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PHASE TRANSITIONS IN THALLOUS NITRATE. A REINVESTIGATION

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ABSTRACT

A detailed reinvestigation of the phase transitions in thallous nitrate using DSC, X-ray, IR and optical microscopy has been undertaken. The DSC measurements on anhydrous samples show that the orthorhombic [OR] → hexagonal [HEX] transition sets in at 349 ± 1 K and peaks around 353 K. However, its intensity depends upon several factors such as particle size, moisture content and thermal history of the sample. The HEX → cubic [C] transition sets in around 405 K and shows two peaks at ~409 K and 413 K. Their relative intensities depend on the moisture content and thermal history of the sample. On cooling, the peaks show hysteresis and, by selective thermal cycling, the pairs of transitions, which correspond to the same process during heating and cooling, have been identified. IR spectra recorded in the OR and HEX phases at room temperature show that the symmetric stretching frequency (~ 1040 cm^{-1}) of the nitrate ion gets damped in the HEX phase. X-ray and optical microscopy data are in good agreement with the DSC observations.

INTRODUCTION

Thallous nitrate is shown [1] to exhibit two crystallographic phase transitions during heating, namely

$$\begin{array}{ccccc} \text{(III)} & \xrightarrow{\sim 350\ \text{K}} & \text{II} & \xrightarrow{\sim 416\ \text{K}} & \text{I} \\ \text{(orthorhombic)} & & \text{(hexagonal)} & & \text{(cubic)} \end{array}$$

It melts around 481 K. Major inconsistencies in the literature regarding the transition temperatures and the heats of transitions prompted us to undertake a detailed reinvestigation of this compound under thermal cycling. It has earlier been demonstrated [2,3] that thermal cycling of certain materials like KNO_3 or Na_2SO_4 brings out features such as the observation of additional transformations (metastable phases) or variation in the heats of transitions. Such fine features can be easily observed by DSC as compared to the conventional DTA.

We report here our observations on the phase transformations in $TlNO_3$ using DSC, X-ray, optical microscopy and IR.

EXPERIMENTAL

Materials

Thallous nitrate was prepared by dissolving thallous carbonate (Analar) in dilute nitric acid (Analar). The solution was then evaporated on a water bath to near dryness. The residue was recrystallized several times from water and dried over P_2O_5 in vacuum. These samples will henceforth be denoted as [A]. A small amount of this sample was taken in a tube and pumped under vacuum in the molten state for 7 h to dryness. It was then cooled to room temperature and stored in a dry box. These samples will be denoted as [B]. All the samples for the various measurements on [B] were prepared in nitrogen atmosphere in a dry box. The samples of [A] were prepared in the open.

Measurements

Differential scanning calorimetry (DSC)

All the measurements were done on a Perkin-Elmer model DSC 1B. The samples were normally powders ranging from 300 to 400 mesh and the amounts varied from 15 to 40 mg. The aluminium pans were crimped. The DSC curves were recorded in flowing dry nitrogen. The heating/cooling rate was 8° min^{-1} and the sensitivity varied from 1 to 32 mcal sec^{-1}. The transition temperatures quoted in this report are the peak temperatures.

X-Ray

Standard X-ray diffractometric techniques were employed. The measurements at higher temperatures were made using a high temperature attachment designed in our laboratory [4]. The temperatures were monitored by means of a chromel—alumel thermocouple.

IR

The IR spectra were recorded on a Perkin-Elmer 577 grating IR spectrometer.

Optical microscopy

A Leitz Ortholux-2 PolBK optical microscope with a Leitz 350 hot stage was used for this work. The heating/cooling rate was 2—3° min^{-1}.

RESULTS AND DISCUSSION

DSC and X-ray

Different batches of samples of [A] and [B] were subjected to detailed DSC scans. The results on samples [A] are as follows.

