

The Dehydration of $\text{CuSr}_2(\text{HCOO})_6 \cdot 8\text{H}_2\text{O}$: A Crystallographic Study

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The isothermal dehydration of $\text{CuSr}_2(\text{HCOO})_6 \cdot 8\text{H}_2\text{O}$ single crystals as well as powdered material has been followed by several techniques, mainly X-ray diffraction and optical microscopy. Evidence was found of a two-stage process, with an early appearance of an amorphous state (attributed to internal dissolution) and further recrystallization of the stable phases. One of these ($\text{CuSr}(\text{HCOO})_4$, monoclinic, P_c , $Z = 2$, $a = 7.345(10) \text{ \AA}$, $b = 8.692(15) \text{ \AA}$, $c = 6.702(10) \text{ \AA}$, $\beta = 97.25(5)^\circ$) has not been reported so far in the literature. When dehydration takes place near room temperature, the remaining product ($\text{Sr}(\text{HCOO})_2$) bears a topotactic relationship to the parent matrix ($\langle(hk0)\rangle/\langle(hk0)'\rangle$; $\langle(0k0)\rangle/\langle(0k0)'\rangle$). A striking metric match between both $(hk0)$ sections, as well as the absence of any common structural motive, suggest an inner epitactic growth as the most probable mechanism for the transformation.

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Introduction

The crystal structure of $\text{CuSr}_2(\text{HCOO})_6 \cdot 8\text{H}_2\text{O}$ (hereafter CSFH) has been recently reported (1). Among other features, the structural work shows the existence of two types of water molecules; viz. the ones strongly held to the Sr atoms through direct coordination and those loosely attached to the structure through rather weak hydrogen bonds. The fact that neither the anhydride nor any lower hydrate has been reported supports the assumption that both types of water molecules must play an important role in stabilizing the structure.

As a result, CSFH is expected to decompose on dehydration into simpler, more stable anhydrous products. We present here a crystallographic study of this process, as well as the relationship between parent and product structures.

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Experimental

CSFH single crystals are easily obtained by slow evaporation at room temperature of a 20% formic acid solution of SrCO_3 and CuCO_3 , in a 2:1 molar ratio. On standing, well-developed single crystals appear, predominantly in the form of triclinic (010) platelets. When evaporation is performed above 45°C , however, a two-phase segregation takes place, with an early precipitation of $\text{Sr}(\text{HCOO})_2$ (hereafter SFA) in the form of white prisms, and the late appearance of deep-blue crystals corresponding to a new phase.

Chemical analysis, as well as single-crystal X-ray diffraction work showed the new phase to be an anhydrous double salt, $\text{CuSr}(\text{HCOO})_4$ (hereafter CSFA), with a different Cu/Sr ratio than the room-temperature hydrate and which could not be traced in the literature. Table I shows the

TABLE I
CRYSTAL DATA FOR $\text{CuSr}(\text{HCOO})_4$

M.W.: 331.2
Monoclinic, P_c , $Z = 2$
$a = 7.345(10) \text{ \AA}$
$b = 8.692(15) \text{ \AA}$
$c = 6.702(10) \text{ \AA}$
$\beta = 97.25(5)^\circ$
$V = 424.4 \text{ \AA}^3$
δ_{obs} (pycnometric) = $2.60(1) \text{ g/cm}^3$;
$\delta_{\text{cal}} = 2.591 \text{ g/cm}^3$

complete crystal data and Table II an indexed powder diagram.

Thermal Behavior

The transformation of CSFH single crystals was followed on a heating stage under an $80\times$ stereoptical microscope for single crystals. Powdered material was studied in a X-ray goniometer, with $\text{CuK}\alpha$ radiation. Several samples were subjected to isothermal treatment up to constant weight. Temperatures ranged from 120 to 40°C and processing times from 15 min to 50 hr.

