

Growth of β -LiNaSO₄ and Li₂SO₄ · H₂O: epitaxy and intergrowth phenomena

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Abstract

Isothermal crystallization in the system Na₂SO₄-Li₂SO₄-H₂O was carried out at 50°C by “salting out” in a tetrametoxysilane (TMS) gel medium. Under these conditions the solid phases that can crystallize are Na₂SO₄, Li₂SO₄ · H₂O and β -LiNaSO₄, depending on the initial composition of the gel interstitial solution. When the initial [Na₂SO₄]/[Li₂SO₄] molar ratio in the interstitial solution is smaller than 1, first β -LiNaSO₄ crystallizes and, subsequently, Li₂SO₄ · H₂O. The nucleation of Li₂SO₄ · H₂O is always heterogeneous and occurs epitaxially on the surface of β -LiNaSO₄ crystals. Occasionally, successive heterogeneous nucleation events promote the development of intergrowth phenomena. In this paper a detailed study of both epitaxial growth and crystal morphology is worked out. Finally, the observed epitaxial relationships are interpreted on the ground of structural considerations.

1. Introduction

The binary-cation sulphates of LiMSO₄ type (M = Na, K, Rb, NH₄, etc.) have been widely studied since several of these compounds exhibit interesting properties of ionic conduction. Particularly, lithium sodium sulphate (LiNaSO₄) undergoes a phase transition at 791 K which is accompanied by an increase of the electrical conductivity by a factor of 10³. This sulphate is classified as a superionic conductor, and its high temperature phase belongs to the class of inorganic rotator phases. The low temperature phase (β) is pyro-

electric and piezoelectric, and it is the starting material in structural and dynamical behaviour studies [1–3]. The growth of single crystals of this phase is usually carried out from aqueous solutions containing equimolar proportions of Na₂SO₄ and Li₂SO₄.

Although crystals of binary-cation salts are generally grown from equimolar solutions, ternary-systems provide an interesting medium to study the influence of the mother solution composition on the crystallization behaviour. The use of non-equimolar solutions leads to different crystallization sequences depending on the specific characteristics of the phase diagram. The solution composition changes continuously as growth proceeds and this affects the morphological evolution of the crystals. Moreover, depending on the structural relationships between the

successive crystallizing phases, different kinds of heterogeneous nucleation may occur.

In this paper we deal with the crystallization behaviour of β -LiNaSO₄ from non-equimolar solutions. In particular, when the initial [Na₂SO₄]/[Li₂SO₄] molar ratio in the solution is smaller than 1, crystals of β -LiNaSO₄ and Li₂SO₄·H₂O can be obtained. Epitactic growth between β -LiNaSO₄ and Li₂SO₄·H₂O crystals is reported as well and interpreted on the base of structural considerations.

2. Experimental procedure

Isothermal crystallization of Li₂SO₄·H₂O and β -LiNaSO₄ crystals was carried out by "salting out" in a gel medium. All the experiments were carried out at 50°C (±0.05°C) by using a two-layer method in test tube [4]. The gel was prepared by mixing volume percentages of tetrametoxysilane (TMS) (10%) and of undersaturated Na₂SO₄-Li₂SO₄ aqueous solutions (90%) [5]. Experiments were carried out with aqueous solutions having different [Na₂SO₄]/[Li₂SO₄] molar ratios. In all cases this ratio was smaller than unity in order to allow the successive crystallization of lithium sodium sulphate (LSS) and lithium sulphate monohydrate (LSM). Gelling was achieved in glass test tubes (16 mm in diameter and 180 mm long) under crystallization temperature (50°C). Then, the top part of the test tube was filled with methanol.

The diffusion of methanol through the gel column modifies the composition of the interstitial solution and promotes the salting out effect. The solubility of both double and single salts, decreases with the increasing concentration of methanol in the interstitial solution; hence nucleation and growth of different crystal phases occur.

The crystallization sequence and the evolution of the crystal morphologies were monitored by optical microscopy. After the growth process, the crystals were recovered from the gel and washed with methanol. The different phases were identified by X-ray diffraction. Finally, polarization microscopy, optical goniometry and scanning elec-

tron microscopy were used to study the crystal morphologies.

