Preparation of Different Solid $CsHSO_4$ Phases by Means of Sample Treatment

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Grinding of $CsHSO_4$ can create a low-energy state which relaxes at 375 K by a first order phase transition with an endothermic enthalpy change of 1.14 kJ/mol. The formed low-energy state can be transferred by one-dimensional pressure to a higher energy state which relaxes at 333 K by a first order phase transition with an endothermic enthalpy change of 0.55 kJ/mol. This striking – previously unknown – behaviour is probably not limited to $CsHSO_4$ only, and it represents a new class of phase transitions. The involvement of the hydrogen bond present and the importance of water content are stressed. The temperatures and enthalpies of all three phase transitions of $CsHSO_4$ are determined by DSC.

Recently it was found that different preparation techniques of a solid sample (grinding, one-dimensional pressing, crystallisation) can lead to considerable differences in several physical properties. This was shown for Ag_2HgI_4 samples whose thermal characteristics of an order-disorder transition were analyzed by differential scanning calorimetry (DSC) [1, 2]. The present paper reports on much more spectacular effects in $CsHSO_4$. Mechanical treatment can create or shift energy states which relax as first order phase transitions with endothermic enthalpy changes. Thus more ordered states can result from mechanical treatment, an effect which is opposite to the well known creation of dislocations or point defects.

During the last years solid-solid transitions of $CsHSO_4$ [3–7] have become of great interest because of the unusual electrical properties of this substance. However the reported data on these transitions disagree: The first paper [3] mentions two transitions, one at 373 K and a second one at 413 K, the first one being characterized by a negligible heat capacity anomaly and more pronounced dielectric constant anomalies. This first transition was not found in the more recent papers [4–6]. We could show that it is due to the relaxation of a low-energy state (called state II below), which is created by grinding. On the other hand, a phase transition at about 333 K, not found in the first paper [3], has been reported in [4–6]. As we shall see, on applying one-dimensional pressure, state II goes over to a state III with a slightly higher energy, which relaxes by a first order phase transition around 333 K with an endothermic enthalpy change. We also shall demonstrate the importance of water vapour for the phase transitions observed, which was completely disregarded before [3–6]. This seems important in connection with the hydrogen bonds surely involved.

As previously [1, 2], a commercial DSC (Rigaku, Japan) equipment was used in our investigations. This enabled a quick and reproducible thermal analysis of differently treated samples, measuring simultaneously the transition temperature and the accompanying enthalpy change. Additional information is available from the shape and structure of the obtained transition peak.

$CsHSO_4$ crystals were obtained by evaporation at room temperature of aqueous solutions of equivalent amounts of Cs_2SO_4 and H_2SO_4 [3]. If the crystals had been annealed for some hours at 440 K and cooled to room temperature, they reached a state I. On heating in the DSC device they gave no phase transition in the temperature range from 320 K up to 416 K, the temperature where the well-known structural transition $\beta \rightarrow \alpha$ occurs (see Table 1). If the sample in state I is ground at room temperature before heating, there occurs a new phase transition around 373 K (transition 2 in terms of Table I) and the previous one at 416 K, both with

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a clearly endothermic first order enthalpy change (see Table 1). Thus grinding creates in the annealed sample a state II with a lower energy. State II relaxes around 373 K to state I, which has a higher energy and thus should be metastable. There is no back transition (from I to II) when lowering the temperature – even to the liquid nitrogen range. But a repeated grinding of a sample relaxed from state II to I leads again to state II. This cycling between states I and II can be repeated many times. Let us remark that this behaviour is opposite to what is expected if the creation of defects, which no doubt takes place during the mechanical treatment, were responsible for the transition observed. Relaxation of such defects – if at all possible as a first order transition – should clearly manifest itself as an exothermic enthalpy effect. This is the general tendency for such transformations from less to more ordered states. Obviously the endothermic enthalpy change observed in our case excludes such a traditional approach. Furthermore, if we neglect the sign of the transition enthalpy, the occurrence in an ionic salt of a relaxation of a defected state by a first order phase transition has, to our knowledge, never been observed, at least not in the temperature range in question. It is obvious that we are dealing with a different phenomenon.

