

Crystallization of β'' -LiNH₄SO₄ and (NH₄)₂SO₄ in gels: growth morphology and epitaxy phenomena

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Abstract

The crystallization sequences in the system (NH₄)₂SO₄–Li₂SO₄–H₂O at 50°C have been studied for solutions with an initial [(NH₄)₂SO₄]/[Li₂SO₄] molar ratio higher than 1. The crystal growth experiments were carried out under isothermal conditions in a gel medium, where supersaturation was achieved by “drowning out”. The phases obtained are β'' -LiNH₄SO₄ (LAS) and (NH₄)₂SO₄ (AS). The similarities exhibited by the structures of both compounds favours the development of orientational overgrowth phenomena. The main epitaxial relationship found is the parallelism between [0 0 1]_{LAS} and [1 0 $\bar{1}$]_{AS}. The most common contact planes are (0 1 0)_{LAS} and (1 0 1)_{AS}. Although less frequent, other epitaxial relationships have also been observed: (0 1 0)_{LAS} \parallel (0 1 0)_{AS} and [1 0 0]_{LAS} \parallel [1 0 0]_{AS}. The development of the overgrowth is interpreted on the grounds of the structural considerations and the characteristics of the crystallization medium.

1. Introduction

β'' -LiNH₄SO₄ (LAS) is included in a group of binary-cation sulphates with the general formula LiMSO₄ (M = Na, K, Rb, NH₄, etc.) that exhibit interesting physical properties and structures. Most of these compounds have been characterized as ionic conductors. Particularly, β'' -LiNH₄SO₄ undergoes two-phase transitions at about 283 and 459.7 K [1]. The room temperature phase (β'' -LiNH₄SO₄) behaves as a ferroelectric. It belongs to the orthorhombic system, with space group P2₁cn.

This phase shows a structure, included in a wide family of structures with the general formula M'M''AX₄ (M' = K, Rb, Cs, NH₄, NH₂; AX₄ = SO₄, BeF₄), that can be described as a distorted derivative of trydimite. In this type of structure, M''X₄ and AX₄ tetrahedra share corners to form a framework enclosing cavities where the large M' ions are “stuffed”. The main difference between β'' -LiNH₄SO₄ structure and a true derivative of trydimite structure is related to the arrangement of M'X₄ and AX₄ tetrahedra in six-membered rings. In the case of β'' -LiNH₄SO₄, those rings are formed by three adjacent tetrahedra pointing “up” the *c*-axis while the other three point “down”. In contrast, in the trydimite-like arrangement, adjacent

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tetrahedra point in opposite directions along the *c*-axis [2]. The distribution of the two types of tetrahedra leads to highly polar structures. This aspect is responsible for the interesting properties exhibited by these compounds.

The fact that most binary-cation sulphates of the LiMSO_4 group exhibit interesting physical properties determined that crystal growth studies of these compounds mainly focused on the obtention of well-developed single crystals. For this purpose, aqueous solutions containing the two cations in the stoichiometric ratio of the solid phase were always used. As a consequence, there is a lack of information about the crystallization behaviour of these substances from non-stoichiometric solutions. However, specific morphologies required in some technological applications can be obtained by employing non-stoichiometric solutions. Moreover, deviations from stoichiometry lead to the successive nucleation of different phases and, depending on the structural relationships between the phases involved, different kinds of heterogeneous nucleation can be observed.

This paper deals with the crystallization sequences in the system $(\text{NH}_4)_2\text{SO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$. We will focus on the crystallization behaviour when solutions with an initial $[(\text{NH}_4)_2\text{SO}_4]/[\text{Li}_2\text{SO}_4]$ molar ratio higher than 1 are employed. In that case, the phases obtained are $\beta''\text{-LiNH}_4\text{SO}_4$ and $(\text{NH}_4)_2\text{SO}_4$. The similarities exhibited by the structures of both compounds favour the development of orientational overgrowth phenomena. The epitaxial relationships are interpreted on the grounds of those similarities.

2. Experimental procedure

Experiments of crystallization of $(\text{NH}_4)_2\text{SO}_4$ and $\beta''\text{-LiNH}_4\text{SO}_4$ were carried out under isothermal conditions in a gel medium. Supersaturation was achieved by “drowning out”, using a two-layer method in a glass test tube. During all the experiments the temperature was kept at 50°C ($\pm 0.05^\circ\text{C}$). The gel was prepared by mixing volume percentages of tetrametoxysilane (TMS) (10%) and of undersaturated $(\text{NH}_4)_2\text{SO}_4\text{-Li}_2\text{SO}_4$ aqueous solutions (90%). Gelling occurred in test tubes

(16 mm in diameter and 180 mm long) under the crystallization temperature (50°C). Subsequently, the top part of the test tube was filled with methanol. This crystallization method represents an alternative to the isothermal removal of solvent by evaporation and can be described as “chemical evaporation” [3]. The diffusion of methanol changes the composition of the interstitial solution and determines a decrease of the solubility of both single and double salts. As a consequence, the crystallization of different crystal phases occurs.

