S. LÓPEZ-ANDRÉS, M. J. SUAREZ, M. PRIETO

Complutense University of Madrid. Crystallography and Mineralogy, Departm., Madrid, Spain, and
University of Oviedo, Geology Departm (IUQOM), Oviedo, Spain

Epitaxial Overgrowth of LiKSO_4 on $\beta\text{-K}_2\text{SO}_4$ Single Crystals

Nucleation of LiKSO_4 (LKS) crystals from non-equimolar solutions may occur epitaxially on the surface of previously nucleated $\beta\text{-K}_2\text{SO}_4$ (KS) crystals. Both compounds evince a profound hexagonal substructure, and have common topological features and similar coordination schemes. Moreover, they may be related by quantitative similarities between their translation parameters and by correspondence between their bond chains along the directions of epitaxy. The planes of epitaxy are $(001)_{\text{KS}}$ and $(0001)_{\text{LKS}}$, and on these planes $[010]_{\text{KS}}$ is always parallel to $[010]_{\text{LKS}}$, with a misfit of 12.19%. Another pair of directions, $[1\bar{1}0]_{\text{KS}}$ and $[100]_{\text{LKS}}$, showing a small angular misfit (0.18°), exhibit an even lower linear misfit (3.09%).

1. Introduction

The binary-cation sulphate LiKSO_4 exhibits many interesting structural and physical properties which have attracted the attention of crystallographers and solid state physicists. This compound undergoes two phase transitions in the high temperature range, at 708 and 950 K (SCHULZ et al.). In addition, at least two further transitions have been found below room temperature, but they are extremely sluggish, the kinetics depending on the thermal treatment of the crystal (BHAKAY-TAMHANE et al.; ZHANG et al.; VARMA et al.). Since 1979 many papers on physical properties and phase transitions of LiKSO_4 have been published (SCHULZ et al.), the pyroelectric room temperature phase being the starting material in all these studies.

The room temperature phase, stable up to 708 K, crystallizes in the hexagonal system, space group $P6_3$. This phase belongs to a family of structures with the general formula $M'M''\text{AX}_4$ ($M' = \text{Li}$; $M'' = \text{K, Rb, Cs, NH}_4, \text{N}_2\text{H}_2$; $\text{AX}_4 = \text{SO}_4, \text{BeF}_4$) which are usually described as distorted derivatives of tridymite. In this approach, the hexagonal tridymite framework is built up of six-membered rings of vertex-connected $M'\text{X}_4$ and AX_4 tetrahedra. The apices of the two types of tetrahedra point in opposite directions along the hexagonal axis, thus leading to a polar (pyroelectric) structure. Finally, the large M'' ions are "stuffed" into the channels of the framework.

Although the "stuffed" tridymite model is convenient to explain certain features of LiKSO_4 crystals, such as twinning by "merohedry" (KAPPLER et al.), other descriptions are possible. MOORE includes room temperature LiKSO_4 in a group formed by $\text{K}_3\text{Na}[\text{SO}_4]_2$, $\alpha\text{-Ca}_2\text{SiO}_4$, $\text{Ca}_3\text{Mg}[\text{SiO}_4]$, $\beta\text{-Ca}_2\text{SiO}_4$, $\beta\text{-K}_2\text{SO}_4$ and other calcium orthosilicate and alkali sulphate structures. All these compounds evince a profound hexagonal substructure, and have been interrelated by MOORE by means of a topological-geometrical approach, the so-called model of "bracelets" and "pinwheels".

Crystals of binary cation salts, such as LiKSO_4 , are usually grown from aqueous solutions containing the two cations in the stoichiometric ratio of the solid phase. However, the use

of non-stoichiometric mother solutions provide an interesting medium to study the influence of the solution composition on the crystallization behaviour. In such a case, the solution composition changes continuously as growth proceeds and this affects the morphological evolution of the crystals. Moreover, according to the specific characteristic of the ternary phase diagram, crystallization from non-stoichiometric solutions involves successive nucleation of several phases. Finally, depending on the structural relationships between the successive crystallizing phases, different kinds of heterogeneous nucleation may occur.

This paper deals with the crystallization sequences in the system $\text{Li}_2\text{SO}_4 - \text{K}_2\text{SO}_4 - \text{H}_2\text{O}$. In particular, when the initial Li/K molar ratio in the aqueous solution is smaller than 1, crystals of LiKSO_4 and $\beta\text{-K}_2\text{SO}_4$ can be obtained. Both compounds show profound structural similarities which can be visualized by the model of "bracelets" and "pinwheels". Overgrowth phenomena and epitactic structural relationships between $\beta\text{-K}_2\text{SO}_4$ and LiKSO_4 are interpreted on this ground.

