

## Structural Transition and Thermal Anomaly in $\text{LiTiSO}_4$

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A survey for discovering new ferroelectric or ferroelastic crystals has been worked in order to get more useful or functional materials or to understand the mechanism of ferroelectricity and ferroelasticity. In the last two decades, a family of crystals with a chemical formula  $A_2BX_4$  have been widely investigated, because they have incommensurate phases.<sup>1)</sup>

If two alkali metal ions  $A$ 's are not the same kind, then the crystal structure and the transition sequence become a little different from the  $A_2BX_4$  family.<sup>1)</sup> Among such  $AA'BX_4$ -type crystals,  $\text{LiNH}_4\text{SO}_4$ <sup>2)</sup> and  $\text{LiRbSO}_4$ <sup>3)</sup> are ferroelectrics and take a general tridymite structure.<sup>4,5)</sup> At high temperature, both crystals belong to an orthorhombic  $Pm\bar{c}n$  ( $Z = 4$ ) system, where each  $\text{SO}_4$  tetrahedron occupies two configurations with equal probability.<sup>6,7)</sup> Ordering of the disordered tetrahedra takes place with lowering temperature. In  $\text{LiRbSO}_4$ , incommensurately and commensurately modulated phases are realized above room temperature.<sup>8)</sup> The  $\text{LiNH}_4\text{SO}_4$  crystal is ferroelectric in the room-temperature phase and takes a superstructure below room temperature.<sup>9)</sup>

Recently Shimizu and Takashige synthesized  $\text{LiTiSO}_4$  by a Bridgman method.<sup>10)</sup> They performed differential thermal analyses and observed two anomalies on cooling and one anomaly on heating, which indicates structural transitions of the crystal. They also measured dielectric constants; the constant perpendicular to the cleavage plane showed three and two anomalies (stepwise change or hump) on cooling and heating runs, respectively. The crystal was considered not to be ferroelectric because no  $DE$ -hysteresis loop was observable.

According to a preliminary study by X-ray scattering,<sup>11)</sup> the room-temperature phase of the crystal belongs to  $Pm\bar{c}n$ . In the low temperature region, superstructure reflections have been found. The diffraction pattern in the  $(h k 0)$  zone seems to be a hexagonal one in the lowest temperature phase, although the degree of crystal symmetry usually decreases with decreasing

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temperature. In  $A_2BX_4$ -type crystals, flopping of  $BX_4$  tetrahedra is necessary to become hexagonal from orthorhombic.<sup>12)</sup> If such flopping takes place at the transition of  $\text{LiTlSO}_4$ , then a large thermal anomaly will be observable. The character of the intermediate phase may also be clarified by thermal analyses. Since no further study has been reported so far as the author's knowledge, we investigated the transition entropy of this crystal.

Single crystals of  $\text{LiTlSO}_4$  were grown by the Bridgman method. The crystal is transparent and colorless. A small amount of crystal was sealed in an aluminum cell and was provided for the thermal analysis. Two kind of samples were prepared; powder of the crystal: 17.87 mg, and a piece of block cut from the bulk: 2.53 mg. Since the piece was selected from a single crystal part, it is called as a single crystal hereafter. A differential scanning calorimeter (Rigaku: DSC8230) was used. The heating rate was 10 K/min. The transition temperature was determined by a cross point of the slope line of the anomalous heat flow and the background line. The transition entropy was estimated from the amount of the excess heat flow.

With decreasing temperature, a differential thermal analysis was recorded on a chart. For the powder sample, two signals were detected; a small anomaly was at 267 K and a large anomaly peaked at 232 K with accompanying a shoulder around 238 K in similar to the first report in ref. 10. For the single crystal, two anomalies were observed; a small one at 267 K and a large one at 243 K. The second transition temperature depended on a cooling rate a little; it was about 253 K under a very slow cooling.

On heating, the excess heat flow at the structural transition was recorded as DSC signal, which is shown in Fig. 1 for the powder sample. We can notice two small anomalies at 236 K and 263 K and



Fig. 1. The DSC signal from  $\text{LiTlSO}_4$  powder observed on a heating run. Two small anomalies are indicated by arrows.

a large one at 288 K. The amount of the enthalpy change  $\Delta H$  was 0.017, 0.027 and 1.65 kJ/mol, respectively. The transition entropy at 288 K was  $5.75 \text{ J}/(\text{mol K}) \simeq R \ln 2.0$ .