A number of experiments were carried out using aqueous solutions with different $[(\text{NH}_4)_2\text{SO}_4]/[\text{Li}_2\text{SO}_4]$ molar ratios. In all the experiments this ratio was higher than unity in order to promote the successive crystallization of lithium ammonium sulphate (LAS) and ammonium sulphate (AS).

The crystallization sequence and the evolution of the crystal morphologies were monitored “in situ” by optical microscopy. After the growth process, the crystals were recovered from the gel and washed with methanol. Their morphologies were studied by means of polarization microscopy, optical goniometry and scanning electron microscopy. The different phases obtained were identified by X-ray powder diffraction.

The isothermal phase diagram for $(\text{NH}_4)_2\text{SO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ was determined at 50°C by the so-called “wet residues” method, in which the composition of the equilibrium solid phase is indirectly obtained by extrapolation [4]. Lithium content of both saturated solutions and “wet residues” was analysed by atomic absorption. Ammonium content was determined by colorimetry.

3. Phase relationships and crystallization sequence

Crystallization sequences in the ternary system $(\text{NH}_4)_2\text{SO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ at 50°C and 1 atm can be predicted by means of the isothermal phase diagram shown in Fig. 1 [5]. In this diagram the dependence of the solubility of $(\text{NH}_4)_2\text{SO}_4$, $\beta''\text{-LiNH}_4\text{SO}_4$ and $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ on the composition of the solution is described by curves *a-b*, *b-c* and *c-d*, respectively. The points *b* and *c* are invariant points where the solution is simultaneously saturated with respect to $\beta''\text{-LiNH}_4\text{SO}_4$ and one of

the simple salts ($(\text{NH}_4)_2\text{SO}_4$, or $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$). Only when the starting composition of the solution is equimolar ($[(\text{NH}_4)_2\text{SO}_4]/[\text{Li}_2\text{SO}_4] = 1$) the crystallization of $\beta''\text{-LiNH}_4\text{SO}_4$ occurs without modifying the $[(\text{NH}_4)_2\text{SO}_4]/[\text{Li}_2\text{SO}_4]$ molar ratio of the solution. Deviations from equimolarity in the initial composition of the solution determine that the solution stoichiometry evolves during the crystallization process of $\beta''\text{-LiNH}_4\text{SO}_4$. This leads to the formation of a simple salt when one of the invariant points is reached.

In this work we will focus on the crystallization sequences in the NH_4 -rich region of the phase diagram. Table 1 summarizes the crystallization runs studied. In all the cases the crystallization sequence

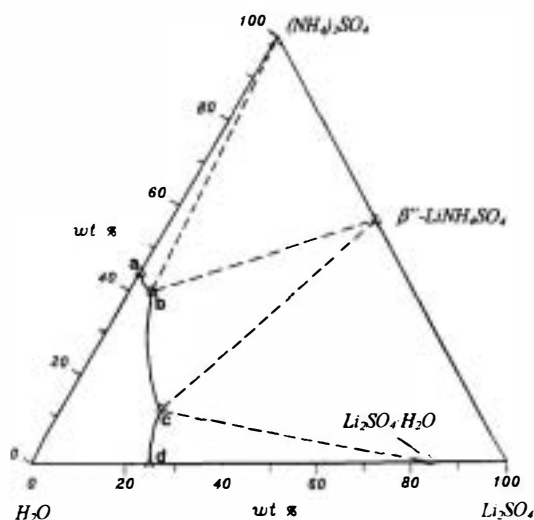


Fig. 1. $(\text{NH}_4)_2\text{SO}_4\text{-Li}_2\text{SO}_4\text{-H}_2\text{O}$ system at 30°C and 1 atm.

