Journal of Solid State Chemistry **156,** 251–252 (2001)
doi:10.1006/jssc.2000.8988, available online at http://www.idealibrary.com on IDEAL®

RAPID COMMUNICATION

Comment on "Thermal Analysis and X-Ray Diffraction Study on $LiKSO_4$: A New Phase Transition"

Xavier Solans,* M. Teresa Calvet,* M. Luisa Martínez-Sarrión,† Lourdes Mestres,† Aniss Bakkali,† Eduardo Bocanegra,‡ Jorge Mata,* and Marta Herraiz†

** Departament Cristallografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, E-08028 Barcelona, Spain; † Departament de Química Inorgànica, and ‡ Departamento de Física Aplicada II, Universidad del Pais Vasco, E-48080 Bilbao, Spain*

Received July 19, 2000; in revised form September 4, 2000; accepted October 6, 2000; published online December 21, 2000

In the preceding manuscript, Tomaszewski comments on our previous paper, X. Solans *et al.*, *J. Solid State Chem.* 148, 316 (1999). These comments can be summarized in two points: (a) The influence of the domain or/and twinning on the obtained results and (b) the poor data obtained in the mentioned paper. An answer is given. © 2001 Academic Press

1. THE DOMAIN/TWINNING STRUCTURE

There is great confusion between twinning and domain formation in the Comment of Tomaszewski. We think that it is necessary to differentiate between the twin crystal obtained from a crystallization process and domain formation (or could be accepted twin formation) due to phase transition. Reference (1) is not the first manuscript on $LiKSO_4$ that deals with an untwinned crystal. An example is reported in (2), and we think that Tomaszewski accepts it, because he states in his introduction "the data obtained below the room temperature are controversial," so as a minimum he accepts the results at room temperature or above room temperature. The phase at room temperature is $P6_3$ (ordered structure), while a twin crystal at room temperature gives a $P6_3$ (disordered structure) or $P2_1$ (3). We remark that the same untwinned crystal was used in all processes on the single-crystal diffractometer in (1). The second point is the domain formation. Here there are two possibilities: These domains can be randomly distributed or ordered. Randomly distributed could produce double or broad peaks in the X-ray diffraction pattern and a high standard deviation in the obtained cell parameters. In the structure determination process a high Flack coefficient for the refined structural model would be obtained, an example of which and how it is solved can be found in (4). An ordered distribution of the domains will give good cell parameters with good standard deviations; surely, a disordered atomic structure and (if the disorder model is correct) will give a correct Flack coefficient. We remark that the authors of (1) are in this second possibility and we state in our results and discussion and in our conclusions that the phase $P6_3mc$ and $Cmc2_1$ "have multiple domains of $P6_3$ and Cc symmetry," which agrees with the comments of Tomaszewski in the preceding manuscript and with the results of (5) and (6). The lack of observation of domains in the phase $P31c$ agrees with the results of (6), of which Tomaszewski is an author. In (6), p. 916, section 3, line 17, the authors state (during a heating process) "Above 194 K the domains disappear ...." Above 194 K corresponds in (1) to the phase $P31c$, which is assumed by Solans *et al.*, to be without domain structure. Could Tomaszewski explain the contradiction between his present comment and that in his paper (6)?

2. THE POOR DATA OF (1)

Tomaszewski states that the cell parameters obtained by X-ray Bond method (7) have an accuracy of 10^{-5}. He confuses the equipment accuracy of 2θ with the accuracy of the cell parameters. An example of our comment is the paper (8) where the Bond method is used. In Table 1 of this manuscript the accuracy of the obtained cell parameters is 2×10^{-4} for *a* and *b* parameters and 10^{-4} for *c* parameter for a crystal of cell volume equal to 400 Å^3. An accuracy of 10^{-4} was obtained in (1).

In Table 1 the measurements of cell parameters of Desert *et al.* (9) and Solans *et al.* (1) are compared. The two measurements are different and give different results because

(a) The higher cooling and heating rates in Solans *et al.* measurements facilitate the kinetics of phase transitions,

0022-4596/01 $35.00
Copyright © 2001 by Academic Press
All rights of reproduction in any form reserved.

