CORRELATION BETWEEN STRUCTURES AND THERMAL PROPERTIES OF HYDRATED THALLIUM(I) DIBORATES; H₂O—Tl₂B₄O₇, PHASE DIAGRAM*

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Two synthetic hydrated thallium(I) diborates have been found in the liquid—solid equilibria of the 100° isotherm of the ternary system H₂O—B₂O₃—Tl₂O; they were characterized via the powder diagrams, but classical chemical analysis does not lead to the correct degree of hydration. Through TG of the powders, a complex process is found with no explanation. Structural resolution and TG of the monocrystals allow a correct explanation of the thermal dehydration: these thallium(I) diborates are two distinct compounds, Tl₂B₄O₇·3H₂O and Tl₂B₄O₇·1.5H₂O, which have their own process of dehydration; they contain infinite chains of polyanions and their structural formulae are Tl₂[B₄O₆(OH)₂]·2H₂O and Tl₄[B₆O₁₆(OH)₄]·H₂O; the latter polyanion may be considered as the dimer of the first.

The H₂O—Tl₂B₄O₇ phase diagram was established by thermal analysis and solubility experiments, both under pressure; it allows the prediction that another hydrated thallium(I) diborate, Tl₂B₂O₇·H₂O, exists, with possible structural formula Tl₆[B₁₂O₁₈(OH)₆]. Actually, only monocrystals of Tl₆[B₁₂O₁₈(OH)₆]·H₂O have been obtained hydrothermally from Tl₂[B₄O₆(OH)₂]·2H₂O.

During establishment of the 100° isotherm of the ternary system H₂O—B₂O₃—Tl₂O [1], the existence of two thallium(I) diborate hydrates became obvious: one with congruent solubility and the other with incongruent solubility and having a very narrow crystallization zone (Fig. 1). Chemical analysis of the solid phases separated from their respective solutions does not allow the exact determination of the degree of hydration; on the other hand, these products were clearly identified by their very different powder diagrams. It therefore became necessary to resort to thermogravimetry (TG) so as to propose plausible chemical formulae.

Experimental

Hydrated thallium(I) diborate, $\text{Tl}_2\text{B}_4\text{O}_7\cdot3\text{H}_2\text{O}$, was synthesized from an aqueous solution of $\text{H}_3\text{BO}_3$ and $\text{Tl}_2\text{CO}_3$. Monocrystals were obtained from moist $\text{Tl}_2\text{B}_4\text{O}_7\cdot3\text{H}_2\text{O}$ powder in a silver tube, itself placed in a larger glass tube which was sealed; heating the material for 15 days at $100^\circ$ led to $\text{Tl}_2\text{B}_4\text{O}_7\cdot3\text{H}_2\text{O}$ monocrystals, and for 7 days at $200^\circ$ to $\text{Tl}_2\text{B}_4\text{O}_7\cdot1.5\text{H}_2\text{O}$ monocrystals [3].

Chemical analysis was performed on the same sample by acidimetry, firstly with 0.1 $N$ HCl, and secondly with 0.1 $N$ NaOH after addition of neutral glycerol [1]. TG on monocrystals needed about 400 mg (Fig. 2a) and 150 mg (Fig. 2b) at a heating rate of $60^\circ$ per hour. The apparatuses used for solubility and thermal analysis under pressure were described in [7]; these techniques needed, respectively, 10 g and 20 g of powders. A classical X-ray diffraction apparatuses for studying powders and monocrystals were also used.

![Fig. 1 100° isotherm of $\text{H}_2\text{O}--\text{B}_2\text{O}_3--\text{Tl}_2\text{O}$ system](image)

![Fig. 2 TG curves of $\text{Tl}_2\text{B}_4\text{O}_7\cdot3\text{H}_2\text{O}$ monocrystals (curve a) and $\text{Tl}_2\text{B}_4\text{O}_7\cdot1.5\text{H}_2\text{O}$ monocrystals (curve b)](image)

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