starts with the formation of $\beta''\text{-LiNH}_4\text{SO}_4$. When the initial $[(\text{NH}_4)_2\text{SO}_4]/[\text{Li}_2\text{SO}_4]$ molar ratio of the solution is higher than 1, but lower than that corresponding to the eutonic point *b* in the phase diagram (runs 2–5), $(\text{NH}_4)_2\text{SO}_4$ nucleates as a second phase. This behaviour is in agreement with that predicted by using the diagram of the ternary system shown in Fig. 1. Nucleation of $(\text{NH}_4)_2\text{SO}_4$ is, in most cases, heterogeneous, occurring on the surface of previously grown $\beta''\text{-LiNH}_4\text{SO}_4$ crystals. During this process, the guest $(\text{NH}_4)_2\text{SO}_4$ adopt specific crystallographic orientations in relation to the host $\beta''\text{-LiNH}_4\text{SO}_4$ crystals, coating them partially. Both the growth morphologies of the crystalline individuals and the epitaxial relationships between them will be discussed in the next sections.

4. Morphological features

4.1. $\beta''\text{-LiNH}_4\text{SO}_4$ crystals

Lithium ammonium sulphate crystallizes in the space group $\text{P2}_1\text{cn}$ with 4 molecules in the unit cell. The lattice parameters are $a_0 = 5.280 \text{ \AA}$, $b_0 = 9.140 \text{ \AA}$, and $c_0 = 8.786 \text{ \AA}$ [2]. Although a PBC (periodic bond chain) analysis is beyond the scope of the present work, the relative importance of crystal forms can be roughly predicted by Donnay–Harker rules. According to Donnay–Harker law, the morphological importance of the different faces decreases with increasing reticular area. D–H method ranks 0 1 1 first, with a reticular area of 66.94 \AA^2 . The faces $110 = \bar{1}10$, 020 , 002 ,

Table 1
Mother solutions and crystallization sequences

Concentration (wt%)		Molar ratio $[(\text{NH}_4)_2\text{SO}_4]/[\text{Li}]$	Phase 1	Phase 2	Evolution
$(\text{NH}_4)_2\text{SO}_4$	Li_2SO_4				
2.562	2.132	1/1	$\beta''\text{-LiNH}_4\text{SO}_4$	–	Growth
5.073	2.110	2/1	$\beta''\text{-LiNH}_4\text{SO}_4$	$(\text{NH}_4)_2\text{SO}_4$	Overgrowth
7.496	2.079	3/1	$\beta''\text{-LiNH}_4\text{SO}_4$	$(\text{NH}_4)_2\text{SO}_4$	Overgrowth
9.869	2.053	4/1	$\beta''\text{-LiNH}_4\text{SO}_4$	$(\text{NH}_4)_2\text{SO}_4$	Overgrowth
12.199	2.030	5/1	$\beta''\text{-LiNH}_4\text{SO}_4$	$(\text{NH}_4)_2\text{SO}_4$	Overgrowth

111 = $\bar{1}\bar{1}\bar{1}$ follow, but their reticular areas are significantly greater (92.74, 92.78, 96.51, 104.55 Å², respectively).

Although D–H method is only an approximation, it can be considered successful in predicting the growth morphology of β'' -LiNH₄SO₄. The crystals obtained in these experiments are elongated along *a*-axis, and their final morphology is invariably dominated by the prism {011} and the side pinacoid {010} (see Fig. 2). The crystals are terminated by two domes, {110} and { $\bar{1}\bar{1}0$ }, and two orthorhombic pyramids, {111} and { $\bar{1}\bar{1}1$ }. The fact that the crystals belong to the point group 2 mm determines that the domes {110} and { $\bar{1}\bar{1}0$ }, as well as the pyramids {111} and { $\bar{1}\bar{1}1$ } are non-equivalent by symmetry and exhibit different morphological importance, in spite of their identical reticular area. Nevertheless, all the forms

observed occupy the first places of the Donnay–Harker ranking for β'' -LiNH₄SO₄.

4.2. (NH₄)₂SO₄ crystals

Ammonium sulphate crystallizes at room temperature in the orthorhombic Pcmn space group. The dimensions of the unit cell are $a_0 = 10.636$ Å, $b_0 = 5.993$ Å, and $c_0 = 7.782$ Å [6]. (NH₄)₂SO₄ is isostructural with β -K₂SO₄ and both compounds form series of solid solutions ranging from pure ammonium sulphate to pure potassium sulphate. The theoretical morphology of β -K₂SO₄ has been determined by Vogels et al. [7] on the basis of a PBC analysis. Following these authors, the most important F-face of β -K₂SO₄ is 101, with an attachment energy 30% lower than the next face, 200. The F-faces 201, 002, 110,