3. Phase relationships

The isothermal diagram of the ternary system Na₂SO₄-Li₂SO₄-H₂O at 50°C and 1 atm pressure is shown in Fig. 1 [6]. As might be expected, the solubility of Na₂SO₄ in solutions of lithium sulphate differs from its solubility in water. This effect is shown by the line *a-b* which represents the composition of a solution saturated for sodium sulphate. Analogously, *c-d* is the solubility curve of Li₂SO₄·H₂O. Furthermore, at this temperature, the system exhibits a binary-cation salt, β -LiNaSO₄, whose solubility curve is represented by the line *b-c*. Obviously, *b* and *c* are invariant points and the solutions having this composition are simultaneously saturated with respect to both β -LiNaSO₄ and the respective single salt. This diagram may be used to predict the course of isothermal crystallization; it ensues that only when the mother solutions are equimolar, the ratio of Na₂SO₄ to Li₂SO₄ remains unaltered during β -LiNaSO₄ growth. On the other hand, when the initial compositions are not equimolar, the growth of LSS crystals induces a continuous variation in the solution stoichiometry, until an invariant point

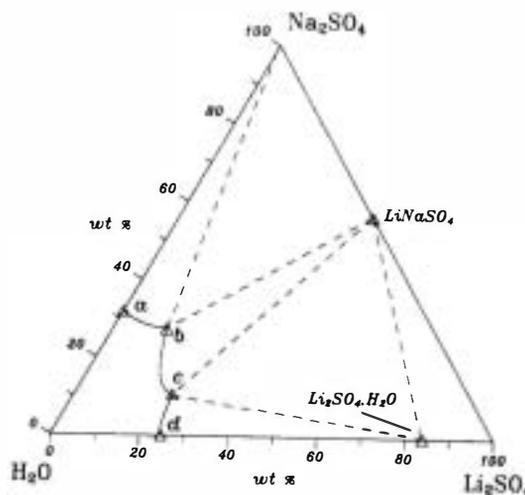


Fig. 1. Na₂SO₄-Li₂SO₄-H₂O system at 50°C and 1 atm.

is reached. At this point the solution will be saturated with respect to β -LiNaSO₄ as well as to the respective simple salt. Then, only when a new critical supersaturation is reached, nucleation of this salt becomes possible. In particular, when the initial [Na₂SO₄]/[LiSO₄] molar ratio in the solution is smaller than 1, only crystals of β -LiNaSO₄ and Li₂SO₄ · H₂O can be obtained.

4. Crystallization sequence and morphological features

4.1. β -LiNaSO₄ crystals

As it is shown in Table 1, in all crystallization runs first LSS crystals appeared and, starting from run No. 3, LSM crystals were observed too. This sequence occurs even for initial solutions with Na/Li molar ratios lower than that corresponding to the invariant point *c* in the phase diagram ([Na₂SO₄]/[Li₂SO₄] = 0.37). This behaviour represents a reversed trend and it must be a consequence of the different nucleation kinetics of the two phases [6]. At moderately high supersaturation values LSS is the first phase to crystallize for a wide range of initial compositions of mother solution. At the moment we are not able to propose a convincing interpretation because we do neither know kinetic factors nor activation energies for both crystal phases.

Lithium sodium sulphate crystallizes in the space group P31c with 6 molecules in the unit cell. The lattice parameters of the hexagonal unit cell are $a_0 = 7.6270 \text{ \AA}$ and $c_0 = 9.8579 \text{ \AA}$ [7]. The



Fig. 2. Scanning electron micrograph of a β -LiNaSO₄ crystal grown in TMS gel. The crystal is twinned on (0001).

morphological importance of a crystal form may be roughly defined by the Donnay–Harker geometrical criterion [8]: the faces are ranked in increasing order of reticular area (decreasing reticular density). The D–H method ranks the forms of LSS in the order {10 $\bar{1}$ 0}, {10 $\bar{1}$ 1}, {0002}, {10 $\bar{1}$ 2}, {11 $\bar{2}$ 0} \equiv {2 $\bar{1}$ 10}, {11 $\bar{2}$ 1} \equiv {2 $\bar{1}$ 11}, {20 $\bar{2}$ 1}, {11 $\bar{2}$ 2} \equiv {2 $\bar{1}$ 12}. The corresponding reticular areas are 75.19, 90.50, 100.75, 125.71, 130.23, 139.53, 158.59 and 164.65 \AA^2 , respectively.

