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Thermal dehydration of lithium sulfate monohydrate. The reaction reversibility and the solid product morphology

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Abstract

Local reversibility caused by a reactant (lithium sulfate monohydrate) crystalline skeleton kept after removal of water molecules ("vacancy structure") was studied via dehydration/rehydration cycles repeated under the same conditions. The dehydration reversibility observed indicates the stability of the "vacancy structure". Solid product morphology was studied using electron microscopy. The initial crystal of $Li_2SO_4 \cdot H_2O$ decomposed in the course of dehydration, and thus the reaction zone, consisted of isolated microcrystalline "blocks".

Keywords: Dehydration; Lithium sulphate; Reversibility

1. Introduction

Observations of changes in the reaction zone of solid-phase transformations involve several problems. Methods for directly measuring the reaction zone dimensions, both its depth and the expansion of the reaction surface, have not yet been developed, although some progress has been made in this area [1].

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In order to understand how the reaction zone of solid-phase transformations forms, extended investigations were performed [2–5] which give rise, among others, to the idea that partial removal of gaseous product molecules during thermal decomposition

$$(AB)_s \rightleftharpoons A_s + B_g$$

leads to the formation of the so-called "vacancy structure". Here, vacancies are assumed to appear in the reactant crystal lattice as a result of water loss, their concentration being far above the thermodynamic equilibrium value. This insight was based on experimental data [2–4] and, later, gave impetus to theoretical mechanistic studies of the propagation of thermal decomposition fronts [5–8].

According to the current approach, vacancies are believed to generate stresses, and their accumulation leads eventually to destruction of that part of the crystal where the ultimate stress is reached. As a result of such destruction microcrystalline "blocks", separated by cracks and voids, appear and keep undergoing dehydration. Reactant structure with a vacancy concentration as high as 100% in the transition layer (quasi-zeolite structure) is responsible for the reversibility of reaction within the reaction zone without essential structural rearrangement. Such a localized reversibility through a "vacancy structure" was observed for alum dehydration [9].

Among the aims of this work was to continue studies of this complex phenomenon with the dehydration of $Li_2SO_4 \cdot H_2O$. As demonstrated before, the reversibility of dehydration of this compound in the above terms occurs until the conversion becomes total [10]. Another aim was to examine the morphology of the reaction solid product.

1.1. *Reversibility of lithium sulfate monohydrate dehydration*

As shown by X-ray studies, dehydration of the above compound occurs through a transition state, the reactant structure being unchanged until the degree of conversion reaches 0.3 [11]. With the particle size specified in this paper (0.1–0.3 mm) the thickness of product layer corresponding to this conversion is estimated as ≈ 0.03–0.1 mm. New data supporting the formation of the "vacancy structure" were later obtained when observing reactant transformation during the reaction by means of a "diffraction movie" technique [12]. The reversibility may be estimated to some extent by studying the dehydration/rehydration of powdered $Li_2SO_4 \cdot H_2O$ during repeated dehydration cycles under the same conditions. (Similar investigations of the reversible release of ammonia were described in [13].)

2. Experimental

Powders used in the experiments were prepared from commercial $Li_2SO_4 \cdot H_2O$ of "chemical purity" grade. The preparation procedure involved disintegration in a centrifugal ball mill for 5 min, i.e. a procedure similar to that described in [14]. The particle sizes were measured using an electron microscopic technique. The major particle size was found to be 0.4–0.5 μm. Reversibility was studied for 20 dehydration/rehydration cycles, which differed from each other by the duration of the rehydration step (several hours through 4 days). Rehydration was performed in a desiccator at ambient temperature over a buffered NaOH solution; the solution was prepared taking into account the equilibrium water vapour pressure over the reactant, calculated using [15]

$$\lg(p/(\mathrm{Torr})) = 10.7587 - 3149/T$$

Dehydration was studied within the temperature range 298–473 K at a heating rate of 5 K min^{-1} using a Paulik–Erdey–Paulik derivatograph.

The experiments showed that the water content was completely regained in ≈ 17 h after dehydration of the substance under study. No variations of the temperature (387–388 K) corresponding to a maximum dehydration rate, the rate itself, or the amount of released water were observed for at least 20 dehydration/rehydration cycles (Figs. 1(b)–(d)) from run to run.

2.1. Morphological studies

Electron microscopic observations confirmed that the initial $Li_2SO_4 \cdot H_2O$ crystal was destroyed during dehydration. There were two directions of the investigation: (1) studies of freshly prepared cleaved surfaces after partial dehydration under isothermal conditions in vacuo, and (2) morphological studies of a solid product formed under the same reaction conditions.