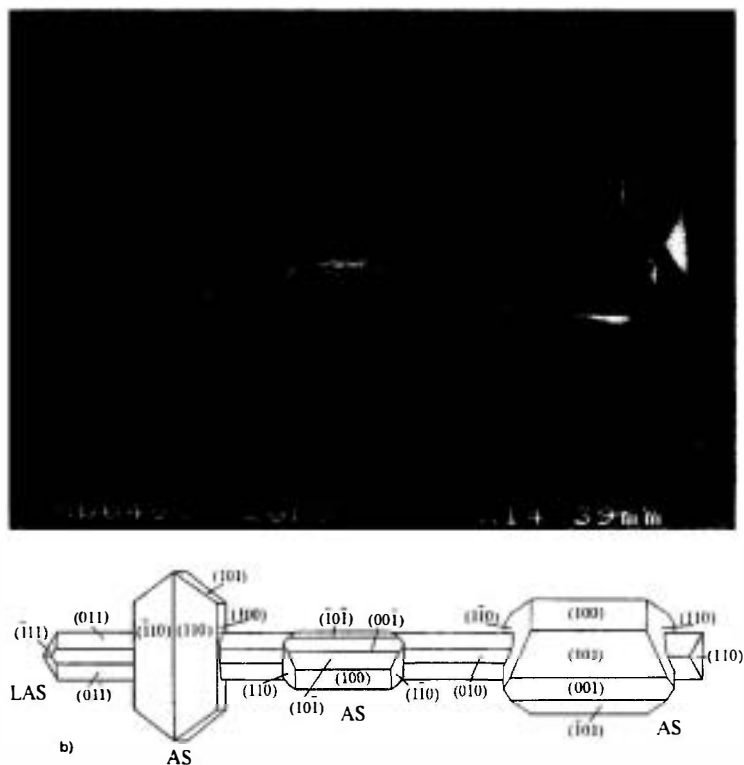


Fig. 2. (a) SEM microphotograph of three (NH₄)₂SO₄ crystals epitaxially grown on β'' -LiNH₄SO₄. Different epitaxial orientations can be observed. (b) Schematic 3D representation showing the epitaxial relationships between (NH₄)₂SO₄ and β'' -LiNH₄SO₄ crystals (see text).

follow, with attachment energies progressively greater. Therefore, a similar ranking of morphological importance is to be expected for the F-faces of $(\text{NH}_4)_2\text{SO}_4$ crystals. In fact, for ammonium sulphate, Donnay–Harker method also ranks 1 0 1 and 2 0 0 first, with reticular areas of 78.98 and 93.27 Å², respectively. The faces 1 1 0, 2 0 1, 1 1 1, 0 0 2, and 1 0 2 follow, with reticular areas of 95.01, 112.97, 114.41, 127.48, and 135.74 Å², respectively. However, in this case the D–H ranking differs slightly from the attachment-energy ranking established by Vogels et al. for $\beta\text{-K}_2\text{SO}_4$.

The habit of the $(\text{NH}_4)_2\text{SO}_4$ crystals obtained in these experiments is defined by the two four-faced prism $\{1 0 1\}$ and $\{1 1 0\}$, and the front pinacoid $\{1 0 0\}$. The orthorhombic dipyrmaid $\{1 1 1\}$ and the basal pinacoid $\{0 0 1\}$ can also appear as minor forms. This morphology fits well with the theoretical morphology predicted by Vogels et al. for the isostructural $\beta\text{-K}_2\text{SO}_4$ and with the D–H ranking computed in this work for ammonium sulphate.

4.3. Epitaxial relationships between $(\text{NH}_4)_2\text{SO}_4$ and $\beta''\text{-LiNH}_4\text{SO}_4$

Heterogeneous nucleation of $(\text{NH}_4)_2\text{SO}_4$ on the surface of $\beta''\text{-LiNH}_4\text{SO}_4$ crystals occurs in a non-random orientation, with specific reticular directions being parallel in both phases. An example of this regularly oriented overgrowth is shown in Fig. 2a. At least two different orientations have been observed. The planes on which the parallelism of the two phases most frequently occurs are $(1 0 1)_{\text{AS}}$ and $(0 1 0)_{\text{LAS}}$. The direction $[1 0 0]$ in $\beta''\text{-LiNH}_4\text{SO}_4$ is then parallel to $[0 1 0]$ in $(\text{NH}_4)_2\text{SO}_4$ (crystals 2 and 3 in Fig. 2a). Moreover, a second preferential orientation, in which $(0 1 0)_{\text{AS}}$ parallels $(0 1 0)_{\text{LAS}}$, has been observed. In this case, the direction $[1 0 0]$ in $\beta''\text{-LiNH}_4\text{SO}_4$ is parallel to $[1 0 0]$ in $(\text{NH}_4)_2\text{SO}_4$ (crystal 1 in Fig. 2a). These epitaxial relationships between crystals of both compounds are schematically shown in Fig. 2b. As can be observed, both orientations can coexist in the same substrate. The number of guests crystals per host individual varies between 1 and 6 and depends on $[(\text{NH}_4)_2\text{SO}_4]/[\text{Li}_2\text{SO}_4]$ initial ratio in the mother solution. So, the higher the ratio, the higher the density of guest crystals.