(i) Figure 1 shows a complete heating run. Qualitatively the transition temperatures and the relative intensity of their peaks appear very similar to

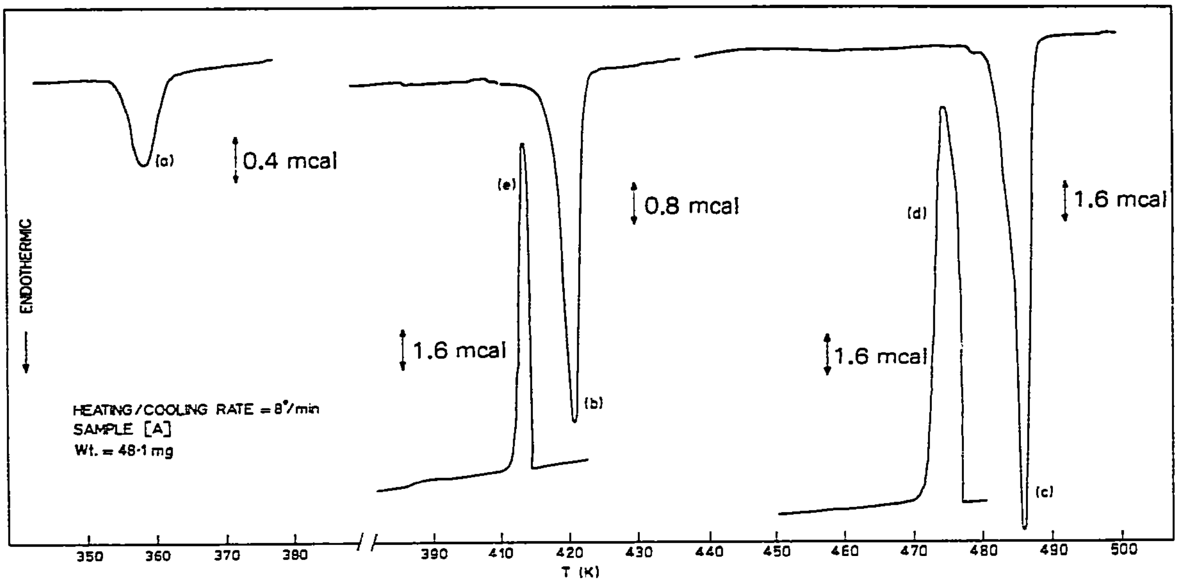

Fig. 1. Complete heating/cooling DSC runs for sample [A] of $TlNO_3$. Peaks (a), (b) and (c) are in the heating mode, (d) and (e) are in the cooling mode.

the DTA heating curve obtained by Clark and Reinhardt [1]. Figure 1 also shows a complete cooling run from 495 K to room temperature. Although both the heating and cooling runs give three peaks each, the sample does not recover to the room temperature OR phase on cooling, details of which will be discussed later. These results are summarized in Table 1. Fresh samples were then subjected to selective thermal cycles to establish the correspondence between the peaks obtained during the heating and the cooling runs.

(ii) Termination of the first heating at 365 K and cooling back to room

TABLE 1

DSC results on sample [A] of $TlNO_3$

Transition	Mode	Temperature (K)	ΔH (kcal mole^{-1})
OR → HEX	1st heating	358	0.13 ± 0.02
	1st cooling	No transition detected	
	Immediate 2nd heating	No transition detected	
HEX → C	1st heating	420.5	0.76 ± 0.01
	1st cooling	404.5(390) *	0.72 ± 0.01
	2nd heating	419.5(409) *	0.77 ± 0.01
	2nd cooling	404.5(390) *	0.73 ± 0.01
C → melt	1st heating	486	2.0 ± 0.1
	1st cooling	474.5	2.0 ± 0.1
	2nd heating	487	2.0 ± 0.1
	2nd cooling	475	2.0 ± 0.1

* The temperatures in parentheses show the position of the shallow peak or shoulder.

temperature did not show any transition; i.e., the sample did not recover from the HEX to the OR phase which was corroborated from the X-ray patterns recorded before and after the heating. However, it was reported [5] that the room temperature phase was recovered only after 12 h on keeping at room temperature. In order to understand this recovery behaviour, samples of totally different particle sizes as well as samples exposed to air for different lengths of time were studied. It was observed that the samples with coarse particle sizes recovered faster than those with extremely small (~400 mesh) particle sizes. The time taken for the complete recovery from HEX → OR at room temperature varied from 3 to 12 h.

In samples exposed to air for longer periods of time, the first transition appeared to be a composite one (at 355 and 359 K) both during the first and subsequent heating runs, but their relative intensities varied remarkably on the moisture content. It may be noted that in all cases the total area of the composite peak remained constant. In view of the above observation, it is possible that the spread in the transition temperatures in literature [1] could very well be due to such small differences in the moisture content in the samples.