The prevailing forms in the crystals obtained are the trigonal prisms {11 $\bar{2}$ 0}, {2 $\bar{1}$ 10}, and the hexagonal prism {10 $\bar{1}$ 0}; pyramids {11 $\bar{2}$ 2}, {2 $\bar{1}$ 12} and {10 $\bar{1}$ 2} truncate the crystals (Fig. 2). The relative development of the most important growth forms depends, obviously, on the initial conditions and, particularly on the [Li/Na] molar

Table 1
Mother solutions and crystallization sequences

Wt%		Molar ratio [Na]/[Li]	Phase 1	Phase 2	Evolution
Na ₂ SO ₄	Li ₂ SO ₄				
9.611	7.439	1/1.00	LiNaSO ₄	–	Growth
8.317	8.047	1/1.25	LiNaSO ₄	–	Growth
7.393	8.584	1/1.50	LiNaSO ₄	Li ₂ SO ₄ · H ₂ O	Intergrowth
6.706	9.083	1/1.75	LiNaSO ₄	Li ₂ SO ₄ · H ₂ O	Intergrowth
6.179	9.566	1/2.00	LiNaSO ₄	Li ₂ SO ₄ · H ₂ O	Intergrowth
5.112	11.869	1/3.00	LiNaSO ₄	Li ₂ SO ₄ · H ₂ O	Overgrowth
3.638	11.263	1/4.00	LiNaSO ₄	Li ₂ SO ₄ · H ₂ O	Overgrowth
2.941	11.383	1/5.00	LiNaSO ₄	Li ₂ SO ₄ · H ₂ O	Overgrowth

sponds to a symmetry element of the substrate. The lattice of one individual is related to that of another individual by a rotation of 60° . This fact gives to the whole the appearance of a twin.

For higher initial $[\text{Na}]/[\text{Li}]$ molar ratios, after nucleation of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ on $\beta\text{-LiNaSO}_4$, often both phases continue to grow. In such a case, the possibility exists that a layer of the $\beta\text{-LiNaSO}_4$ spread out on the uppermost layer of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, covering it wholly. As a result, the $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystals become included in the substrate. Successive events of heterogeneous nucleation of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ on $\beta\text{-LiNaSO}_4$ lead to the development of intergrowth phenomena.

5. Discussion

Epitaxy is a particular case of heterogeneous nucleation in which the overgrowing phase shows a non-random orientation. Many attempts have been made to explain the phenomenon of epitaxy both from vapour and solution [10–13] in order to justify the development of an oriented overgrowth the structure matching with respect to the substrate must be considered. For this purpose it is necessary to compare the geometrical features of the crystal lattices and the structural elements that they have in common.

$\beta\text{-LiNaSO}_4$ and $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystals belong to two non-centrosymmetric point groups whose polar directions $[010]_{\text{LSM}}$ and $[001]_{\text{LSS}}$ constitute the main coincident pair in the oriented overgrowth. Along both directions, chains of sulphate–cation–sulphate strong bonds can be observed [14]. In the case of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ crystals, all the SO_4 tetrahedra point up along $[010]$. How-

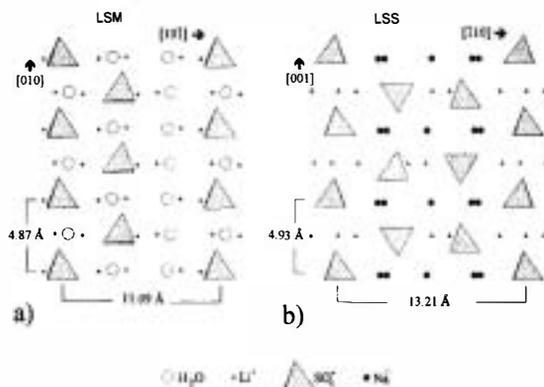


Fig. 5. Projection of (a) $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and (b) $\beta\text{-LiNaSO}_4$ structures on (101) and $(11\bar{2}0)$, respectively.

ever, in the $\beta\text{-LiNaSO}_4$ structure, two types of sequences of SO_4 can be distinguished along $[001]$. In the first type, SO_4 tetrahedra point alternatively up and down. In the second, all the tetrahedra are oriented pointing up. This is shown in Fig. 5 where the structures of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\beta\text{-LiNaSO}_4$ are projected on (101) and $(11\bar{2}0)$, respectively, i.e., on the most frequent contact planes.