2. Experimental

Isothermal crystallization in the system $\text{Li}_2\text{SO}_4 - \text{K}_2\text{SO}_4 - \text{H}_2\text{O}$ was carried out at 50°C ($\pm 0.05^\circ\text{C}$) by "solubility reduction" in a gel medium. The gel was prepared by mixing 10 vol% of tetramethoxysilane (AREND, CONNELLY) and 90 vol% of undersaturated $\text{K}_2\text{SO}_4 - \text{Li}_2\text{SO}_4$ aqueous solutions. Experiments were carried out with aqueous solutions of different $[\text{Li}_2\text{SO}_4]/[\text{K}_2\text{SO}_4]$ molar ratios. A two layer single-diffusion arrangement (HENISH) in glass test-tube (16 mm diameter and 180 mm long) was used. Gelling was achieved in the test tube under crystallization temperature (50°C). Then the top part was filled with methanol. In these conditions, the methanol diffusing to the gel reduces the solubility of the solutes, leading to nucleation and growth of successive phases according to the phase diagram.

The crystallization sequence was monitored "in situ" by optical microscopy. After the growth process, the crystals were recovered from the gel, identified by X-ray diffraction, and their morphologies were studied by polarization microscopy, optical goniometry and scanning electron microscopy.

The isothermal phase diagram for $\text{Li}_2\text{SO}_4 - \text{K}_2\text{SO}_4 - \text{H}_2\text{O}$ 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 mathematical extrapolation (SCHOTT). Potassium and lithium content of both saturated solutions and "wet residues" was analyzed by atomic absorption spectrophotometry.

3. Phase relationships and crystallization sequence

The isothermal diagram of the ternary system $\text{K}_2\text{SO}_4 - \text{Li}_2\text{SO}_4 - \text{H}_2\text{O}$ at 50°C and 1 atm pressure is shown in Figure 1. In this diagram the lines L-M and N-O are the solubility curves of K_2SO_4 (KS) and $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (LSM), respectively. Moreover, at this temperature, the system exhibits a binary cation salt, LiKSO_4 , with its solubility curve represented by the line M-N. The point LKS on the $\text{K}_2\text{SO}_4 - \text{Li}_2\text{SO}_4$ side represents the composition of the double salt. Solutions having compositions corresponding to the eutonic points M and N are simultaneously saturated with respect to both LiKSO_4 and the respective single salt. The molar Li/K ratios corresponding to M and N are 0.85 and 10.46, respectively.

Figure 1 shows that only when the mother solutions are equimolar, the ratio $[\text{Li}_2\text{SO}_4]/[\text{K}_2\text{SO}_4]$ remains unaltered during growth of LiKSO_4 . An equimolar solution represented on the line W-LKS behaves as a solution of single solute: only the double salt crystallizes and neither of the single salts is deposited at any stage. On the contrary, when the initial compositions are not equimolar, the growth process involves a continuous change of solution stoichiometry, thereby leading to successive crystallization of two phases when the fluid composition reaches the dashed lines which separate the different fields.

Fig. 1. The system $\text{Li}_2\text{SO}_4\text{--K}_2\text{SO}_4\text{--H}_2\text{O}$ at 50 °C and 1 atm

Table 1 shows crystallization sequences for the experimental runs reported in this work. Except for $\text{Li/K} = 0.8 < 0.85$, these sequences are in agreement with the phase diagram. It is, however, worth noting that nucleation occurs when a certain supersaturation level has been reached. Therefore, one cannot strictly apply equilibrium Li/K transitional values to account for the behaviour of supersaturated solutions. The effective transitional ratios for successive nucleation events depend on kinetic factors and can result considerably deviated

Table 1
Mother solutions and crystallization sequences

Molar Ratio Li/K	Weight % $\text{Li}_2\text{SO}_4\text{--K}_2\text{SO}_4$	Phase 1	Phase 2
0.0	0.00–8.71	$\beta\text{-K}_2\text{SO}_4$	—
0.2	1.10–8.71	$\beta\text{-K}_2\text{SO}_4$	LiKSO_4
0.4	2.19–8.71	$\beta\text{-K}_2\text{SO}_4$	LiKSO_4
0.6	3.30–8.71	$\beta\text{-K}_2\text{SO}_4$	LiKSO_4
0.8	4.39–8.71	LiKSO_4	$\beta\text{-K}_2\text{SO}_4$
0.9	4.39–7.75	LiKSO_4	$\beta\text{-K}_2\text{SO}_4$
1.0	4.39–6.97	LiKSO_4	—

from the equilibrium values (PRIETO et al.) Non-equilibrium effects have been widely observed in ternary solid solution-aqueous solution systems (PUTNIS et al.) and they are to be expected in ternary systems involving the formation of double salts.