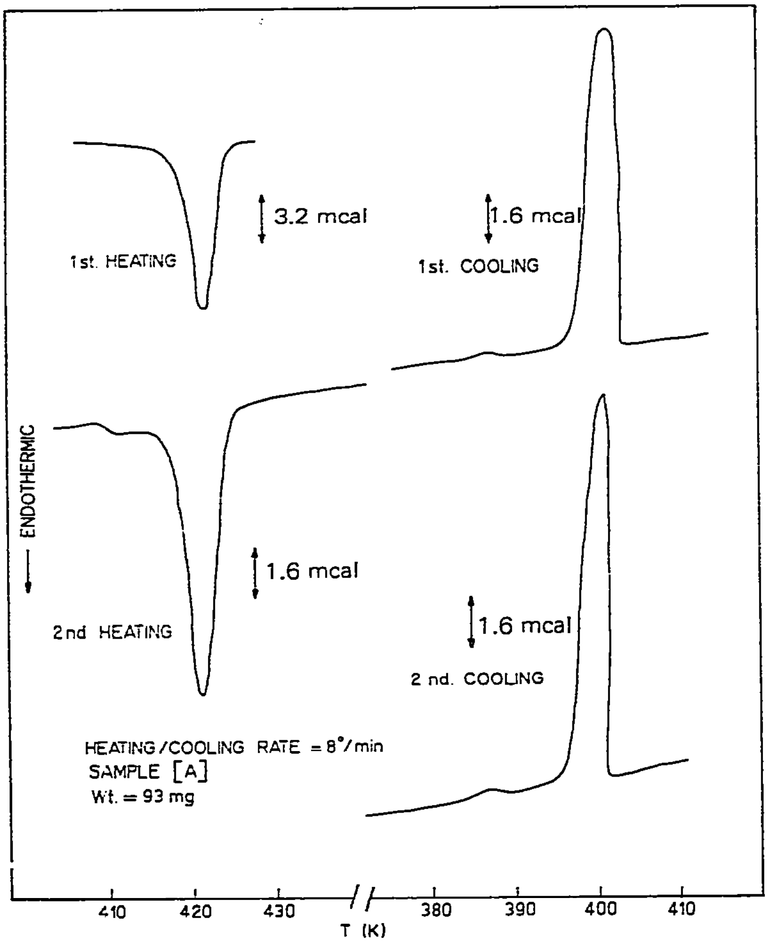

Fig. 2. Thermal cycling of the HEX → C transition for sample [A] of $TlNO_3$ in DSC.

(iii) Fresh samples [A] were thermally cycled through the HEX → C transition by heating them to 450 K and cooling back to room temperature. During the first heating, the transition sets in around 407 K and peaks around 421 K [cf. Fig. 2]. The peak is asymmetric on the low temperature side. On cooling, this peak showed a hysteresis of about 18° and became sharper and symmetrical around 403 K. A small shallow peak appeared around 390 K [cf. Fig. 2]. On second and subsequent heating the peak at 421 K became broader with a shallow shoulder around 408 K [cf. Fig. 2]. By suitable thermal cycling it was established that the shallow peak around 390 K during cooling and the shallow shoulder around 408 K are correlated.

The combined heats of transition during heating and cooling modes were 0.77 ± 0.03 and 0.73 ± 0.03 kcal/mole^{-1}, respectively. It may, however, be noted that the value of ΔH obtained during the cooling mode may be lower than the actual value due to the insignificant intensity of the shallow peak around 390 K, thus making the interpolation of the base line difficult.

(iv) The samples cycled around the melting point gave an average ΔH value of 2.0 ± 0.1 kcal mole^{-1} for melting. In order to eliminate the role played by at least one of the factors, namely, moisture (if any), measurements on the samples [B] were made. Previous workers [1] have dried samples at 120°C under vacuum for 24 h. We were unable to judge to what extent moisture could be removed by this treatment, since no DSC traces were presented by them.

The DSC results on samples [B] are summarized below.