For $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ the distance between successive SO_4 groups along $[010]$ is 4.87 \AA , i.e., it coincides with the parameter b_0 . For $\beta\text{-LiNaSO}_4$, the distance between SO_4^{2-} anions within a chain with all the tetrahedra pointing up is a half of the repeating period along the c -axis, i.e., 4.93 \AA . In the case of the chains of strong bonds with sulphate groups pointing up and down, there are two different distances between successive SO_4^{2-} anions, 5.56 and 4.29 \AA . So, the chains where all the tetrahedra point up are the main element that both structures have in common. The similar

Table 2
Epitaxial relationships

$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$		$\beta\text{-LiNaSO}_4$		Misfit	
Contact plane	Parameter (\AA)	Contact plane	Parameter (\AA)	Linear	Angular
(101)	$2 \times [010] = 9.741$	$(11\bar{2}0)$	$[001] = 9.858$	1.20%	–
	$[10\bar{1}] = 11.088$		$[\bar{1}10] = 13.210$	19.14%	–
	$[12\bar{1}] = 14.760$		$[\bar{1}11] = 16.483$	11.67%	4.56°
	$d_{101} = 3.823$		$d_{11\bar{2}0} = 3.814$	0.26%	–

distance between successive tetrahedra along these chains explains the good matching between $[010]_{\text{LSM}}-[001]_{\text{LSS}}$. The misfit is only 1.20% (see Table 2), when it is calculated considering a 1:2 ratio between the repeating periods along these directions.

The matching is not so clear between $[10\bar{1}]_{\text{LSM}}$ and $[\bar{1}10]_{\text{LSS}}$, two directions lying within the contact planes $(101)_{\text{LSM}}$ and $(11\bar{2})_{\text{LSS}}$ that are orthogonal to $[010]_{\text{LSM}}$ and $[001]_{\text{LSS}}$, respectively. The repeating periods along $[10\bar{1}]_{\text{LSM}}$ and $[\bar{1}10]_{\text{LSS}}$ are 11.09 and 13.21 Å, which means a misfit of 19.14%. This is a high mismatch for coherent nucleation [15,16]. However, another pair of directions lying within the contact planes, $[\bar{1}11]_{\text{LSS}}$ and $[12\bar{1}]_{\text{LSM}}$, show similar repeating periods (16.48 and 14.76 Å, respectively). The corresponding linear misfit is 11.67%. Even though these two directions are not exactly coincident, the angular misfit between them is very small (4.56°). It appears that from a geometrical standpoint, the epitaxy can be considered two-dimensional.

On the other hand, both structures exhibit a good fit perpendicularly to the faces of adherence. The spacings of the contact planes, $(d_{101})_{\text{LSM}}$ and $(d_{11\bar{2}})_{\text{LSS}}$, differ less than 0.26%, as Table 2 shows. This fact can explain the development of intergrowth subsequent to epitaxy [17]. Intergrowth occurs when layers of the substrate spread out on the uppermost deposit, and this process is favoured by the good match in the third dimension.

6. Conclusions

(1) Crystallization in the system $\text{Na}_2\text{SO}_4-\text{Li}_2\text{SO}_4-\text{H}_2\text{O}$ was carried out from non-equimolar solutions. When the initial $[\text{Na}]/[\text{Li}]$ molar ratio is smaller than 1, first $\beta\text{-LiNaSO}_4$ (LSS) crystallizes, and $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (LSM) subsequently.

(2) Nucleation of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ occurs epitaxially on the surface of $\beta\text{-LiNaSO}_4$ crystals. The main relation is the parallelism between $[010]_{\text{LSM}}$ and $[001]_{\text{LSS}}$; the most frequent contact faces are $(101)_{\text{LSM}}$ on $(11\bar{2})_{\text{LSS}}$ or $(2\bar{1}1)_{\text{LSS}}$.

(3) The misfits between the coincident directions $[010]_{\text{LSM}} \parallel [001]_{\text{LSS}}$, and $[10\bar{1}]_{\text{LSM}} \parallel [\bar{1}10]_{\text{LSS}}$, lying in the faces of adherence, are 1.20% and 19.14%, respectively. Another pair of directions, $[12\bar{1}]_{\text{LSM}}$ and $[\bar{1}11]_{\text{LSS}}$, showing a small angular misfit (4.56°), exhibit also a good match (misfit 11.67%). The epitaxy can be considered two-dimensional.

(4) The development of intergrowth is favoured by the small mismatch in the direction perpendicular to the face of adherence (misfit 0.26%).

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