4. Morphological features

4.1. β -K₂SO₄ crystals

Potassium sulphate crystallizes at room temperature in the orthorhombic Pcmn space group. The dimensions of the unit cell at 25 °C are $a_0 = 10.072 \text{ \AA}$, $b_0 = 5.772 \text{ \AA}$, $c_0 = 7.483 \text{ \AA}$ (WYCKOFF) (many authors use a different choice of crystallographic axes which lead to the space group Pnma). VOGELS et al. determine the theoretical morphology of β -K₂SO₄ by means of a PBC (Periodical Bond Chain) analysis (HARTMAN) and compare the results obtained to experimentally observed growth forms. Following these authors, there are 21 F-forms (out of 228) corresponding to 21 connected nets. In order to rank these forms according to their relative importance, the authors use the attachment energy E_{hkl}^{att} , and the inverse of the interplanar distance d_{hkl} . Both parameters rank {101} first, with E_{hkl}^{att} 30% lower than the next form, {200}. The forms {201}, {002}, {110}, {111}, {102}, {211}, {020}, and {310} follow, but in this case the rankings corresponding to E_{hkl}^{att} and d_{hkl} differ.

The habit of the β -K₂SO₄ crystals obtained in these experiments varies from crystal to crystal and seems to be rather dependent on the initial [Li₂SO₄]/K₂SO₄ molar ratio. Crystals grown in gels from pure K₂SO₄ (lithium-free) mother solutions are elongated along [010]. The forms {101} and {201} are the largest, followed by {001}, {100}, {310}, {111}, and {112} (Fig. 2a). This morphology is in reasonable agreement with the theoretical one and fit well with the ranking of frequency measured by VOGELS et al. on crystals grown from solution. However, as the relative lithium content of the mother solution increases, the crystals become slightly tabular {100} with the pinacoid {001} and the bipyramid {111} as side faces. The forms {101}, {310}, {201}, and {112} vanish and thus the morphology becomes rather poor (Fig. 2b).

Fig. 2. Growth morphologies of β -K₂SO₄ single crystals

Fig. 3. Single crystal of LiKSO_4

4.2. LiKSO_4 crystals

Lithium potassium sulphate crystallizes at room temperature in the space group $P6_3$ with $Z = 2$. The lattice parameters at 25°C are $a_0 = 5.1452 \text{ \AA}$ and $c_0 = 8.6343 \text{ \AA}$ (KARPPINEN et al.). Although a PBC analysis is beyond the scope of the present work, the relative importance of crystal forms may be roughly predicted by ranking the faces in increasing order of reticular area, according to the DONNAY HARKER rules. The D-H method ranks $\{10\bar{1}0\}$, $\{0002\}$, and $\{000\bar{2}\}$, $\{10\bar{1}1\}$ and $\{10\bar{1}\bar{1}\}$ first. The forms $\{10\bar{1}2\}$ and $\{10\bar{1}\bar{2}\}$ follow, but their reticular area is significantly greater.

Although the D-H method is only an approximation it can be considered very successful in predicting the growth morphology of LiKSO_4 . The crystals grown in these experiments are invariably formed by a combination of one prism $\{10\bar{1}0\}$, two pedions $\{0002\}$ and $\{000\bar{2}\}$, and two pyramids $\{10\bar{1}1\}$ and $\{10\bar{1}\bar{1}\}$ (Fig. 3). Moreover, crystals usually exhibit microscopic and macroscopic "twinning by merohedry", with twin laws $m \parallel [001]$, $2 \perp [001]$ and $m \perp [001]$ (KAPLER et al.). Because the crystals belong to point group 6, the pyramids $\{10\bar{1}1\}$ and $\{10\bar{1}\bar{1}\}$, as well as the pedions $\{0002\}$ and $\{000\bar{2}\}$, are non-equivalent and often occur with different morphological significance. Sometimes, however, due to twinning, the two pyramids and the two pedions show equal development, thus simulating a bipyramid and a pinacoid.