Starting from state II or state I the energy can be raised or lowered, respectively, to that of a new state III by applying one-dimensional pressure. This is simply realized by pressing a pellet from the powdered sample in a small piston-cyclinder device, applying pressures in the range 0.1–0.6 GPa. If such a pressed pellet is heated from room temperature in the DSC device, we obtain a first order transition peak already around 333 K with an endothermic enthalpy change of only nearly 50% of the II → I transition (see Table 1). The transition at 416 K is again obtained. The new state III relaxes to another new state I′, which for reasons given below we consider to be different from state I in spite of the fact that we cannot detect any difference between I and I′ at the 416 K structural transition.

We face in the II → III case a new class of transitions: Contrary to grinding, one-dimensional pressing increases the energy of the salt. So far no other example of such a drastic shift of a first order phase transition by one-dimensional pressure treatment has come to our knowledge. First of all let us eliminate the obvious explanation that the pressure treatment creates a metastable phase which is present in the T-p phase diagram of the component considered. This simple interpretation can be definitely excluded:

Transitions between states II and III are possible by grinding (III → II) or one-dimensional pressing (II → III). It is also possible to get II by grinding I′. State III can be reached from state I′ by cooling to room temperature (sometimes a few minutes are sufficient). Thus the transition III ⇄ I′ is reversible notwithstanding the transition III → I′ can easily be recorded by DSC but not the reverse transition I′ → III because of its sluggishness.

State III can also be reached from I by controlled contact with water vapour (again sometimes a few minutes may be sufficient), the shift to state III being identified by the same transition around 333 K and the corresponding enthalpy change (see Table 1). Samples of III obtained from state I by treatment with water vapour go over to state II by grinding. Vapour pressure treatment of II also leads to III. The opposite transformation (III → II) was studied by keeping a sample in state III for some weeks in an exsiccator. The observation in this case, that phase III had disappeared completely before phase II had been built up, suggests that the transformation goes in the two steps III → I → II, state I being metastable, as has been mentioned.

All the details given above prove clearly that the transitions 2 and 3 are not independent. In other words, it has so far not been possible to prepare samples which would simultaneously realize both transitions with the total enthalpies involved as summarized in Table 1. We can either observe one or the other transition in full extent (in respect to the enthalpy given) or – under certain conditions – we can detect both these transitions, and the corresponding enthaplies can be taken as a measure of the percentage of both states responsible for the transformations involved. Figure 1 presents an example of a DSC record where all three transitions were detected.

The above observations indicate in a convincing way the importance of water content in the treated sample. This was overlooked in all previous papers [3–7]. But it is excluded that we meet here a simple formation and decomposition of hydrates. This is obvious from the reversibility of the III to I′ transitions by temperature changes only as well as from weight control before and after the transitions.

Table 1. Phase transitions observed in $CsHSO_4$. Transition 1 occurs for both heating and cooling, and its temperature and enthalpy are nearly independent of the sample history. The transitions 2 and 3 are detectable only when a sample is heated, and their intensity depends on how the sample has been treated. Neither of them if the sample has been annealed thoroughly (e.g. kept at 440 K for a few hours) before heating. Grinding (shear stress) as well as slow, intense drying tend to increase the intensity of transition 2 and, simultaneously, decrease that of transition 3, while one-dimensional pressure as well as exposure to water vapour have the opposite effect. Crystals prepared by evaporation at ambient temperature will undergo transition 3 upon heating. All temperatures are determined from the slope of the transition peak.