5. Discussion

The development of epitaxial phenomena is generally related to structural similarities between the substratum and the overgrowing crystal. Normally, the existence of common structural elements, like coordination polyhedra or cation distribution, and the good matching of the two lattices along certain directions control the epitaxial relationships. On the other hand, epitaxial growth is strongly controlled by the characteristics of the crystallization medium, mainly by the transport properties and the supersaturation that can be reached with respect to the overgrowing phase [8]. In this section, the epitaxial overgrowth observed between $\beta''\text{-LiNH}_4\text{SO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ will be explained by attending to the structural features that these phases share. Main attention will be paid to the basis of both structures: the distribution and orientation of the sulphate groups. Finally, the influence of the particular properties of the TMS gel as a crystallization medium will be discussed.

Although $\beta''\text{-LiNH}_4\text{SO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ crystals belong to different orthorhombic spatial groups, both compounds evidence a profound pseudo-hexagonal substructure. In the case of $\beta''\text{-LiNH}_4\text{SO}_4$, the pseudo-hexagonal character is evidenced by the structural similarities along $[1 0 0]$ and $[1 1 0]$. The distance between successive $[\text{SO}_4^{2-}]$ tetrahedra along $[1 0 0]$ is 5.280 Å, coinciding with the parameter a_0 . This parameter is very similar to the distance (5.277 Å) between two adjacent $[\text{SO}_4^{2-}]$ tetrahedra along $[1 1 0]$. Moreover, as shown in Fig. 3a, both directions form an angle 59.99°

the sulphate groups within the $(\text{NH}_4)_2\text{SO}_4$ structure also reveals an hexagonal appearance. The distance between successive tetrahedra along $[0 1 0]$ and $[1 1 0]$ is very similar (5.99 and 6.10 Å, respectively), and the angle between both directions (60.60°) emphasizes the pseudo-hexagonal character of the c -axis projection (Fig. 3b).

The previous considerations imply that both $\beta''\text{-LiNH}_4\text{SO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ have common topological features and similar coordination schemes. Moreover, they may be related by quantitative similarities between their translation lattices and by correspondence between their bond chains.

