CORRELATION BETWEEN STRUCTURES AND THERMAL PROPERTIES OF HYDRATED THALLIUM(I) DIBORATES; H_2O—$Tl_2B_4O_7$ 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 H_2O—B_2O_3—Tl_2O; 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, $Tl_2B_4O_7 \cdot 3H_2O$ and $Tl_2B_4O_7 \cdot 1.5H_2O$, which have their own process of dehydration; they contain infinite chains of polyanions and their structural formulae are $Tl_2[B_4O_6(OH)_2] \cdot 2H_2O$ and $Tl_4[B_8O_{12}(OH)_4] \cdot H_2O$; the latter polyanion may be considered as the dimer of the first.

The H_2O—$Tl_2B_4O_7$ phase diagram was established by thermal analysis and solubility experiments, both under pressure; it allows the prediction that another hydrated thallium(I) diborate, $Tl_2B_4O_7 \cdot H_2O$, exists, with possible structural formula $Tl_6[B_{12}O_{18}(OH)_6]$. Actually, only monocrystals of $Tl_4[B_8O_{12}(OH)_4] \cdot H_2O$ have been obtained hydrothermally from $Tl_2[B_4O_6(OH)_2] \cdot 2H_2O$.

During establishment of the 100° isotherm of the ternary system H_2O—B_2O_3—Tl_2O [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, $Tl_2B_4O_7 \cdot 3H_2O$, was synthesized from an aqueous solution of H_3BO_3 and Tl_2CO_3. Monocrystals were obtained from moist $Tl_2B_4O_7 \cdot 3H_2O$ powder in a silver tube, itself placed in a larger glass tube which was sealed; heating the material for 15 days at 100° led to $Tl_2B_4O_7 \cdot 3H_2O$ monocrystals, and for 7 days at 200° to $Tl_2B_4O_7 \cdot 1.5H_2O$ monocrystals [3].
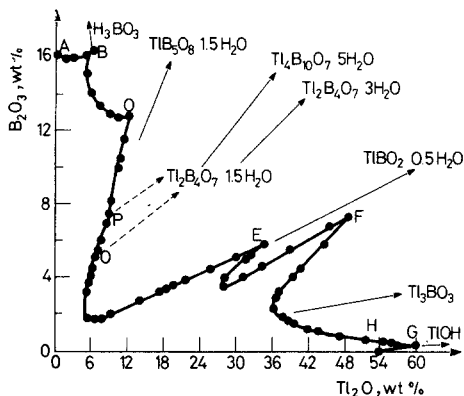
Fig. 1 100° isotherm of H_2O—B_2O_3—Tl_2O system

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° per hour. The apparatuses used for solubility and thermal analysis under pressure were described in [7]; these techniques needed, respectovely, 10 g and 20 g of powders. A classical X-ray diffraction apparatuses for studying powders and monocrystals were also used.
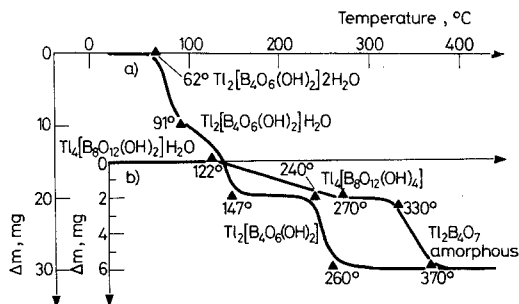
Fig. 2 TG curves of $Tl_2B_4O_7 \cdot 3H_2O$ monocrystals (curve a) and $Tl_2B_4O_7 \cdot 1.5H_2O$ monocrystals (curve b)
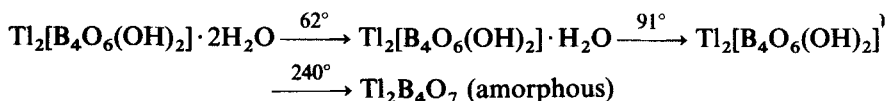
Results