The results of many such observations can be summarized as follows:

(1) The early stages of higher temperatures dehydration ($90\text{--}120^\circ\text{C}$) consisted in the release of water molecules in the innermost parts of the crystal, leading to the formation of a syrup-like solution confined by an outer, very thin solid shell. Sometimes, this solution managed to drip out through some crack in the external wall, but more often than not it was kept tightly enclosed, and then from the external appearance nothing suggested the kind of process that was taking place inside. It was only through puncturing the very thin, solid shell that the internal dissolution became evident.

(2) Further heating resulted in increasing opacity of the sample, with a gradual change to a reddish brown color. The diminishing of water content was accompa-

nied by the recrystallization of the now supersaturated solution. As previously observed in crystal-growth experiments from a saturated solution at similar temperatures, there was an early appearance of $\text{Sr}(\text{HCOO})_2$, as myriads of tiny, well-developed crystallites (Fig. 1a) and a late precipi-

TABLE II
OBSERVED AND CALCULATED
SPACINGS (\AA), NORMALIZED
INTENSITIES AND ASSIGNED
INDICES FOR THE X-RAY
POWDER DIFFRACTOGRAM OF
 $\text{CuSr}(\text{HCOO})_4$
(DIFFRACTOMETRIC, $\lambda(\text{CuK}\alpha) =$
 1.54178 \AA)

d_{obs}	d_{cal}	I/I_0	hkl
5.58	5.58	64	110
5.26	5.28	50	011
4.07	4.08	1	111
3.72	3.73	3	120
3.63	3.64	11	200
	3.64		021
3.35	3.35	4	$12\bar{1}$
3.32	3.32	4	002
3.15	3.15	100	$21\bar{1}$
2.97	2.99	31	$11\bar{2}$
2.88	2.89	6	$10\bar{2}$
2.62	2.63	17	$20\bar{2}$
2.51	2.51	5	$21\bar{2}$
2.33	2.34	3	310
2.19	2.19	5	$30\bar{1}$
	2.19		$10\bar{3}$
	2.19		$23\bar{1}$
2.135	2.132	13	$11\bar{3}$
2.116	2.120	2	320
2.092	2.091	1	$30\bar{2}$
2.085	2.087	3	$32\bar{1}$
2.044	2.046	5	132
	2.043		$22\bar{2}$
2.031	2.033	7	$31\bar{2}$
1.953	1.958	19	$21\bar{3}$
	1.958		$23\bar{2}$
1.859	1.861	10	330
	1.854		123
	1.853		302
1.754	1.758	7	213
	1.752		$13\bar{3}$