TABLE 1

Comparison of the Method Used to Determined the Cell Parameters at Different Temperatures in Refs. (1) and (9)

	Desert *et al.* (9)	Solans *et al.* (1)
Geometry	Reflection	Transmission
Beam	Divergent	Parallel
Sample	Single crystal	Powder
Scan	Missing ($\omega/2\theta$ from Figs. 1 and 4?)	Detector: fixed Sample: Phi rotation
Wavelength	Missing	Cu$K\alpha$
Primary monochromator	Missing (None from figures)	Quartz monochromator
Exposure time for each value	Scan speed is missing	> 1 h
Temperature range	100–298 K	163–298 K
Cooling and heating rate	0.43 K/min	10 K/min
No. of reflections used to determine cell parameters	2 (0 0 8 and 0 4 0)	All between 2 and 120°

while the lower rate in Desert *et al.* measurements facilitates the observation of metastable phases.

(b) The number of reflections used to determine the cell parameters by Solans *et al.* give an average information for the entire sample. The use of one reflection to determine each cell parameter in Desert *et al.* implies that systematic errors in the measurements of this peak will be reflected in the obtained cell parameter.

(c) The phi scan used by Solans *et al.* diminishes the domain effects on the determination of cell parameters. In the Desert *et al.* study a phi scan is not used in order to study the domain effects, as is stated in (9).

(d) The shortest temperature range in (1) does not allow the study of the $Cmc2_1$ phase.

The results of Desert *et al.* are different because

(a) Desert *et al.* use reflection geometry and divergent beam, so the width and the asymmetry effects of the peak are higher than those obtained by Solans *et al.* The overlapping of Kα_1 and Kα_2 in the 0 4 0 reflection is important and the number of counts per peak is different in the two measurements because different type of sample and exposure time are used. All that produces less accuracy in the determination of the peak position in the measurements of Desert *et al.* than that obtained by Solans *et al.*

(b) The main problem in the measurements reported in (7) and (9) is the tilt angle between the crystal face and the goniometer plane, a test of which is not stated in either manuscript.

Despite all that, it is well known that all phase transition processes depend on their history, so the two measurements are not readily comparable.

The enthalpies of the phases transitions in (1) were measured during the heating process. The peak overlap of phase transitions II and III was solved by a multipeak computer fit, using an asymmetric pseudo-Voight function. The onset temperatures were determined using the maximum slope method.

As a last remark, we agree with Tomaszewski's comment concerning the phase at 189 K. The space group is $P31c$.

REFERENCES

1. X. Solans, M. T. Calvet, M. L. Martínez-Sarrión, L. Mestres, A. Bakkali, E. Bocanegra, J. Mata, and M. Herraiz, *J. Solid State Chem.* **148,** 316 (1999).
2. J. Ortega, J. Etxebarria, and T. Breczewski, *J. Appl. Cryst.* **26,** 549 (1993).
3. S. Bhakay-Tamhane, A. Sequeira, and R. Chidambaram, *Acta Crystallogr. Sect. C* **40,** 1648 (1984).
4. X. Solans, J. Mata, M. T. Calvet, and M. Font-Bardia, *J. Phys.: Condens. Matter* **11,** 8995 (1999).
5. W. Kleemann, F. J. Schaefer, and A. S. Chaves, *Solid State Commun.* **64,** 1001 (1987).
6. R. Cach, P. E. Tomaszewski, and J. Bornarel, *J. Phys. C: Sol. State Phys.* **18,** 915 (1985).
7. P. E. Tomaszewski and K. Lukaszewicz, *Phase Transit.* **4,** 37 (1983).
8. P. E. Tomaszewski and A. Pietraszko, *Phys. State Sol.* (*a*) **56,** 467 (1979).
9. A. Desert, A. Gibaut, A. Righi, U. A. Leitao, and R. L. Moreira, *J. Phys.: Condens Matter* **7,** 8445 (1995).