(1) As a result of partial dehydration, cracks appear on cleaved surfaces normal to [010] (Fig. 2). "Blocks" with apparent interfaces form in the process (dehydration was achieved at 333–363 K for 1 h in each run). The average block size is slightly dependent on temperature; statistical analysis of the microscopy data shows it to be equal to 50–70 μm. If the sample is left longer in the reactor, the blocks undergo further cracking to generate smaller fragments, down to 1–2 μm in size (Fig. 3).

(2) The results of morphological studies of the solid product obtained by dehydration of single crystals in various crystallographic directions are presented in Figs. 4–6. Obvious product particles and a "product–reactant" interface are seen here.

The crystallographic orientations of the samples ((010) and (101) planes) were chosen because they represent the anisotropy of the reactant crystal structure. Just before the microscopic studies the samples were fractured normally to the direction of the interface propagation; the cleaved surfaces so obtained were flat and smooth, with no visible imperfections.

2.2. Genesis of local reversibility

The reversibility of the reaction $(Li_2SO_4 \cdot H_2O)_s \rightleftharpoons (Li_2SO_4)_s + (H_2O)_g$ may be connected with the retained skeleton of the reactant crystal lattice even after releasing water molecules. As a result, the surrounding water molecules become capable of re-insertion into vacancies to reproduce the initial solid structure. The reaction reversibility will thus depend on the stability of the "vacancy structure" mentioned above. The kinetic behaviour of dehydration, which is observed to be unchanged during repeated experiments, indicates the stability of the structure.

The idea that this "vacancy structure" causes the cyclic reversibility is supported by Fig. 1(e). The same sample as used before to study dehydration/rehydration cycles (Figs. 1(b)-(d)), but "crystallized", was dehydrated again. Judging from the XRD data, the "vacancy structure" was no longer observed. The "crystallized"

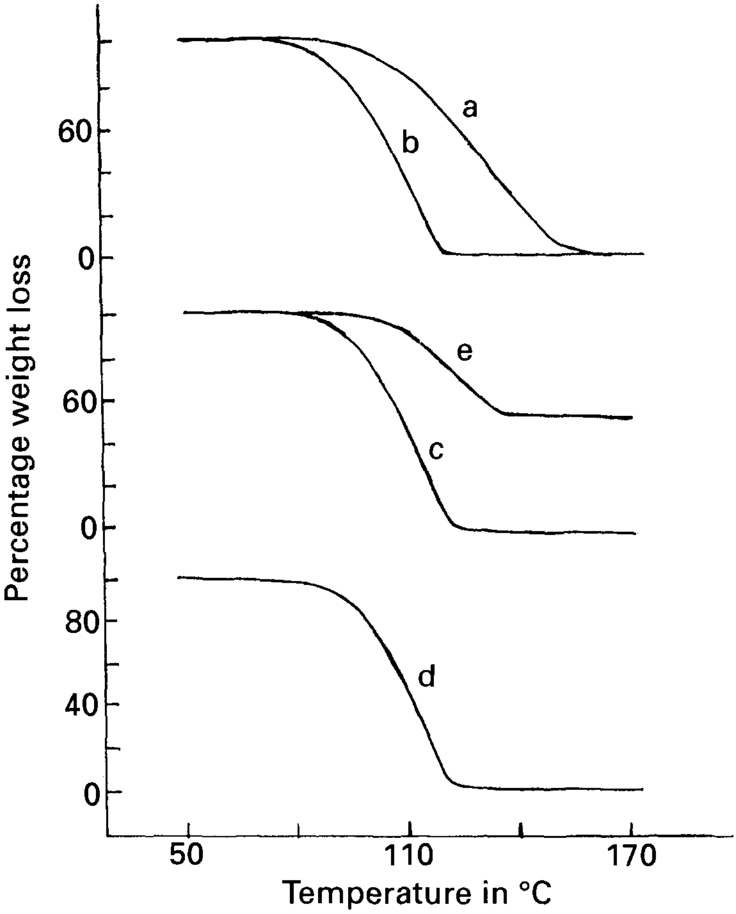

Fig. 1. Changes in the weight upon dehydration of $Li_2SO_4 \cdot H_2O$: (a) the reactant powder was not pre-milled; (b), (c), (d) dehydration cycles of the pre-milled reactant powder (the majority of particles being 0.4-0.5 μm in size): (b) first cycle; (c) ninth cycle (exposed to water vapour for 17 h before dehydration); (d) eighteenth cycle (kept in water vapour for 19 h); (e) the same sample as in (b), (c) and (d), but "crystallized" after studies of dehydration/rehydration cycles were complete (according to XRD data, the pattern corresponding to the "vacancy structure" was not observed). Exposed to water vapour for 17 h before dehydration.