Cutoff at $d = 1.500 \text{ \AA}$

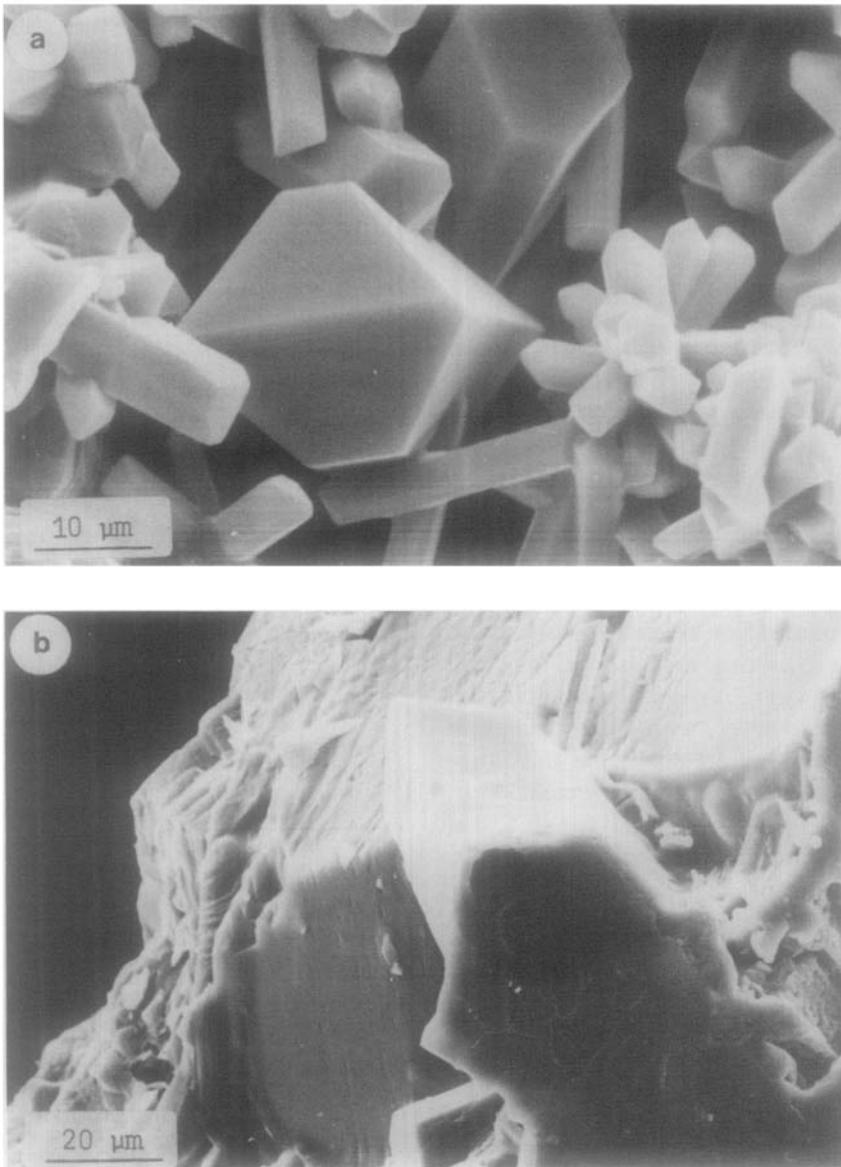


FIG. 1. (a) SEM micrograph of the core of a completely transformed CSFH sample, showing perfectly developed SFA single crystals. (b) An outer part of the same specimen showing SFA single crystals covered by a late precipitation of CSFA.

tation of CSFA, cementing the former together (Fig. 1b). Both phases were identified by means of powder X-ray diffractograms. SFA crystals appeared slightly reddish in color, probably due to some Cu contamination, as detected by

EDAX. Another striking feature was the fact that SFA crystallites did not appear to grow at random, but a moderate correlation between their orientations could be observed.

(3) Lower temperature treatments (60–

90°C) led to a honeycomb-like structure with the solution trapped in the small cavities bridged by solid material. Complete dehydration of these structures led to SFA crystallites showing a much stronger corre-

lation. The lower the temperature, the stronger the spatial correlation observed (Figs. 2a and b).