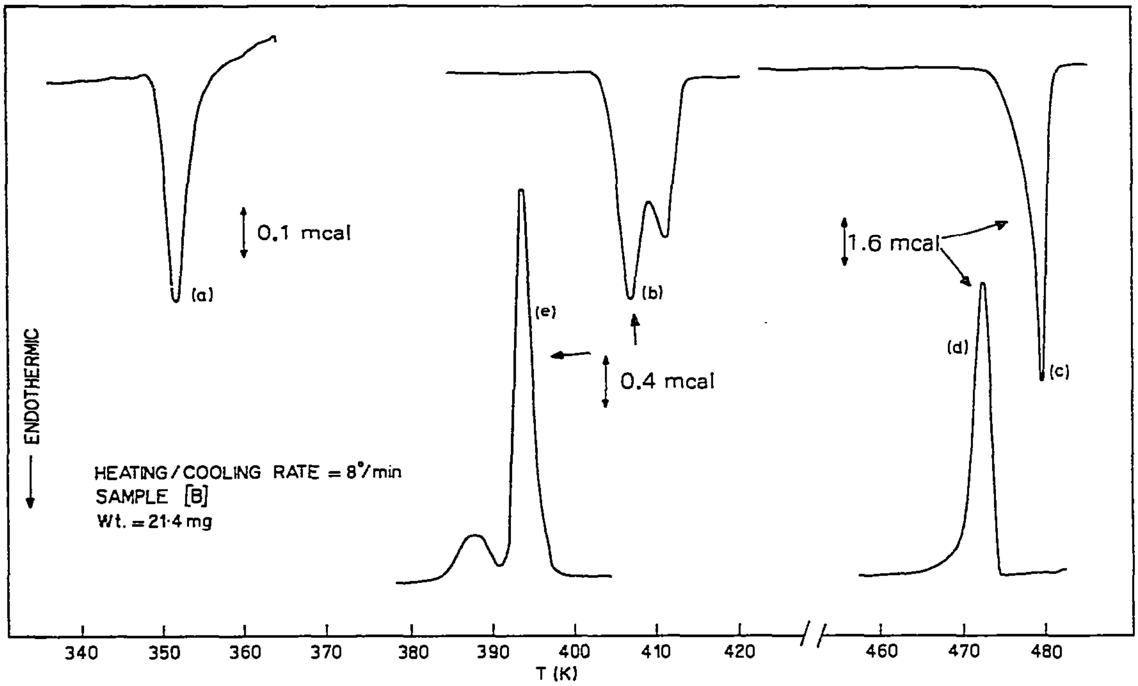

Fig. 3. Complete heating/cooling DSC curves for sample [B] of $TlNO_3$. Peaks (a), (b) and (c) are in the heating mode, (d) and (e) are in the cooling mode.

(i) Complete heating and cooling curves for samples [B] are shown in Fig. 3. All the transitions in sample [B] occur at lower temperatures as compared to those in samples [A]. The first peak corresponding to the OR → HEX transition is more symmetric and sharper in samples [B]. The asymmetric peak (421 K) in [A] developed into a very well resolved doublet in [B] at 408 K and 412 K, with hysteresis remaining the same as in [A]. However, in contrast to the observations in samples [A], there is an intensity reversal between the components of the HEX → C transition during the heating and cooling cycles. This feature is shown in Fig. 4.

In order to confirm the above observation, samples of [A] were taken in uncrimped Al pans in the DSC apparatus so that when heated the moisture would escape with the flowing nitrogen. The samples were heated to melting in the DSC apparatus. The first heating and cooling runs were identical to those shown in Fig. 1. On subsequent melting of the sample and cooling, the