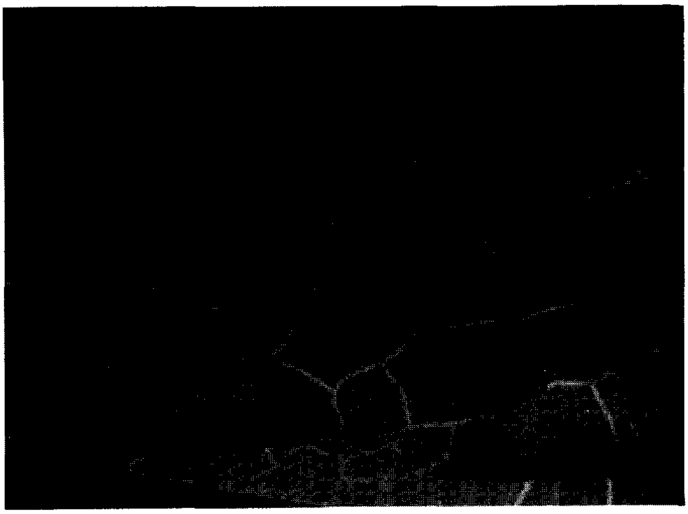

Fig. 2. Cracking of the cleaved surface of $Li_2SO_4 \cdot H_2O$ single crystal after dehydration. $T = 353$ K, duration of the experiment ≈ 1 h.

sample (i.e. the sample taken after complete restructuring into a final, waterless, product) was exposed to water vapour for ≈ 17 h. This period corresponds to that of complete rehydration of the "vacancy structure" (Fig. 1(c)). With the "crystallized" sample, rehydration was less than half complete during this period and the shape of the kinetic curve was rather different from that shown in Figs. 1(b)-(d).

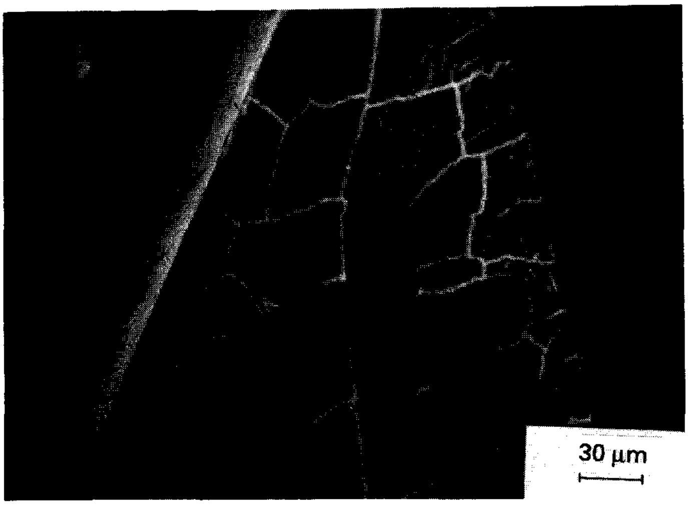

Fig. 3. Destruction of the cleaved surface followed by the formation of smaller fragments after ≈ 2 h; $T = 353$ K.