(4) CSFA could only be traced down to 45°C. Below this temperature, only SFA

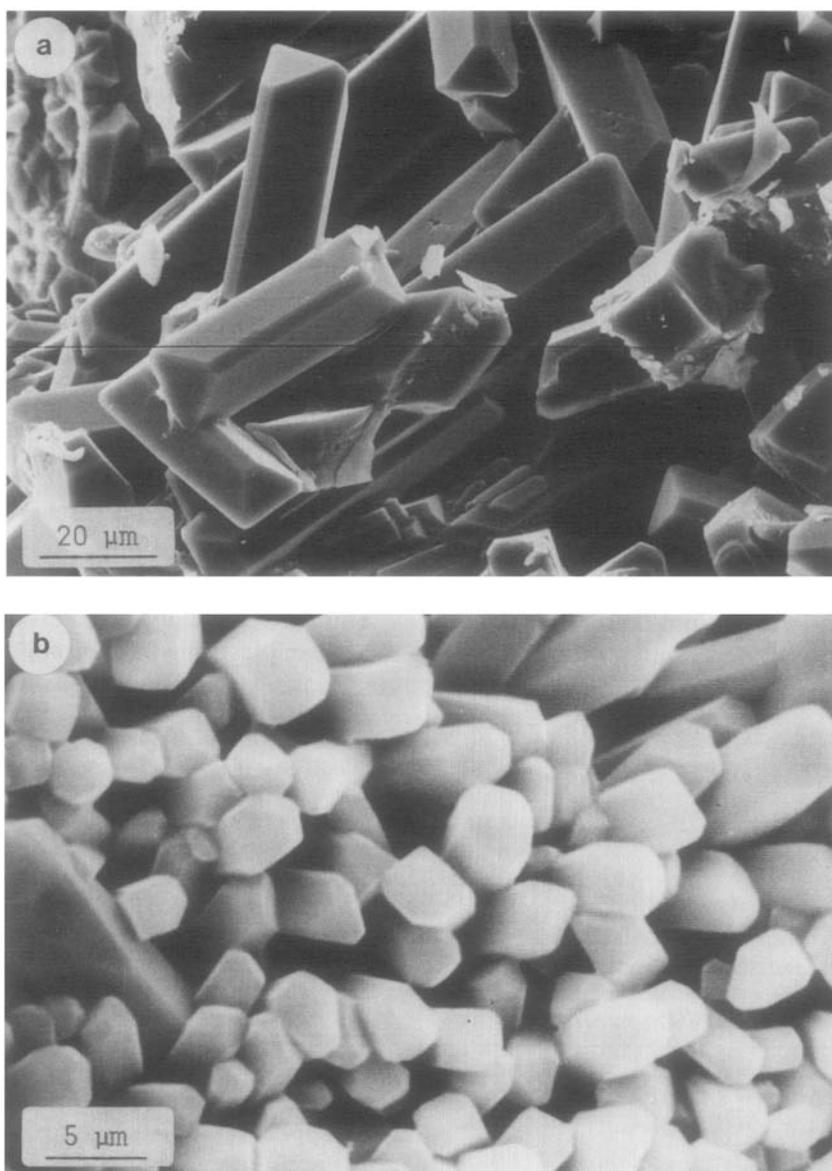


FIG. 2. SEM micrograph showing relative orientation of SFA crystallites. (a) Random orientation (transformation temperature 120°C). (b) A nearly ordered arrangement (transformation temperature 70°C).

was detected in a crystalline form. Correlation was now so good as to make the whole aggregate diffract as a single crystal, with a minimum spread. In crystals not fully transformed, both coexistent lattices, (parent and product) were found to have a fixed (topotactic) relationship.

The Topotactic Transformation

To study this topotactic relationship a bit further, a systematic X-ray study of the transformation of single crystals of CSFH, near room temperature was undertaken. It was found that the probe ($\text{CuK}\alpha$ radiation) also acted as nucleating agent, accelerating the process so as to render studies at about 45°C feasible (complete transformation for previously irradiated crystals takes place in about 3 days, against 6 to 8 weeks for virgin samples). The work was performed at $T \approx 45^\circ\text{C}$ in a precession camera provided with a heating device, and the results of many trials in different crystals are reported in Table III.

The relative orientation of the two phases in direct as well as in reciprocal space are shown in Fig. 3 and summarized in the following relationships:

in reciprocal space:

$$(h0l)_{\text{CSFH}}^* // (h0l)_{\text{SFA}}^*, (00l)_{\text{CSFH}}^* // (00l)_{\text{SFA}}^*$$

and

TABLE III

CRYSTALLOGRAPHIC PARAMETERS FOR THE
TOPOTACTICALLY RELATED PHASES

CSFH (1)	SFA (2)	Topotactic phase
$a = 6.61(1) \text{ \AA}$	$a = 6.874(1) \text{ \AA}$	$a = 6.86(2) \text{ \AA}$
$b = 8.84(1) \text{ \AA}$	$b = 8.748(1) \text{ \AA}$	$b = 8.76(2) \text{ \AA}$
$c = 8.90(1) \text{ \AA}$	$c = 7.267(1) \text{ \AA}$	$c = 7.26(2) \text{ \AA}$
$\alpha = 104.5(1)^\circ$		
$\beta = 96.0(1)^\circ$		
$\gamma = 88.5(1)^\circ$		
$P\bar{1}$	$P2_12_1$	$P2_12_1$