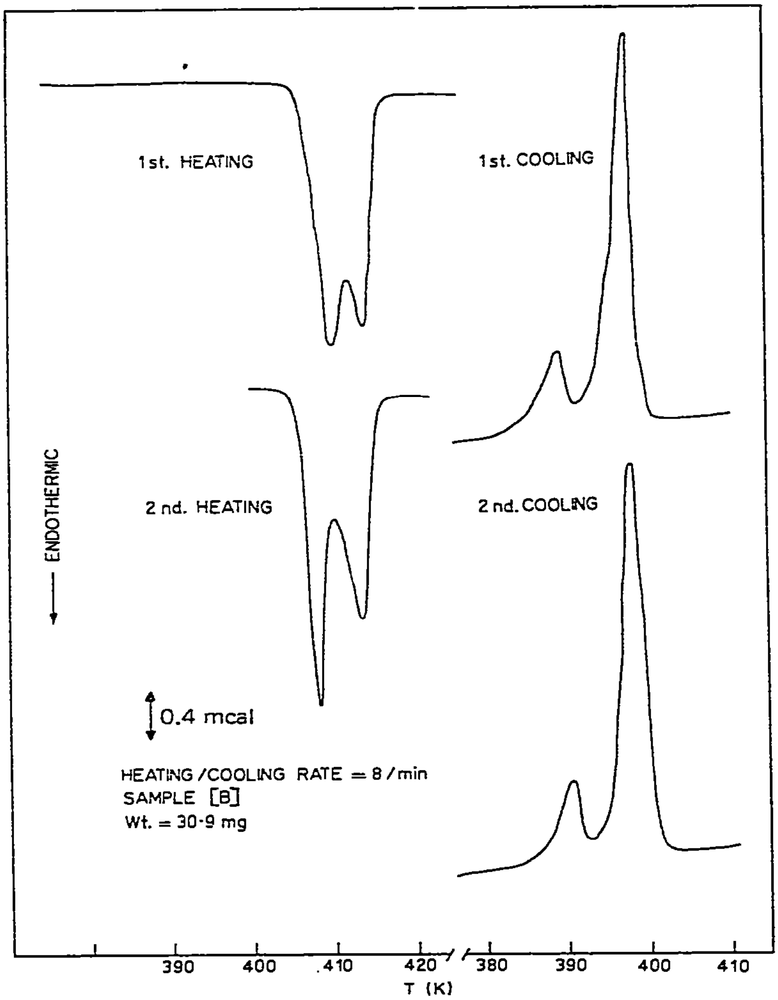

Fig. 4. Thermal cycling of the HEX → C transition for sample [B] of $TlNO_3$ in DSC.

TABLE 2

DSC results on sample [B] of $TlNO_3$

Transition	Mode	Temperature (K)	ΔH (kcal mole^{-1})
OR → HEX	1st heating	351.5	0.12 ± 0.02
	1st cooling	No transition detected	
	Immediate 2nd heating	No transition detected	
HEX → C	1st heating	409.5, 413.5	0.75 ± 0.01
	1st cooling	389, 396.5	0.70 ± 0.01
	2nd heating	408, 413	0.74 ± 0.01
	2nd cooling	390, 398	0.70 ± 0.01
C → melt	1st heating	480.5	1.9 ± 0.1
	1st cooling	473.5	1.9 ± 0.1
	2nd heating	480	1.9 ± 0.1
	2nd cooling	473	1.9 ± 0.1

peak ~421 K in the initial moist samples shifted to ~414 K, with the peak ~408 K growing at the cost of the main peak. By this it was not possible to obtain the well resolved doublet or the intensity reversal as in [B]. However, it is clear that moisture does play a very significant role in these transitions. The melting peak (~480 K) was much sharper in [B] than in [A]. The ΔH values and the transition temperatures are listed in Table 2.

(ii) The recovery of the HEX → OR phase in samples [B] was then studied in detail. In well powdered (400 mesh) samples of [B] heated up to 370 K and cooled back to room temperature, it was observed that the OR phase did not recover completely even after several days, as measured by DSC and X-ray. However, in much coarser samples the recovery was faster and varied between 1 and 12 h. Even in well powdered samples, if heated beyond the melting point and cooled back to room temperature, the OR phase recovered relatively quicker, as evidenced both in the DSC and X-ray measurements.

(iii) DSC runs between 180 and 300 K did not show any phase transitions as has been reported earlier [6].

Optical microscopy

The use of optical microscopy in the study of phase transitions was demonstrated in the case of Na_2SO_4 [7]. A tiny single crystal of $TlNO_3$ subjected to the same drying process as in [A] was examined under crossed polars at 45° position on a hot stage of the microscope. The thickness of the crystal was such that at room temperature it was pale yellow. At about 348 K polarization colours developed and changed rapidly at 352 ± 0.5 K, suggesting the onset of a crystallographic phase transition. On further heating, the polarization colours developed at about 413 K and quickly changed at 421 ± 0.5 K to give a colourless isotropic solid. On cooling, brilliant polarization colours appeared at 413 ± 0.5 K. Both the 421 K and 413 K transitions in the heating and cooling modes, respectively, were highly reproducible. This is consistent with the DSC results on samples [A].

The melting point of the isotropic material was found to be 482 ± 0.5 K. It was not possible to determine the freezing point accurately due to poor contrast of the isotropic solid phase resulting from the melt.