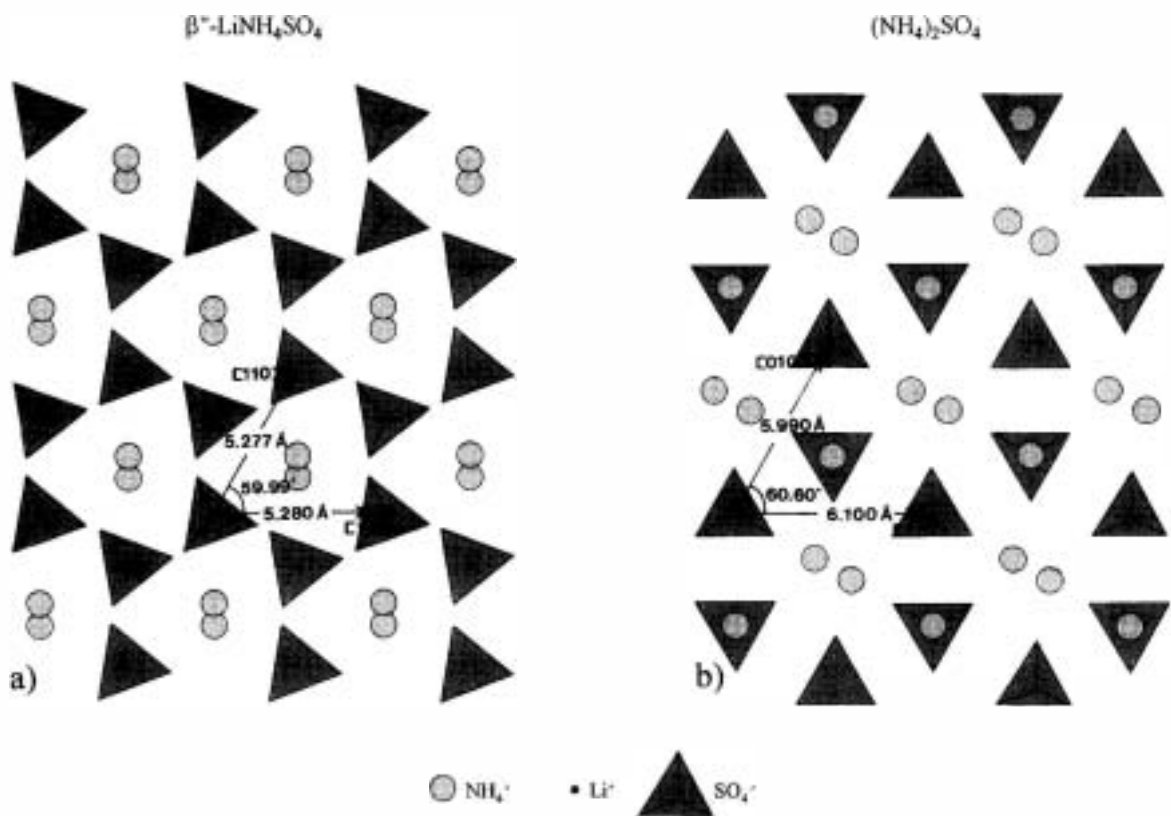


Fig. 3. Projection of (a) $(\text{NH}_4)_2\text{SO}_4$ and (b) $\beta''\text{-LiNH}_4\text{SO}_4$ structures on (001). A pseudo-hexagonal appearance can be observed.

This is clear from Fig. 3 where both structures are projected on (001). However, epitaxial overgrowth involving parallelism between $(001)_{\text{AS}}$ and $(001)_{\text{LAS}}$ has not been observed, mainly because the face (001) does not appear in the growth morphology of $\beta''\text{-LiNH}_4\text{SO}_4$. As we have reported above, $(\text{NH}_4)_2\text{SO}_4$ crystals nucleate on the surface of $\beta''\text{-LiNH}_4\text{SO}_4$ in a non-random way, but the most frequently related faces are $(101)_{\text{AS}}$ and $(010)_{\text{LAS}}$, and the first pair of coincident directions within these planes is $[010]_{\text{AS}}$ and $[100]_{\text{LAS}}$. In the $\beta''\text{-LiNH}_4\text{SO}_4$ structure, chains of $[\text{SO}_4^{2-}]$ tetrahedra point alternatively right and left along $[100]$, and a similar configuration can be observed in the $[010]$ direction of $(\text{NH}_4)_2\text{SO}_4$ (Fig. 4a and Fig. 4b). The distances between successive tetrahedra in both structures are a half of the repeating periods along the coincident directions

($b_0 = 5.993 \text{ \AA}$ for $(\text{NH}_4)_2\text{SO}_4$ and $a_0 = 5.280 \text{ \AA}$ for $\beta''\text{-LiNH}_4\text{SO}_4$), which implies a rather high misfit (13.5%). However, along the second pair of coincident directions, $[10\bar{1}]_{\text{AS}}$ and $[001]_{\text{LAS}}$, the misfit is nearly null if one compare the distance between successive $[\text{SO}_4^{2-}]$ tetrahedra. The repeating period for $[10\bar{1}]_{\text{AS}}$ is 13.179 \AA , but the distance between successive tetrahedra along this direction is a third of this period, i.e., 4.393 \AA . In the same way, the repeating period for $[001]_{\text{LAS}}$ is 8.786 \AA , but the distance between successive tetrahedra along this direction is a half of this value, i.e. again 4.393 \AA . (see Table 2).

As shown in Fig. 2, in some cases, crystals of $(\text{NH}_4)_2\text{SO}_4$ grown on an unique $\beta''\text{-LiNH}_4\text{SO}_4$ substrate exhibit more than one epitaxial relationship. Another common pair of related planes is $(010)_{\text{AS}}$ and $(010)_{\text{LAS}}$, with $[100]_{\text{AS}}$ and $[100]_{\text{LAS}}$