On the other hand, only one DSC signal was observed for the single crystal. It was found that the anomaly depended on the turning temperature at which a cooling run was changed to a heating run. If the crystal was cooled enough, say below 230 K, then the single crystal sample showed a large anomaly at 288 K with  $\Delta H = 1.47 \text{ kJ}/\text{mol}$  on the heating. The excess heat flow amounts to the entropy change of  $5.10 \text{ J}/(\text{mol K}) \simeq R \ln 1.8$ . Since the single crystal sample was very small, this value is not so accurate as the powder one.

On the contrary, if the turning temperature was above 250 K, the small anomaly appeared at 267 K with  $\Delta H \simeq 0.12 \text{ kJ}/\text{mol}$  and the anomaly at 288 K disappeared, as shown in Fig. 2. If the

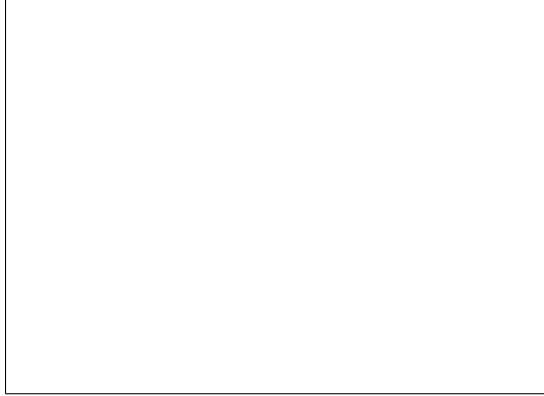


Fig. 2. The temperature dependence of the DSC signal from  $\text{LiTlSO}_4$  single crystal on heating runs. The sample temperature was changed from cooling to heating at 235 K (a), 245 K (b) and 260 K (c).

turning temperature was near the transition temperature of 243 K, then weaker anomalies were detectable at 267 K and 288 K. This result shows that once the low temperature phase is realized, it is easily super-heated and the intermediate phase does not appear on heating. If the crystal transforms to the room-temperature phase, then the intermediate phase appears on cooling. The phase sequence and the transition temperatures are summarized in Table I.

The transition temperatures and the shape of the anomaly depended slightly on the part of the crystal from which the sample was prepared. However, the transition at 267 K, if it takes place, seems to be a second order one. Meanwhile the transition at 243 K (cooling) and 288 K (heating) is a first-order one with accompanying a large thermal hysteresis. The powder sample might be contaminated from a non-stoichiometric part synthesized by the Bridgman method. We attribute

Table I. Phase sequence of LiTiSO<sub>4</sub>.

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Phase	III	←	II	↔	I
		243 K		267 K	
Phase	III	→	I		
		288 K			

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the additional small anomalies at 236 K and 263 K in the powder sample to such imperfection of the sample.

The transition entropy at 288 K on heating is almost  $R \ln 2$  per one mole and the transition is an order-disorder type. Taking the LiNH<sub>4</sub>SO<sub>4</sub> type structure into account, the SO<sub>4</sub> tetrahedra are disordered in the room temperature phase of *Pmcn*. Each tetrahedron occupies, with an equal probability, two configurations related by the mirror symmetry perpendicular to the *a* axis. In the low temperature phase, the tetrahedron occupies one configuration, dominantly. Then the expected entropy change is  $R \ln 2$ . If the lowest temperature phase is hexagonal, then the SO<sub>4</sub> tetrahedra should have additional freedom to turn the apex upside down, which needs further entropy change of  $R \ln 2$ , and the total entropy change may be  $R \ln 4$ ; however this is not the case.

Finally we note about the thermal anomaly at 267 K, below which superstructure reflections were observed by the preliminary X-ray scattering study.<sup>11)</sup> The estimated transition entropy is about 0.45 J/(mol K), small enough to indicate a displacive type transition. On further cooling, the intensity of the superstructure reflections increased discontinuously below 243 K. Between 267 K and 243 K, the cell dimension is fourfold along the *a*-axis. Below 243 K, the unit cell volume becomes six times of the room-temperature phase. Therefore, the existence of the intermediate phase in LiTiSO<sub>4</sub> is clear. A detailed diffraction study is now on progress.

