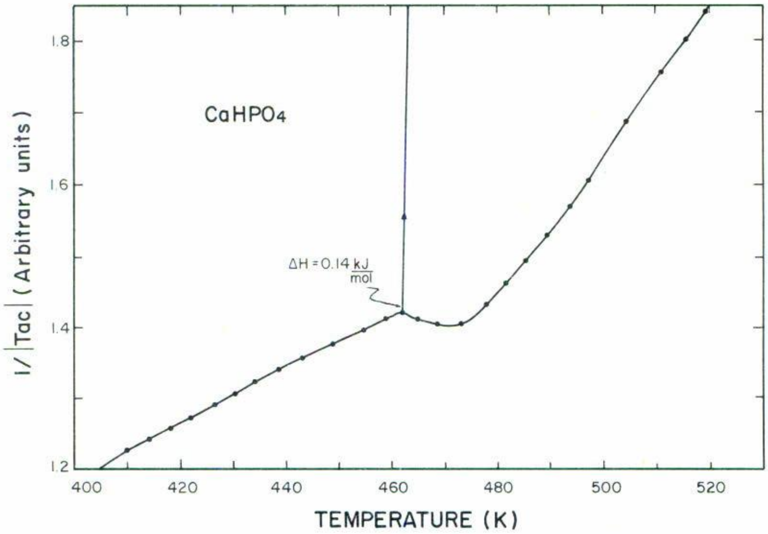

FIGURE 2. Ac-calorimetric heating curve, $1/|T_{ac}|$, which is proportional to the heat capacity, $C_P(T)$, in the 400–530 K temperature range, for a $CaHPO_4$ sample. The solid line is drawn as a guide to the eye.

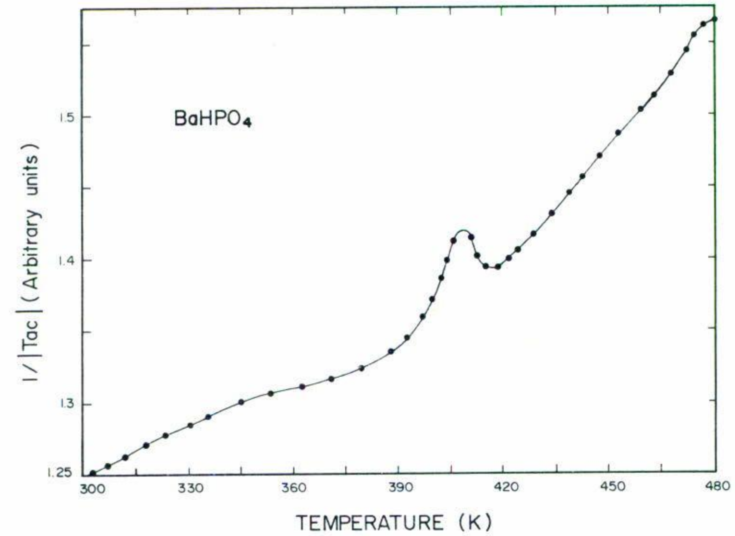

FIGURE 3. Ac-calorimetric heating curve, $1/|T_{ac}|$, in the 300–500 K temperature range, for a $BaHPO_4$ sample. Full curve is guide to the eye.

3.3. Ion-mobility characteristics

Appreciable changes in the electrical resistivity of CHP and BHP cells were observed at their phase transitions above room temperature. This might indicate either large deformation of the crystalline framework as a conducting proton passes or a change in the motional state of the anions which affects the rate of proton transports.

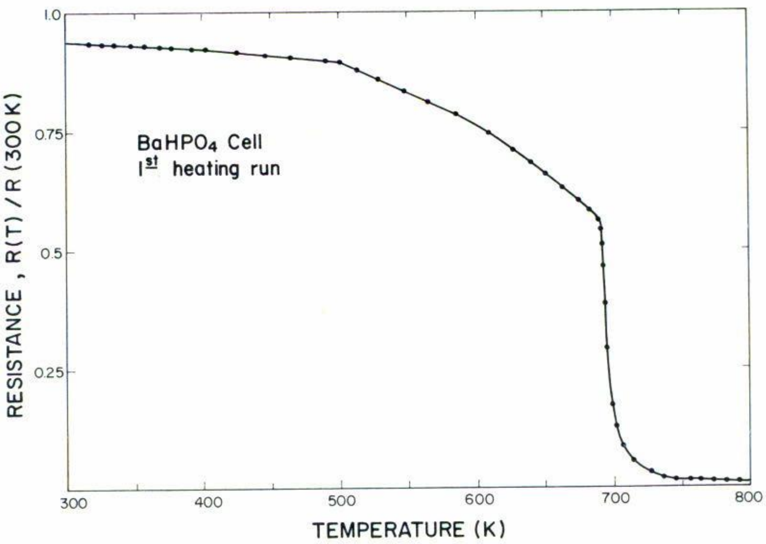

FIGURE 4. Relative resistance, R(T)/R(300 K), of a $BaHPO_4$ cell on a first heating run in the 300–800 K temperature range. Full curve is guide to the eye.

A typical temperature variation of a BHP cell resistance is shown in Fig. 4, which exhibits three distinct domains: a low temperature domain, namely between room temperature and the first-order phase transition at 498 K, characterized by a very low ionic conductivity with almost no temperature variation; an intermediate temperature region between 498 K and 686 K where the resistance decreases rapidly with increasing temperature; and a high temperature region above 686 K and after a steeper fall of the resistance to a value that remains almost constant with increasing temperature. It is worth noticing that above 686 K the sample decomposes.

Both from the thermal and the ion-transport analysis of two distinct hydrogen phosphate salts, in which alkali atoms were replaced by alkaline-earth atoms (Ca, Ba), the conclusion is clear that the same thermal effects observed previously [14,15] for the first type of salts also occurred for the second one. This was demonstrated in the recently ac-calorimetry study of the tetragonal-monoclinic phase transition of KH_2PO_4 at 453 K: the high-temperature monoclinic phase remains metastable below this transition point on cooling the sample to the low temperature region [18].

In summary, we have investigated the complex thermal behavior of two hydrogen-bonded salts, $CaHPO_4$ and $BaHPO_4$, in their solid states and in the temperature region where is expected a fast-ion mobility, and found that both salts show thermal effects that are very similar to those found in many alkali acid salts: relaxation effects, thermal hysteresis, phase separation and metastable states. It seems then plausible the involment of hydrogen bonds in the disordering process that takes place in all these acid salts with increasing temperature.

The conclusions of the present study might have some importance also for other types of materials with structural protons and, in general, for protonic behavior in solids.

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