4.3. Epitaxial relationships between LiKSO_4 and $\beta\text{-K}_2\text{SO}_4$ crystals

As mentioned above, the use of non-equimolar mother solutions leads to different crystallization sequences, in agreement with the phase diagram. So, the initial crystallization of $\beta\text{-K}_2\text{SO}_4$ involves a continuous rise of the relative lithium concentration in the interstitial solution. The advancement of methanol diffusion, together with the Li-enrichment, produces an increase of supersaturation with respect to LiKSO_4 , which, finally, nucleates. Nucleation of LKS is often heterogeneous and occurs on the surface of previously grown $\beta\text{-K}_2\text{SO}_4$ crystals.

All observations of LKS crystals growing on KS suggest a non-random orientation, which means parallelism between specific reticular directions of the two phases. As shown in Fig. 4, the planes on which parallelism of the two lattices occurs are $(001)_{\text{KS}}$ and $(0001)_{\text{LKS}}$, and on these planes $[010]_{\text{KS}}$ is always parallel to $[010]_{\text{LKS}}$. The number of epitaxial crystals

Fig. 4. SEM view of a LiKSO_4 crystal epitaxially grown on a $\beta\text{-K}_2\text{SO}_4$ crystal

per host individual is initially not very high in most cases. However, the subsequent evolution depends on the initial composition of the mother solutions. So, for $[\text{Li}_2\text{SO}_4]/[\text{K}_2\text{SO}_4] > 0.6$, nucleation and growth of epitaxial crystals continues until the substrate is completely encompassed by an aggregate of parallel LiKSO_4 individuals (Fig. 5).

5. Discussion

Despite the fact that we are dealing with matching between an orthorhombic crystal and an hexagonal one, the similarities that make epitaxial overgrowth possible are not surprising. This becomes apparent when one compare the structural elements which both LiKSO_4 and $\beta\text{-K}_2\text{SO}_4$ have in common. Both compounds have been included by MOORE in a group formed by glaserite and over 100 alkali sulphates and calcium orthosilicate structures. Although they belong to different crystal systems, all these compounds evince a profound hexagonal substructure and can be described by the so-called model of "bracelets and pinwheels".

Fig. 5. Encompassing of $\beta\text{-K}_2\text{SO}_4$ by LiKSO_4 crystals

Fig. 6. Polyhedral diagram of the $\beta\text{-K}_2\text{SO}_4$ structure

The structure of $\beta\text{-K}_2\text{SO}_4$ appears as a polyhedral diagram in Figure 6. The large cation K^+ is 9-coordinated by oxygen atoms, six of which define the vertices of an elongated pseudo-trigonal antiprism (Fig. 7a). The grouping of six $[\text{SO}_4]^-$ tetrahedra around the antiprism defines a "pinwheel" where the apical oxygens points either up (4) or down (2). The circles represent the three additional oxygens, at tetrahedral apices, coordinating the cation. The K atoms are split away from the ideal pinwheel centre and oriented towards these meridional oxygens. Following MOORE's model, this configuration corresponds to $(4 + 2)_a$, which is one of the thirteen distinct "bracelets" involving six nodes and two symbols (u-up or d-down) distributed over trigonal antiprismatic vertices. The c -direction is the pinwheel repeat and $b_0 = 5.772 \text{ \AA} \sim a_0/\sqrt{3} = 5.815 \text{ \AA}$ emphasizes the pseudo-hexagonal character of the c -axis projection.

In the same way, the LiKSO_4 structure reveals the tetrahedral pinwheel $(6 + 0)_a$ -six up an zero down- and its selfcomplement. Such a configuration is shown on Figure 7b. In this pinwheel, the large cation K^+ also possesses 9-coordination, with the three meridional oxygens rotated away from the trigonal antiprism. The Li atoms occur in tetrahedral coordination with the oxygens and are not shown in Figure 7b. Obviously, the hexagonal c -direction is also in this case the pinwheel repeat. The previous considerations imply that both $\beta\text{-K}_2\text{SO}_4$ and LiKSO_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. This is clear from Figure 8 where the structures of $\beta\text{-K}_2\text{SO}_4$ and LiKSO_4 are projected, respectively, on (001) and (0001), i.e., on the epitaxy contact planes.