Thermogravimetry

The thermal curves of the *polycrystalline* products were similar to those presented in Fig. 2, but accompanied by a loss of some moisture under 50° [2]. Curve 2a (Fig. 2) concerns the compound with congruent solubility, which is also easily synthesized from aqueous solutions of H_3BO_3 and Tl_2CO_3. By a simple calculation of the total water loss, we can ascribe the formula $Tl_2B_4O_7 \cdot 3H_2O$; three steps of dehydration occur according to the scheme below:

$$Tl_2B_4O_7 \cdot 3H_2O \xrightarrow{62°} Tl_2B_4O_7 \cdot 2H_2O \xrightarrow{91°} Tl_2B_4O_7 \cdot H_2O \xrightarrow{240°} Tl_2B_4O_7.$$
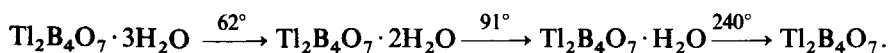
From curve 2a, it is possible that the second hydrate which appeared with incongruent solubility in the 100° isotherm might be formulated as $Tl_2B_4O_7 \cdot 2H_2O$ and might be obtained by simple dehydration of the former hydrate.

To verify this hypothesis, the TG of the solid phase with incongruent solubility, separated from its solution at 100°, was carried out (Fig. 2b): the formula obtained from the calculation was not $Tl_2B_4O_7 \cdot 2H_2O$, but was close to $Tl_2B_4O_7 \cdot 1.5H_2O$ for the first step; there is another step corresponding to $Tl_2B_4O_7 \cdot H_2O$ before $Tl_2B_4O_7$.

To resolve the problem of the formulation of these two hydrates, monocrystals were synthesized [3] to permit structural resolution and also thermogravimetric analysis (Fig. 2). Structural resolution led to the formulae $Tl_2B_4O_7 \cdot 3H_2O$ [4] and $Tl_2B_4O_7 \cdot 1.5H_2O$ [5]. These compounds contain infinite chains of polyanions $[B_4O_6(OH)_2]^{2-}$ and $[B_8O_{12}(OH)_4]^{4-}$, the thallium atoms and the water molecules being localized between these chains. Their structural formulae are, respectively, $Tl_2[B_4O_6(OH)_2] \cdot 2H_2O$ and $Tl_4[B_8O_{12}(OH)_4] \cdot H_2O$. The TG curves of the *monocrystals* (Fig. 2) may readily be explained. The TG of $Tl_2[B_4O_6(OH)_2] \cdot 2H_2O$ and systematic X-ray verification at each step of dehydration lead to the same scheme, but which is better written (curve 2a):

$$Tl_2[B_4O_6(OH)_2] \cdot 2H_2O \xrightarrow{62°} Tl_2[B_4O_6(OH)_2] \cdot H_2O \xrightarrow{91°} Tl_2[B_4O_6(OH)_2]$$
$$\xrightarrow{240°} Tl_2B_4O_7 \text{ (amorphous)}$$

The water of crystallization is of the zeolitic type and is removed easily at relatively low temperature, without destruction of the network; at 240°, destruction of the network occurs and the rupture of the chains leads to an amorphous anhydrous product, $Tl_2B_4O_7$.

A correct explanation may also be given of the TG of $Tl_4[B_8O_{12}(OH)_4] \cdot H_2O$ (curve 2b) with the scheme below:

$$Tl_4[B_8O_{12}(OH)_4] \cdot H_2O \xrightarrow{122°} Tl_4[B_8O_{12}(OH)_4] \xrightarrow{330°} Tl_2B_4O_7 \text{ (amorphous)}$$
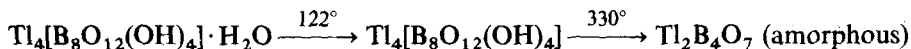
Elimination of the water of crystallization of zeolitic type takes place at 122°; rupture of the chains and destruction of the network occur at higher temperature, 330°, and lead to the same amorphous product, $Tl_2B_4O_7$.