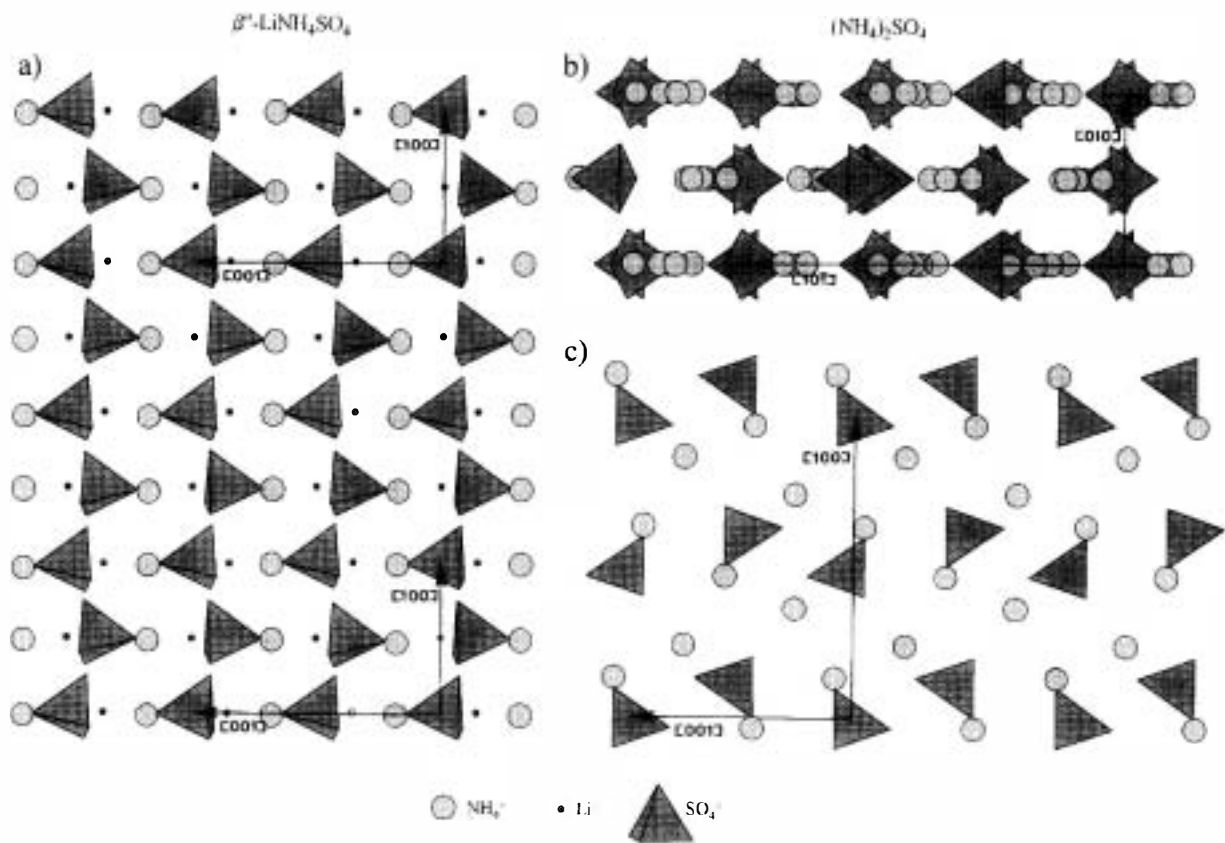


Fig. 4. Projection of (a) β' - LiNH_4SO_4 structure on (0 1 0), (b) $(\text{NH}_4)_2\text{SO}_4$ structure on (1 0 1), and (c) $(\text{NH}_4)_2\text{SO}_4$ structure on (0 1 0).

Table 2
Epitaxial relationships

$(\text{NH}_4)_2\text{SO}_4$		β' - LiNH_4SO_4		Linear misfit (%)
Contact plane	Parameter (\AA)	Contact plane	Parameter (\AA)	
(1 0 1)	$[0 1 0] = 5.993$ $\frac{1}{3}[1 0 \bar{1}] = 4.393$	(0 1 0)	$[1 0 0] = 5.280$ $\frac{1}{2}[0 0 1] = 4.393$	13.50 0.0
(0 1 0)	$[1 0 0] = 10.636$ $[0 0 1] = 7.782$	(0 1 0)	$2[1 0 0] = 10.560$ $[0 0 1] = 8.796$	0.72 12.

as main coincident directions within these planes. For $(\text{NH}_4)_2\text{SO}_4$ the repeating period along $[1 0 0]$ is 10.636 \AA , while the repeating period for β' - LiNH_4SO_4 along the same direction is 5.280 \AA (Fig. 4a and Fig. 4c). However, if we take two identity periods along $[1 0 0]$ in the structure of β' - LiNH_4SO_4 , the misfit is only 0.72%. Other coinci-

dent directions lying within the contact planes $(0 1 0)_{\text{AS}}$ and $(0 1 0)_{\text{LAS}}$ are $[0 0 1]_{\text{AS}}$ and $[0 0 1]_{\text{LAS}}$. For these directions the repeating periods are 7.782 and 8.786 \AA , respectively, which means a mismatch of 12.90% (Table 2). Again the misfit values are reasonably within the limits required for epitaxial nucleation from solution [8–11].