Fig. 7. a) Pinwheel $(4 + 2)_a$ of $\beta\text{-K}_2\text{SO}_4$. b) Tetrahedral pinwheel $(6 + 0)_a$ corresponding to LiKSO_4

Fig. 8. Projection of β - K_2SO_4 and $LiKSO_4$ structures on (001)

As reported above, $[010]_{KS}$ and $[010]_{LKS}$ constitute the most obvious coincident pair in the oriented overgrowth. For β - K_2SO_4 the distance between successive $[SO_4^-]$ tetrahedra along $[010]$ is $5.772 \text{ \AA}$, coinciding with the parameter b_0 . Moreover, $[010]_{KS}$ is the direction of the strongest PBC in this structure. For $LiKSO_4$, the distance between successive $[SO_4^-]$ groups along $[010]$ also coincides with the repeating period $b_0 = 5.145 \text{ \AA}$. Stoichiometric chains of strong sulphate-cations-sulphate bonds extend parallel to this direction and form an important PBC of $LiKSO_4$. The similar repeating period along $[010]_{KS}$ and $[010]_{LKS}$ explains the good matching between these directions. The misfit is 12.19%, which is reasonably inside the limits required for epitaxial nucleation both from vapour and solution (WALTON; VAN DER MERWE; TURNBULL, BONNEGUT).

Another pair of directions lying within the contact planes are $[100]_{LKS}$ and $[1\bar{1}0]_{KS}$ (see Fig. 8). In the hexagonal $LiKSO_4$, the direction $[100]$ is symmetrical to $[010]$ by a rotation of 120° . So, repeating periods ($5.145 \text{ \AA}$) and bond chains are equal along both directions. On the contrary, in β - K_2SO_4 the directions $[010]$ and $[1\bar{1}0]$ are obviously not symmetrical. Along $[1\bar{1}0]_{KS}$, cations and sulphate groups form strong bond chains of repeating period $11.608 \text{ \AA}$. However, the $[SO_4^-]$ tetrahedra point alternatively up and down along these chains, in such a way that the distance between successive tetrahedra is half of the repeating period, i.e., $5.304 \text{ \AA}$. It is worth noting that $[1\bar{1}0]_{KS}$ and $[010]_{KS}$ form an angle of 119.82° , which again shows the pseudo-hexagonal character of $(001)_{KS}$.

The similar distance between successive tetrahedra along $[100]_{LKS}$ and $[1\bar{1}0]_{KS}$ explains the good matching between these directions. The misfit is only 3.09%, when calculated considering a 2:1 ratio between the repeating periods. Even though these two directions are not exactly coincident, the angular misfit between them is very small (0.18°). It therefore appears that from a geometrical standpoint, the epitaxy is favoured by good match in two directions on the contact planes, which means it can be considered two-dimensional.

This work was supported by CICYT (Science and Technology Commission of Spain), Grant MAT 90-0775-CO3-03.

References

- AREND, H., CONNELLY, J. J.: *J. Cryst. Growth* **56** (1982) 642
BHAKAY-TAMHANE, S., SEQUEIRA, A., CHIDAMBARAM, R.: *Solid State Commun.* **53** (1985) 197
DONNAY, J. D. H., HARKER, D.: *Amer. Mineral.* **22** (1937) 446
HARTMAN, P.: in: *Morphology of Crystals* (Ed. I. SUNAGAWA), Terra Sci., Tokyo 1987
HENISH, H. K.: *Crystals in gels and Liesegang's rings*, Cambridge University Press, Cambridge 1989
KARPPINEN, M., LUNDGREN, J. O., LIMINGA, R.: *Acta Cryst.* **C39** (1983) 34
KLAPPER, H., HAHN, TH., CHUNG, S. J.: *Acta Cryst.* **B43** (1987) 147
MOORE, P. B.: *Amer. Mineral.* **58** (1973) 32
PRIETO, M., PUTNIS, A., FERNÁNDEZ-DÍAZ, I., LÓPEZ-ANDRÉS, S.: *J. Cryst. Growth* **142** (1994) 225
PUTNIS, A., FERNÁNDEZ-DÍAZ, L., PRIETO, M.: *Nature* **358** (1992) 743
SCHOTT, H.: *J. Chemical Engineering Data* **6** (1961) 324
SCHULZ, H., ZUCKER, U., FRECH, R.: *Acta Cryst.* **B41** (1985) 21
VAN DER MERWE, J. H.: *J. Appl. Phys.* **34** (1963) 117
VARMA, V., BHATTACHARJEE, R., FERNANDES, J. R., RAO, C. N. R.: *Solid State Commun.* **76** (1990) 627
VOGELS, L. J. P., VERHEIJEN, M. A., BENNEMA, P.: *J. Cryst. Growth* **110** (1991) 604
WALTON, A. G.: in: *Nucleation* (Ed. A. C. ZETTMAYER), Dekker, New York 1969
WYCKOFF, R. W. G.: *Crystal structures*, Wiley, New York 1965
ZHANG, P. L., YAN, Q. W., BOUCHERLE, J. X.: *Acta Cryst.* **C44** (1988) 592