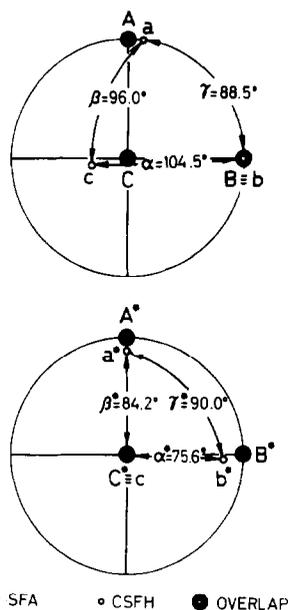


FIG. 3. Schematic stereographic projections showing the relative orientations of both direct and reciprocal lattices of topotactically related CSFH and SFA.

in direct space:

$$\langle 0k0 \rangle_{\text{CSFH}} // \langle 0k0 \rangle_{\text{SFA}}, (hk0)_{\text{CSFH}} // (hk0)_{\text{SFA}}$$

This was the only orientation found in many samples transformed under different conditions.

Discussion

The results presented so far can be briefly summarized as follows: $\text{CuSr}_2(\text{HCOO})_6 \cdot 8\text{H}_2\text{O}$ (CSFH) decomposes under thermal treatment into $\text{CuSr}(\text{HCOO})_4$ (CSFA) and $\text{Sr}(\text{HCOO})_2$ (SFA), if the temperature is high enough as to render the former stable. The process is clearly one of internal dissolution and recrystallization, and closely resembles the behavior of mother liquors at the same temperature. At lower T , only SFA appears in crystalline form.

Different temperature treatments disclosed two main features:

(1) The generalized internal dissolution process which takes place at higher temper-

ature (90–120°C), changes into a localized one at lower T (60–90°C) giving rise to a honeycomb-like structure with the saturated solution trapped in the small holes supported by solid material.

(2) There is a decreasing randomness in SFA crystallites orientation at lower transformation temperatures.

This seems to be in qualitative agreement with the dehydration behavior of CSFH as studied by DTA (1). Above 100°C both types of water molecules detach from the structure. This means plenty of water is available to form a solution, and there is a complete lack of memory for the parent structure, as the heavy ions coordination polyhedra are basically destroyed. As a result, good single crystals of SFA grow but with a random distribution. Between 90 and 60°C, just one type of water molecules (those attached to the structure by weak H bonds) are readily available for the process. The coordination polyhedra are, in the short term, basically preserved and with them some memory of the orientation of the original structure is kept. A correlation between SFA crystallites orientation is accordingly observed. But it is below 60°C, when dehydration is not yet a generalized process, and the mobility of the molecules involved certainly very low, that the painstaking growth of the new phase occurs in a truly topotactic manner, as myriads of oriented crystallites. The process must take place at a submicroscopic level but the main characteristics can be inferred from some systematic X-ray powder diffraction work. This clearly shows a fast disappearance of the triclinic phase, with the onset of

an "amorphous" state and, over this, the laborious growth of the recrystallized products. This results are clearly compatible with the recrystallization observed at higher temperatures.

In comparing CSFH (1) and SFA (2) crystal structures, no common structural motives seem to be present, suggesting that the reason for the topotactic growth is more likely to be found in some metric match between both lattices rather than in the conservation of structural units. In fact, a comparison between both unit cells shows a striking similarity between both ($hk0$) planes (the ones whose orientations are preserved in the transformation); compare a , b , and γ in Table III.

This match on two otherwise very different structures could be responsible for an inner epitactic growth (3), later generalized to the whole core of the crystal.

The oriented character of the recrystallization at lower temperatures would be then a manifestation of the gentle dehydration leaving behind a recognizable pattern over which the new structure builds up; higher temperatures, instead, would mean the appearance of a solution-like state with partial or total loss of this structural information.

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