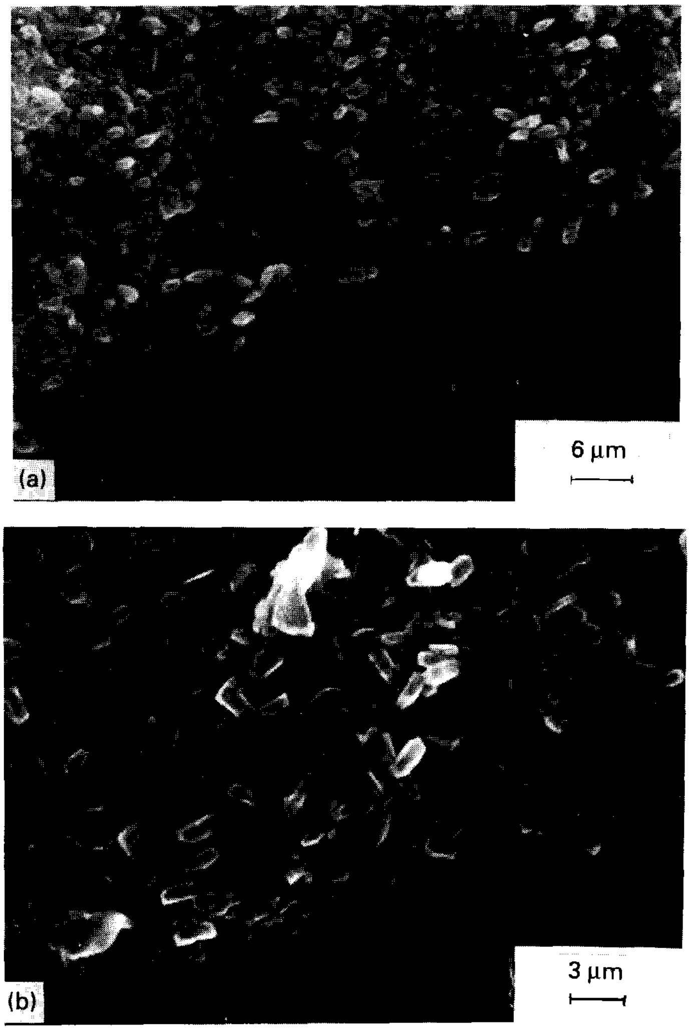

Fig. 4. The "product–reactant" interface (a) and product morphology after single crystal dehydration. (b) The sample was broken normally to a (010) plane. $T = 353$ K, experiment duration 3 h.

It should be emphasized that, when a single crystal is decomposed to form blocks during the reaction, the kinetic reproducibility (beginning from a first dehydration cycle) can be obtained only with powders of particle size no larger than that of a minimum microcrystalline block. As suggested in [7], the size of a particle resulting from crystal cracking is governed by the elastic parameters of the crystal, and no further destruction of the minimum sized particles is observed. The size of the majority of particles in the powder used for the study of reversibility was no more than 0.4–0.5 μm from the outset, owing to preliminary milling (electron microscopic data [14]). Therefore, the particles were no larger than the minimum "blocks" formed as a result of destruction of the single crystals (0.5–1 μm). This may be why particles of the sample under study were not cracked, even after repeated dehydration, and the reaction surface did not change during dehydration.

To verify these observations, test experiments were performed under the same conditions but the powder used was not pre-milled. Dehydration of such a powder proceeds in a different way: over a wider temperature range (353–433 K) and with the maximum rate reached at 408 K (Fig. 1(a)). The distinction is easily explained, as particles of various sizes, mostly larger (>100 μm), are involved in the reaction; in this case, changes in the rate and time of dehydration appear, and an endothermic peak in DTA shifts to higher temperature. In subsequent cycles the kinetics are not reproduced, but the kinetic behaviour of this sample and that of the pre-milled powder (Figs. 1(b)–(d)) become identical. Evidently there is "chemical" comminution of the powder in the reaction zone, and particles formed as a result of the reaction are not decomposed further.

Thus, not only is the "vacancy structure" formed stable, but also the sizes of blocks produced by the destruction of a single crystal are responsible for the dehydration kinetic behaviour.

2.3. Morphological features of the solid product

In the case under consideration, the relaxation of internal stresses due to the formation of the "vacancy structure" proceeds through cracking of the initial crystal along cleavage planes; these are the (101), (100), (110) planes [16]. As a consequence, particles of the partially dehydrated reactant appear in the reaction zone. Most likely these "blocks" can further break down into smaller fragments until the minimum size of particles is attained.

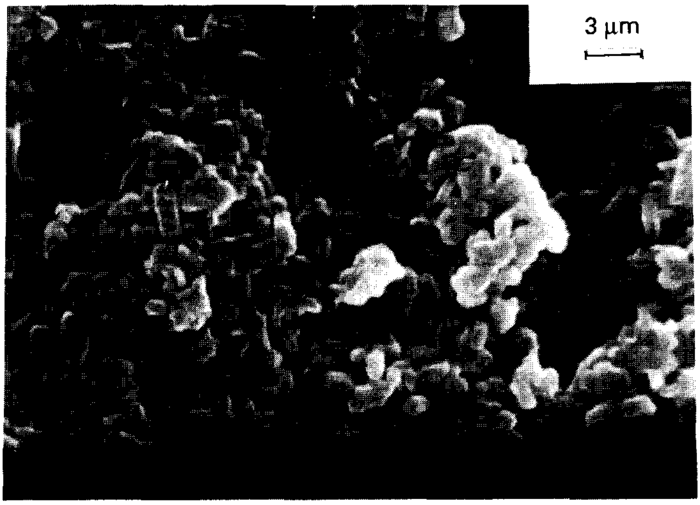

Fig. 5. Dehydrated product for a sample of (101) crystallographic orientation under reaction conditions as in Fig. 4. The sample was broken normally to the studied plane.