A very frequent feature of β'' -LiNH₄SO₄ and (NH₄)₂SO₄ epitaxy is the coating of all $\{0k1\}$ faces of β'' -LiNH₄SO₄ by (NH₄)₂SO₄ crystals. The existence of at least two different epitaxial orientations, in addition to the relatively high number of equivalent faces in orthorhombic crystals and the coincidence of many interfacial angles, is probably responsible for this phenomenon.

Although the two epitaxial relationships determined are well represented in the population of crystals studied, a number of guest crystals appears slightly misoriented with respect to the "correct" epitaxial orientation. Glikin and Kaulina (1988) [12] proposed a model for epitaxial growth that distinguishes two stages. During the first stage, overgrowing crystals nucleate in an orientated way as a result of the chemical similarity between the two phases. In the second stage, the overgrowing crystals turn under the influence of the growth of the substratum layers. Therefore, the lower is the growth rate of the substrate and the higher is the growth rate of the overgrowing crystals, the higher is the degree of epitaxy. The model by Glikin and Kaulina is in agreement with our observations. Initially, crystals of (NH₄)₂SO₄ nucleate and grow at high rate on β'' -LiNH₄SO₄ surfaces. These crystals show a high degree of epitaxy. As time passes by, the growth rate of (NH₄)₂SO₄ decreases. At one stage, both overgrowing and substrate growth rates are roughly the same. As a result, the deposition of substrate layers becomes important, leading to the misorientation of the (NH₄)₂SO₄ epitaxial crystals.

The development of epitaxial overgrowth between double and single sulphates is a common phenomenon when crystallization occurs in a gel medium. Several examples have recently been reported [13, 14] and in all the cases the similarity between structural elements of the two phases involved seems to control the development of the epitaxial overgrowth. However, epitaxial phenomena are rare when crystallization occurs from free solutions. This is because the transport properties of the medium affect the nucleation behaviour. When crystallization in gels is compared with crystallization from free solutions, one of the main differences is caused by the degree of supersaturation. Prieto et al. [15] have reported the high metastability level that can be achieved in a gel medium.

Such a supersaturation level in a free solution would involve a catastrophic nucleation and a high density of crystalline individuals. The fact that only a small number of crystals nucleates proves that the gel medium is very effective at suppressing nucleation. In this situation, heterogeneous nucleation on pre-existing phases is an alternative way to decrease the free energy of a highly supersaturated unable to nucleate homogeneously. Moreover, the system exploits the crystalchemical similarities between host and guest by developing epitaxial relationships.

6. Conclusions

(1) Crystallization in the system (NH₄)₂SO₄-Li₂SO₄-H₂O was carried out from non-equimolar solutions. When the initial [(NH₄)₂SO₄]/[Li₂SO₄] ratio of the solution is higher than 1, but lower than that corresponding to the eutonic point *b* in the ternary diagram, β'' -LiNH₄SO₄ crystallizes first, and (NH₄)₂SO₄ subsequently.

(2) Nucleation of (NH₄)₂SO₄ on the surface of β'' -LiNH₄SO₄ is, in most cases, epitaxial. The most common contact planes are (1 0 1)_{AS} and (0 1 0)_{LAS}. Moreover, parallelism between (0 1 0)_{AS} and (0 1 0)_{LAS} has also been observed.

(3) When (1 0 1)_{AS} parallels (0 1 0)_{LAS}, the misfit between [0 1 0]_{AS} and [1 0 0]_{LAS} is 13.50%, another pair of directions lying within these planes, [1 0 $\bar{1}$]_{AS}-[0 0 1]_{LAS}, shows a nearly null misfit, when the distances between successive tetrahedra along this directions are compared. When (0 1 0)_{AS} and (0 1 0)_{LAS} are parallel, the misfits between the coincident directions [1 0 0]_{AS}-[1 0 0]_{LAS} and [0 0 1]_{AS}-[0 0 1]_{LAS} are 0.72% and 12.90%.

(4) Deviations from the "correct" epitaxy relationships can be interpreted as a consequence of differences between the growth rates of the substratum and overgrowing phases.

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