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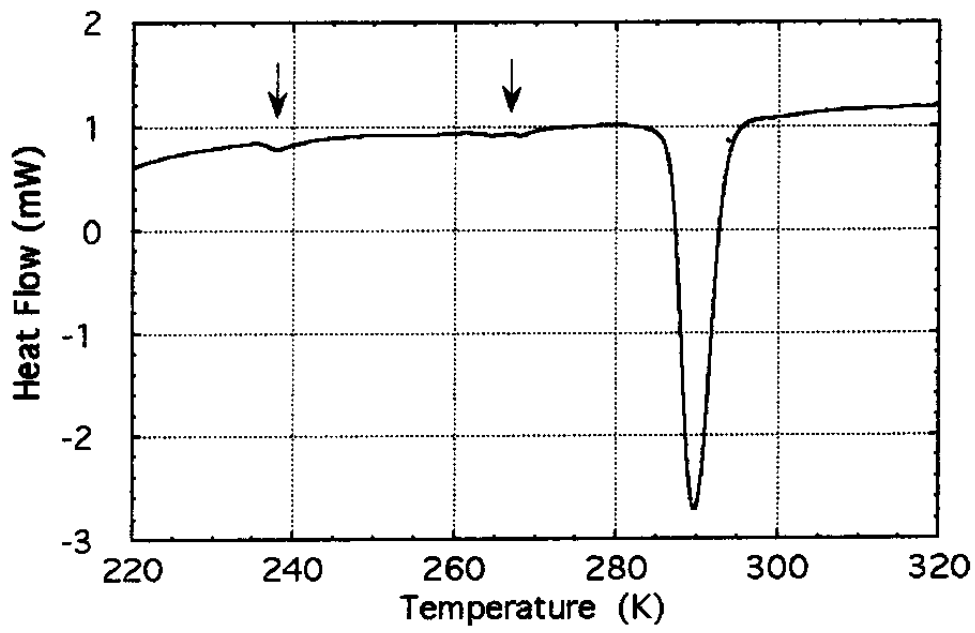


Fig. 1

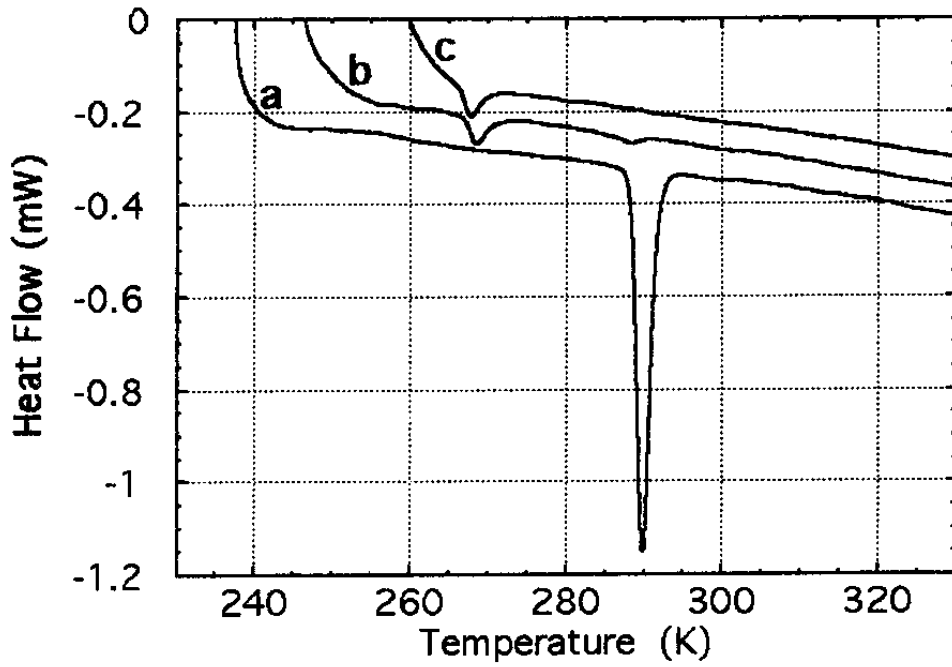


Fig. 2