IR

The IR spectra (4000—200 cm^{-1}) in Nujol mull in the OR phase agrees very well with those reported earlier [8—10]. The relevant sections of the spectra with their assignments are shown in Fig. 5. ν_1, ν_2, ν_3 and ν_4 are the totally symmetric stretching, out-of-plane, the doubly degenerate stretching, and the bending modes of the nitrate ion, respectively. After recording the spectra at room temperature, the sample with the sample holder was heated to 370 K in an oven for 1 h. It was then taken out, cooled to room temperature, and the spectra were recorded immediately. The spectra shown in Fig. 5 indicates that the bands at ~1040 cm^{-1}, ~2670 cm^{-1} and the doublet at 2420 cm^{-1} and 2320 cm^{-1} in the OR phase get damped in the HEX phase as is evident from their intensities. It may be recollected that the HEX phase has a sluggish recovery for very fine particles as seen from our X-ray and DSC measurements. The IR mull has very fine powder (~400 mesh) dispersed in it. Such a damping of the symmetric stretching frequency has also

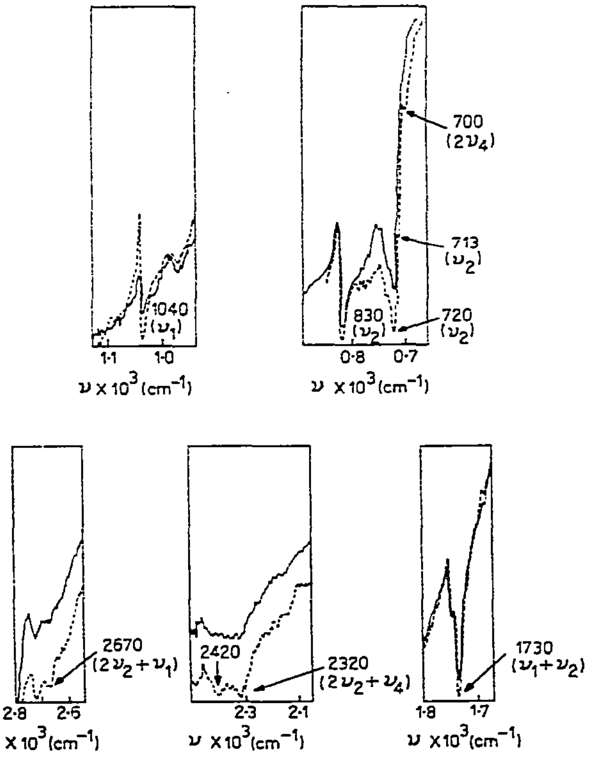

Fig. 5. IR spectra of sample [B] in the OR and HEX phases. (———), HEX phase; (- - - - -), OR phase.

been observed in the case of KNO_3 as it passes from the OR to trigonal phase [11].

CONCLUSIONS

From the above discussions it is seen that thallous nitrate passes through two principal phase transitions in addition to fusion. Both these transitions involve more than one step, an aspect which was completely missed in earlier investigations. The first transition, i.e., OR → HEX is not reversible for extremely fine particle sizes and anhydrous conditions, whereas in the case of coarser particles and in the presence of moisture the transition is reversible and time dependent. Such a physical effect on the stability of the polymorph has also been demonstrated in the case of ZrO_2, where the high temperature tetragonal phase could be made stable, indefinitely at ordinary temperatures if the particle size is small [12]. The effect of particle sizes on phase transformations in KNO_3 [13—15] or the presence of "residual paramagnetism" in systems exhibiting a high spin ⇌ low spin crossover [16,17] has also been observed. The stabilization of a high temperature phase at room temperature is probably due to the excess surface energy of the small particle size samples.

During the thermal cycling, in the case of $TlNO_3$, the HEX → C transition shows up as a composite peak both during the heating and cooling modes. However, in anhydrous samples the intensities of the components show an intensity reversal. This has been found to be sensitive to moisture.

The role of moisture in these transitions is to inhibit the low temperature component of the composite peak, thereby causing a superheating of the sample so that both the processes occur simultaneously at higher temperature (as in samples [A]). It may also be concluded that moisture enhances or reduces one of the processes during the phase transformation at the cost of the other. Such a catalytic effect of moisture in the phase transitions is also known in NH_4NO_3 [18].

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