H_2O—$Tl_2B_4O_7$ diagram

These results and the procedure for obtaining monocrystals (see experimental section) necessarily lead to a reexamination of the interpretation of the binary phase diagram H_2O—$Tl_2B_4O_7$, which was studied *under pressure* by thermal analysis and solubility measurements [2]. From these latter experimental results which remain valid, a correct interpretation may be given (Fig. 3). The trihydrate,
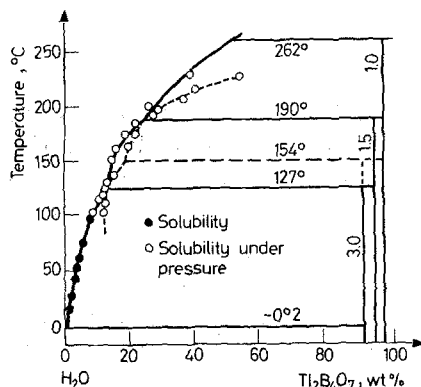

Fig. 3 H_2O—$Tl_2B_4O_7$ system; dashed lines represent metastable equilibrium

$Tl_2B_4O_7 \cdot 3H_2O$, is in equilibrium at room temperature with the saturated solution. Its solubility depends on the temperature and it melts incongruently at 127° to give $Tl_2B_4O_7 \cdot 1.5H_2O$ and liquid. However, it is possible that this latter compound does not appear and then a metastable peritectic reaction leads to the formation of a monohydrate $Tl_2B_4O_7 \cdot H_2O$. At 190°, $Tl_2B_4O_7 \cdot 1.5H_2O$ gives, by a peritectic process, $Tl_2B_4O_7 \cdot H_2O$, which leads to an anhydrous product, $Tl_2B_4O_7$, at 262° (peritectic reaction). In Fig. 3, full lines represent stable equilibrium, and dashed lines represent metastable equilibrium.

Considerations

These results allow us to foresee that another hydrated thallium(I) diborate exists, $Tl_2B_4O_7 \cdot H_2O$. We can predict its structure by analogy with those of the two

other hydrates, from the monocrystal-forming process and from thermal analysis and solubility experiments: we can see that the polyanion $[B_8O_{12}(OH)_4]^{4-}$ (Fig. 4b) is the dimer of the polyanion $[B_4O_6(OH)_2]^{2-}$ (Fig. 4a); the dimerization resulted from elevation of the temperature in a closed apparatus. It is possible that trimerization occurs at higher temperature and leads to the polyanion
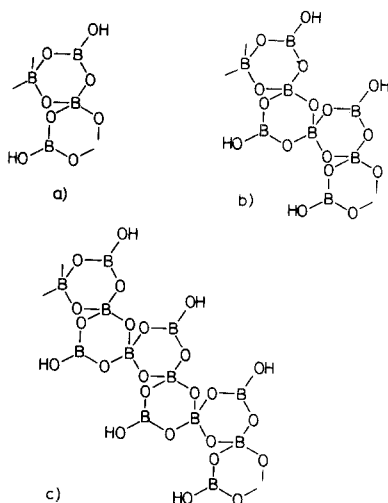

Fig. 4 Real polyanions $[B_4O_6(OH)_2]^{2-}$ (a); and $[B_8O_{12}(OH)_4]^{4-}$ (b); possible polyanion $[B_{12}O_{18}(OH)_6]^{6-}$ (c)

$[B_{12}O_{18}(OH)_6]^{6-}$ (Fig. 4c). The structural formula of $Tl_2B_4O_7 \cdot H_2O$ might be $Tl_6[B_{12}O_{18}(OH)_6]$ with no water molecule of crystallization. Additional proofs were the facts that, by thermal analysis under pressure, two exothermic effects occur, at 370° and 420°, which correspond, respectively, to the crystallization of anhydrous $Tl_2B_4O_7$-γ and to the monotropic transformation to $Tl_2B_4O_7$-β [1, 2, 6].

