

New Phase Transitions in CsHSeO_4 , CsH_2PO_4 , RbHSO_4 , RbHSeO_4 , and RbH_2PO_4

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Z. Naturforsch. **41a**, 981–982 (1986);
received April 22, 1986

Alkali metal hydrogen double salts can have more than one stable phase at ambient temperature. These phases can be identified by the enthalpy and temperature of the endothermic phase transitions they undergo when heated. Transitions to these phases at ambient temperature depend on mechanical treatment (grinding, one-dimensional pressure) as well as on the water vapour pressure above a sample. Eight phase transitions (of which five were not known before) have been studied by means of differential scanning calorimetry.

It has recently been shown for CsHSO_4 [1] that solid-solid phase transitions can be created, annihilated or shifted by mechanical and thermal treatment as well as by varying the water vapour pressure. The most important feature is the occurrence of first order phase transitions due to simple mechanical treatment (grinding or one-dimensional pressing). Here we meet a new type of phase transitions which should not be limited to CsHSO_4 . Therefore it seemed worthwhile to look for similar transitions in compounds of related composition and structure [2–6].

All samples were crystallized from aqueous solutions of the corresponding acids and the alkali metal salts. Differential scanning calorimetry (DSC) measurements were carried out with a commercial Rigaku instrument. If the crystals are simply crushed to a coarse powder, the transitions of interest either do not appear at all, or the results are irreproducible. Combinations of grinding, exposure to water vapour (over pure water at about 393 K or 36.4 wt% H_2SO_4 at the same temperature) or one-dimensional pressure were used to obtain well defined, reproducible first order phase transition peaks. Sometimes repeated grinding and water contact was necessary in order to obtain the transi-

tion again if the sample is heated a second time. Figures 1 and 2 represent two examples (RbHSeO_4 and RbH_2PO_4) where a sequence of two phase transitions was recorded. For RbHSeO_4 besides the previously reported transition at about 372 K [4–6], a new one follows after 14 degrees. This combination of two transitions was not always obtained and it usually required a prolonged pretreatment by repeated grinding. For RbH_2PO_4 the first transition (352 K) could be achieved easily if the sample had been subject to one-dimensional pressure or a proper contact with water vapour, while the second one (380 K) was obtained if the sample had been ground. Neither of them could be detected during

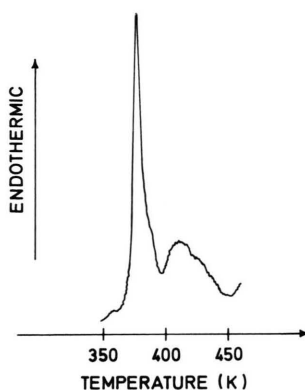


Fig. 1. DSC heating curve of a RbHSeO_4 sample, pretreated by combined action of grinding and exposing to water vapour. The transition temperatures are 372 K and 386 K, respectively. The scanning rate is 0.5 mcal/s and the heating rate is 5 K/min.

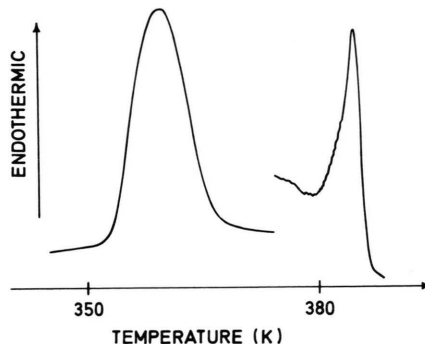


Fig. 2. DSC heating curve of a RbH_2PO_4 sample, pretreated by combined action of grinding and exposing to water vapour (or one-dimensional pressing). The transition temperatures are 352 K and 380 K, respectively. The scanning rate is 8 mcal/s for the transition at 352 K and 1 mcal/s for the transition at 380 K. The heating rate is 5 K/min.

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Table 1. Endothermic phase transitions measured for heating runs.

Salt	T/K	$\Delta H/kJ/mol$	$dT/dp / \frac{K}{GPa}$	$\Delta V \frac{cm^3}{mol}$
CsHSeO ₄	355 ± 3	0.61 ± 0.1	+ 110	0.14
CsH ₂ PO ₄	380 ± 1.5	0.45 ± 0.14	− 205	− 0.25
RbHSO ₄	439 ± 1	0.22 ± 0.08	+ 200	0.1
RbHSeO ₄	372 ^a ± 2.5	0.31 ± 0.12	− 120	− 0.1
RbHSeO ₄	386 ± 2	0.14 ± 0.05	− 20	− 7 × 10 ^{−3}
RbHSeO ₄	447 ^b ± 3	10.6 ± 0.4	− 30	− 0.7
RbH ₂ PO ₄	352 ± 3	4.04 ± 0.28	− 50	− 0.6
RbH ₂ PO ₄	380 ± 3	0.52 ± 0.1	0	0

^a known before [4–6].^b known before [7, 8].

the cooling of the sample. If the sample was reheated, the 380 K transition was reproduced straight away, while the 352 K transition required a repeated pretreatment of the sample.

The results achieved are summarized in Table 1. All data are for heating since only the 447 K transition of RbHSeO₄ is detectable when the sample is cooled. The transition temperatures and enthalpies are given as mean values of 6 to 40 runs taken from at least 3 different samples. Besides the thermal characteristics the transition volume was estimated by measuring the dT/dp slope in a high pressure device (maximally up to 0.1 GPa) and taking the Clausius-Clapeyron relation into account. These numbers have to be considered as rough estimates only.

As mentioned above, a certain water content seems to be required in the samples if the transi-

tions are to be recorded by the DSC technique. The importance of water can be easily demonstrated by annealing the powdered samples for some hours around 420–440 K and cooling them to room temperature in a dry atmosphere. If such samples are heated the “new” phase transitions usually do not occur. But a proper contact with water vapour combined with mechanical (grinding or one-dimensional pressing) treatment leads to a repetition of the previous transition. A systematic search for the existence of a critical water vapour activity for the onset of a similar transition (around 330 K) in CsHSO₄ was carried through and will be published with DSC results achieved in an extended pressure range [9].

From the results reported above one can conclude that at ambient temperatures all six salts MHSO₄, MHSeO₄ and MH₂PO₄ (M = Rb, Cs) can exhibit several ordered states, and the transformation between these states is strongly enhanced by a minute water content. These states are very sensitive to mechanical treatment, which proves their flexibility in energy and degree of order. In other words, there is only a weak coupling between these states and the crystalline matrix. This weak coupling explains the scatter of the transition temperatures and enthalpies. Water probably plays the role of a “molecular lubricant”, which facilitates the occurrence of the observed phase transitions. However, it cannot be excluded that part of the measured enthalpy change might be due to some loss of water from the salt. Anyway, we face here a different class of order-disorder transitions than those occurring at somewhat higher temperatures in CsHSO₄ [10], CsHSeO₄ [11] and RbHSeO₄ [7, 8].

Acknowledgements

This investigation is supported by the Swedish Natural Science Research Council and by the Erna and Victor Hasselblad Foundation.

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