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RAPID COMMUNICATION

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

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In a recent paper (*J. Solid State Chem.* 148, 316 (1999)) Solans *et al.* presented the structure of different phases of $LiKSO_4$ and a new phase transition at about 226 K (268 K on heating). We believe that most of the results commented on are not credible. © 2001 Academic Press

Key Words: **lithium potassium sulphate; phase transition; domain structure.**

INTRODUCTION

In a recent publication Solans *et al.* (1) present the results of their studies of $LiKSO_4$ in the temperature range 123–1000 K. The data obtained below room temperature are controversial and of different scientific value.

$LiKSO_4$ is one of the most interesting ferroelastic crystals studied since 1855 (2–4). Now, the $LiKSO_4$ bibliography contains more than 600 papers (5). Despite this there are many controversies even in establishing a definitive phase diagram of $LiKSO_4$. Thus, it is necessary to be careful with the "discovery" of new phases and phase transitions. Furthermore, each new paper about this compound should present better and more reliable data than those previously published. Unfortunately, the paper commented on here does not present such a case. The authors published rather poor data obtained, as it seems, on multidomain samples and presented it in a unconventional manner, and without critical review of the previously published results. Below some of the questioned statements will be discussed.

NOMENCLATURE

First, it is necessary to preserve the nomenclature established by previous works (6–9) to avoid the misinterpretation of new data. The authors, contrary to the above rule, proposed their own new sequence of phase names starting from low-temperature phase (in the literature numbered as phase V) instead of highest-temperature phase as widely used in the literature concerning phase transitions. With this inconvenient nomenclature, the numerous phases below 150 K could not be included in the coherent scheme of phase transitions.

DOMAIN STRUCTURE

One of the most important problems to solve in all crystals with a ferroelastic phase transition is the occurrence of twinning (domain formation) of an initially single-domain sample. In $LiKSO_4$ such domain structures are very complicated (6, 10–14) and depend strongly on the thermal treatment of the sample (6). The influence of such domains on the X-ray diffraction pattern is perfectly demonstrated by Desert *et al.* (8). In general, it is not possible to remove these domains by using external stress. Thus, it is of great importance to know what procedure was used by the authors to avoid the creation of ferroelastic domains when the sample passes from one phase to another, changing crystal systems (especially below 190 K) (14–16). How was the sample maintained in the single-domain state at all temperatures? It is not sufficient to write "without using a twin structure" (p. 319). Thus, it is very difficult to believe the accuracy of the structure determination results, especially when the authors write about some disorder in the structures due to the domain structure (p. 323). The "working conditions" mentioned in the paper should have been described in detail. It seems that if there is an efficient procedure known to the authors it would be an important result, more so than the structural data.

The existence of domains in the sample may be a source of errors in the structure determination—the domain structure disturbs the final results leading to the "average structure."

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If the amount of both types of domains is equal, the "average structure" has a symmetry higher than the true basic structure. It seems that such misinterpretation concerns the data at 260 and 125 K. There is no scientific meaning to publish such results when the correct data are available in the literature. Moreover, the space group at 189 K should be written as $P31c$ instead of $P3_1c$, which occurs several times in the text commented on.

LATTICE PARAMETERS

The Authors published data of insufficient quality on the changes of the lattice parameters calculated from the powder diffraction data, and do not compare them with the precise results (of the accuracy of 10^{-5}) obtained by the X-ray Bond method (17). There were no peculiarities found in the thermal dependence of lattice parameters obtained from single-crystal experimentation, which could suggest supplementary phase transitions in $LiKSO_4$. Similar good data were published several times and more recently by Desert *et al.* (8).

The values of lattice parameters calculated from powder data (see Fig. 2 of Ref. (1)] do not coincide with the data from single-crystal experiments (reported in Table 3 of the discussed paper). Moreover, the low-temperature lattice parameters (below 190 K, i.e., within phase I) are totally different and with opposite behavior from other published data (8, 17).

The lack of estimated error bars in Fig. 2 of Ref. (1) provides no opportunity to assess the goodness of data and the significance of the "anomalies." One could suppose that the standard deviations for the presented data are at least of about 10^{-3} Å, thus "hiding" all anomalies on the curves.

Moreover, the great difference in the lattice parameter c above 260 K with respect to the literature data was not explained at all. The assumption of new phase transition is not sufficient. This result seems to be due to change in the proportion of different coexistent phases (17).

DSC DATA

The transition temperature for phase transition III on heating should be 260 K instead of 268 K (the onset was erroneously taken from the high-temperature site). Moreover, there is an unexplained discrepancy between the data from Table 2 and that from Fig. 1. Similar DSC peaks I and III correspond to the ΔH of 46 and 9 J/mol^{-1} respectively; i.e., the first is five times greater than the latter.

The situation in $LiKSO_4$ is still far from being clear. The recent paper by Scherf *et al.* (18) is a good example—the authors presented the well-refined structure of phase V made in the centrosymmetric space group *Pcmn* instead of acentric subgroup $Pc2_1n$ chosen in the paper commented on. The commented paper does not bring us closer to the desired understanding of the nature of structure and phase transitions.

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