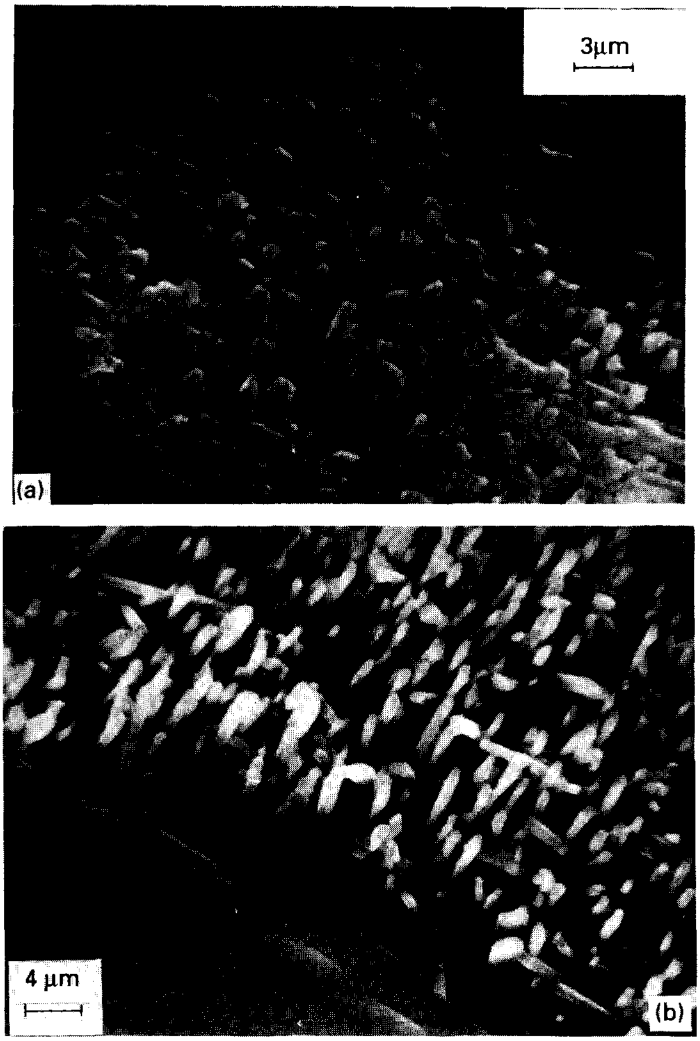

Fig. 6. The same crystallographic orientation of the sample as in Fig. 5, but the product particles are different in appearance. Moreover, the product morphology for (a) differs from that for (b), despite the same experimental conditions: dynamic vacuum $\approx 6 \times 10^{-5}$ Pa, $T = 353$ K.

As seen from micrographs (Figs. 4 and 5), most of the particles formed have elongated shape ("parallelepiped"). Their minimum dimensions are ≈ 0.5 μm. Product particles resulting from dehydration of the samples at the (101) crystallographic plane look like ordered ones (they are mainly "packed" in two perpendicular directions; see Figs. 5 and 6). Nothing like this is observed with dehydration from the (010) plane (Figs. 4(a), (b)).

Dehydration of two (101) orientated samples (Figs. 5 and 6) resulted in the formation of particles which differ from each other by their dimensions and shapes, though the principal features of product shape are the same in both cases.

Again, an exciting point is that product particles which differ somewhat from each other in their appearance and dimensions are formed as a result of the same sample dehydration (Figs. 6(a), (b)). This seems to be connected with an inhomogeneity throughout the reaction zone which, in its turn, can be attributed to different defects present in various parts of the initial crystal.

The most important results of this investigation are

(1) reversibility within the reaction zone (local reversibility) is possible due to the partial stability of the "vacancy structure". Moreover, this phenomenon itself is additional evidence in favour of reaction development through the "vacancy structure" formation;

(2) the reaction zone of $Li_2SO_4 \cdot H_2O$ dehydration was found (a) to form through the initial crystal destruction connected with instability of the "vacancy structure", owing to accumulation of elastic stresses during the reaction, and (b) to possess, as a consequence, a "block" structure. Some differences in "block" sizes observed for the same sample are likely to be a result of inhomogeneity within the reaction zone.

The results obtained are in good agreement with the model of thermal decomposition proceeding through "vacancy structure" formation [2–5].

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