Transition number	Transition temperature [K]	Transition enthalpy [kJ/mol]	Comment
1	416 ± 1	5.24 ± 0.12	Heating
1	412 ± 1	5.43 ± 0.12	Cooling
2	375 ± 3	1.14 ± 0.14	
3	333 ± 1	0.55 ± 0.03	Crystals
3	331 ± 1	0.51 ± 0.03	One-dimensional pressure
3	329 ± 1	0.54 ± 0.03	Water vapour present

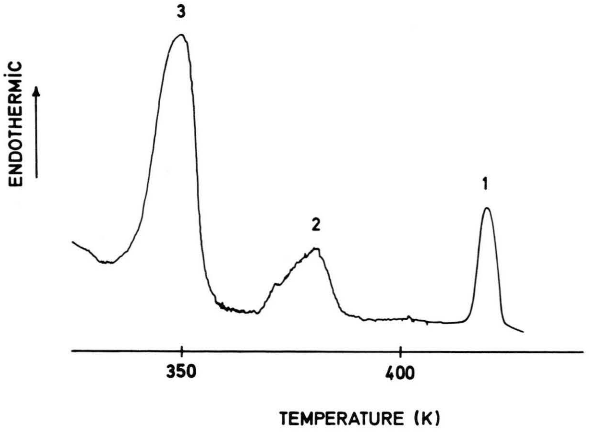

Fig. 1. DSC heating curve showing three transitions. The sample was prepared by grinding followed by exposure to saturated water vapour for 5 min at 318 K. The heating rate was 5 K/min. Transition 1 was measured with another scanning range than the other two ones, corresponding to a change by a factor of 16 of the energy scale. The combination of these two competing treatments results in a mixture of the "phases" that undergo transition 2 or 3, respectively, and this affects not only the measured enthalpies (which both are lower than according to Table 1) but also the transition temperatures: 366 K for no. 2 and 339 for no. 3 in this experiment. Transition 1 occurs at 416 K with its full enthalpy.

The transition around 333 K (transition 3 in Table 1) was reported earlier [4–6] as being found in crystals obtained by slow evaporation at room temperature (without further annealing). However, the enthalpy effect was never measured, and the reversibility by suitable cooling was overlooked in the previous papers [4–6]. We have confirmed the observation of transition 3 in fresh crystals. This proves clearly that the energy state III obtained from II by one-dimensional pressing, is not a metastable high pressure phase. State III is surely identical, from the energetic point of view, with non-annealed crystals obtained at room temperature by slow evaporation of aqueous solutions.

Besides the transitions 2 and 3 (in terms of Table 1), which are easily manipulated by mechanical treatment, $CsHSO_4$ exhibits a more energetic structural transition around 416 K [3, 4–7]. Our DSC values associated with this transition (see Table 1) agree in respect to both the temperature [3, 6] and the enthalpy [3] with earlier results. When the sample is cooled, the transition to the β phase (state I) takes place at about 4 degrees lower temperature, as it was already indicated earlier [7], but the exothermic enthalpy is always somewhat higher (up to 8%; average 3%) than the endothermal enthalpy of the immediately preceding $\beta \rightarrow \alpha$ transition. This indicates that the process of disordering is accompanied by a sluggish tail which is not detected by the DSC peak. In other words, the transition to the β phase occurs completely during the time range corresponding to the integrated part of the scanning curve. Just an opposite behaviour was found for the order-disorder process in Ag_2HgI_4 (see [8]).

Let us repeat that the enthalpy change for transition 2 is nearly twice that for transition 3. Thus from a purely energetic point of view the state II seems to be twice as ordered as the state III. The shear stress applied during the grinding creates a more ordered state than the one-dimensional pressure does. The possibility of such double-ordered states should clearly be reflected in the structure of $CsHSO_4$. It is an open structure where only two of the SO_4 oxygens are H-bonded [9]. These bonds are probably actively involved in the interesting variations of phase transitions created in solid $CsHSO_4$ by heating, drying, shear stress, one-dimensional pressure and contact with controlled water activity in the gaseous phase. It seems obvious that other techniques are desirable to clear up the mechanism of the phase transitions involved and the properties of the states between which these transitions occur.

Work is in progress on a study of the pressure dependence of the three phase transitions.

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