Conclusions

$Tl_2B_4O_7 \cdot 3H_2O$ and $Tl_2B_4O_7 \cdot 1.5H_2O$ are two distinct compounds, which have their own process of dehydration; in the H_2O—$Tl_2B_4O_7$ phase diagram, another hydrated thallium(I) diborate is clearly shown: $Tl_2B_4O_7 \cdot H_2O$. The structural formulae of these three hydrates are: $Tl_2[B_4O_6(OH)_2] \cdot 2H_2O$, $Tl_4[B_8O_{12}(OH)_4] \cdot H_2O$ (proved by structural resolution) and possibly $Tl_6[B_{12}O_{18}(OH)_6]$; the second and third hydrates contain polyanions which are the dimer and trimer of the polyanion existing in the first hydrate. This polymerization

may occur on heating of the material under pressure. At the present moment, monocrystals of $Tl_4[B_8O_{12}(OH)_4] \cdot H_2O$ and only powder of "$Tl_6[B_{12}O_{18}(OH)_6]$" have been obtained by this process.

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Zusammenfassung — Im ternären System H_2O—B_2O_3—Tl_2O liegen bei 100° bei Einstellung des Gleichgewichtes flüssig-fest zwei hydratisierte Thallium(I)-diborate vor; diese wurden durch Pulverdiagramme charakterisiert, die klassische chemische Analyse ergab jedoch nicht den richtigen Hydratationsgrad. Bei TGA von Pulvern verläuft ein komplexer Prozeß, für den keine mögliche Erklärung gegeben werden kann. Strukturaufklärung und TGA mit Einkristallen ermöglichen eine korrekte Erklärung der thermischen Dehydratisierung: die hydratisierten Thallium(I)-diborate sind zwei verschiedene Verbindungen der Zusammensetzung $Tl_2B_4O_7 \cdot 3H_2O$ und $Tl_2B_4O_7 \cdot 1.5H_2O$ mit unterschiedlichem Dehydratisierungsverlauf, die Polyanionketten enthalten und durch die Strukturformeln $Tl_2[B_4O_6(OH)_2] \cdot 2H_2O$ bzw. $Tl_4[B_8O_{12}(OH)_4] \cdot H_2O$ zu beschreiben sind. Das Polyanion der zweiten Verbindung kann als Dimeres des der ersten angesehen werden. Das Phasendiagram H_2O—$Tl_2B_4O_7$ wurde durch unter Druck ausgeführte thermische Analyse und Löslichkeitsexperimente aufgestellt. Aus diesem Phasendiagramm kann die Existenz eines anderen hydratisierten Thallium(I)-diborats, $Tl_2B_4O_7 \cdot H_2O$, mit der möglichen Strukturformel $Tl_6[B_{12}O_{18}(OH)_6]$ vorausgesagt werden. In Wirklichkeit wurden aber nur Einkristalle von $Tl_4[B_8O_{12}(OH)_4] \cdot H_2O$ durch hydrothermale Behandlung von $Tl_2[B_4O_6(OH)_2] \cdot 2H_2O$ erhalten.

Резюме — В тройной системе H_2O—B_2O_3—Tl_2O при 100° и при наличии равновесия типа жидкость твердое тело были найдены два гидрата дибората одновалентного таллия, охарактеризованных порошковыми диаграммами. ТГА исследования порошков показали сложный процесс, не находящийся объяснения. Структурные и ТГА исследования монокристаллов дали возможность корректного объяснения процесса дегидратации: данные гидраты являются двумя различными соединениями $Tl_2B_4O_7 \cdot 3H_2O$ и $Tl_2B_4O_7 \cdot 1.5H_2O$, имеющих свой собственный процесс дегидратации. Оба соединения содержат бесконечные цепи полианионов и их структурные формулы $Tl_2[B_4O_6(OH)_2] \cdot 2H_2O$ и $Tl_4[B_8O_{12}(OH)_4] \cdot H_2O$. Последнее соединение можно считать димером первого. С помощью термического анализа и двумя методами определения растворимости под давлением была определена фазовая диаграмма системы H_2O—$Tl_2B_4O_7$. Это также позволило установить, что для другого гидрата дибората таллия $Tl_2B_4O_7 \cdot H_2O$ возможна структурная формула $Tl_6[B_{12}O_{18}(OH)_6]$. Действительно, только монокристаллы $Tl_4[B_8O_{12}(OH)_4] \cdot H_2O$ были получены гидротермическим синтезом из $Tl_2[B_4O_6(OH)_2] \cdot 2H_2O$.