で、従来からガラス化しないとされていた RO-GeO₂ 系 (R: Ca, Sr, Ba) はかなり発達した相分離が存在するために失透した分相ガラスであると考えられる。

5. 結 言

2元ゲルマン酸塩系の不混和領域を著者らが開発、自作したホットサーモカップル法を用いて測定した。その結果 CaO-GeO₂ 系の一部及び MgO-GeO₂ 系, ZnO-GeO₂ 系には安定不混和(2液相)が存在し、また PbO-GeO₂ 系, Bi₂O₃-GeO₂ 系ではケイ酸塩系にも認められる準安定不混和領域が存在した。CaO-GeO₂ 系の一部及び SrO-GeO₂ 系, BaO-GeO₂ 系には液相線以下、結晶化温度以上の高温に準安定不混和が確認できた。

測定した全系の不混和領域を Rowlinson の式によって整理するとともに、従来ガラス化しないとされていた2元ゲルマン酸塩系での組成域が、超急冷によっても避けられない高温での不混和領域の存在に起因し、これらの系ではかなり発達した相分離のために失透した分相ガラスであることを見いだした。

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論 文・Paper

Stability and Bond Energy of RBO₄ Units

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Thermochemical quantities such as the heats of formation and solution of alkali borate crystals are assumed to be the sum of the partial molar quantities of the component borate units such as BO₃, RBO₄ and ROBO₂. According to examination of composition dependence of the heats of solution of the alkali borate crystals reported previously (*Yogyo-Kyokai-Shi*, **84**, 62-70 (1976)), the ΔH_f data of the crystals are calculated. The stabilization energy H_{stab} of an RBO₄ unit relative to an ROBO₂ unit, defined as the heat of decomposition $RBO_{4/2} \rightarrow ROBO_{2/2} + H_{stab}$, has been evaluated for several crystals based on reported and calculated heats of formation data. The composition dependence of the fraction N_4 of the four-coordinated boron atoms has been interpreted in terms of H_{stab} . The B-O bond energies of the RBO₄ units in some crystals have also been calculated, ranging from 130 to 135 kcal/mol.

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RBO₄ 単位の安定性と結合エネルギー

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アルカリホウ酸塩結晶の生成熱や溶解熱等の熱化学量はそれらを構成する BO₃, RBO₄ 及び ROBO₂ なる単位の部分分子量の和であると仮定した. この系の結晶の溶解熱-組成関係 (窯協, **84**, 62-70 (1976)) に基づき, 結晶の生成熱を算出した. RBO_{4/2} → ROBO_{2/2} + H_{stab} なる反応の反応熱として, RBO₄ 単位の ROBO₂ 単位に対する安定化エネルギー H_{stab} を定義し幾つかの結晶について生成熱の引用値及び計算値より見積もった. H_{stab} に基づいて 4 配位ホウ素の割合 N_4 の組成変化を解釈した. また二, 三の結晶中の RBO₄ 単位の B-O 結合エネルギーは 135~130 kcal/mol の範囲であった.

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Key-words : Alkali borate crystals, Borate units, RBO₄, ROBO₂, Stability, N_4 , B-O bond energy

1. Introduction

The thermochemical quantities of glasses or crystals such as the heat of solution ΔH_s , the heat of formation ΔH_f and the free energy of formation ΔG_f depend upon their atomic arrangements. Takahashi and Yoshio¹⁾ discussed the structures of the alkali borate glasses based on the ΔH_s data. Shartsis and Capps²⁾ reported those of the alkali borate crystals from which the JANAF Thermochemical Tables³⁾ (later denoted as JANAF) yielded ΔH_f 's of the crystals. In the previous paper Osaka and Takahashi⁴⁾ predicted that an RBO₄ unit bonded to the other RBO₄ units was unstable than that bonded to four BO₃ units. In this paper, it is intended to interpret thermochemically the decomposition of the RBO₄ units to the ROBO₂ units by means of evaluating the stabilization energy of the RBO₄ units relative to the ROBO₂ units. It is also intended to calculate the B-O bond energy of the RBO₄ units.

2. The thermochemical data of the alkali borate crystals

Figure 1 schematically shows molar heats of solution ΔH_s 's of the alkali borate crystals, $xR_2O \cdot B_2O_3$, plotted as a function of x according to Takahashi and Yoshio where R=Li, Na and K. When B₂O₃(c) crystallizes completely, ΔH_s 's in the range $x < 0.25$ vary along the broken lines¹⁾. The ΔH_s data in the range $0.5 < x$, approximated by the solid lines, have been extrapolated to $x=1$, giving ΔH_s (RBO₂(c))'s as the heats of reaction of Eq. (1),

With the ΔH_s (RBO₂(c)) and ΔH_f data of the chemical species in Eq. (1), ΔH_f (RBO₂(c))'s for R=Li, Na and K have been calculated through a thermochemical cycle and shown in **Table 1**. ΔH_f (LiBO₂(c)) is in good agreement with that given by JANAF. The disagreement on ΔH_f (NaBO₂(c)) can be attributed to the wrong value of ΔH_s (NaBO₂(c)) obtain-

Fig. 1. The heats of solution of the alkali borate crystals, $xR_2O \cdot B_2O_3$, plotted as a function of x , after Takahashi and Yoshio (Ref. 1).

Table 1. The thermochemical data for several chemical species. $\Delta H_f(\text{RBO}_2(\text{c}))$'s adopted are indicated by (o).

	ΔH_f (kcal/mol)	references
$\text{LiNO}_3(27.75\text{H}_2\text{O}, \text{aq})$	-115.9	3b, $\text{LiBO}_2(\text{c})$
$\text{NaNO}_3(27.75\text{H}_2\text{O}, \text{aq})$	-106.3	3b, $\text{NaBO}_2(\text{c})$
$\text{KNO}_3(27.75\text{H}_2\text{O}, \text{aq})$	-111.1	3b, $\text{KBO}_2(\text{c})$
$\text{HNO}_3(27.75\text{H}_2\text{O}, \text{aq})$	-49.4	3b, $\text{KBO}_2(\text{c})$
$\text{H}_3\text{BO}_3(27.75\text{H}_2\text{O}, \text{aq})$	-256.4	3b, $\text{KBO}_2(\text{c})$
$\text{H}_2\text{O}(\text{l})$	-68.3	3a

	ΔH_s^a (kcal/mol)	ΔH_f (kcal/mol)	references
$\text{LiBO}_2(\text{c})$	-11.1 ^a	-243.6	3b
	-10.8 ^b	-243.9	o this work
$\text{NaBO}_2(\text{c})$	-11.8 ^a	-233.2	o 3b
	-10.2	-234.7	this work
$\text{KBO}_2(\text{c})$	-11.9	-237.8	3b
	-14.1 ^b	-235.6	o this work

a] Heats of solution in 2N-HNO₃ aqueous solution.

b] Ref. 1.

*] Calculated reversely from the ΔH_f data of JANAF(ref.3).

o] The data adopted in this work.

ed by the extrapolation. $\Delta H_f(\text{NaBO}_2(\text{c}))$ of JANAF, obtained in the other way than using Eq. (1), gives $\Delta H_f = -11.8$ kcal/mol for Eq. (1). Thus, it has been shown that $-\Delta H_s$'s of the sodium crystals in the range $0.5 < x < 1.0$ increase along the finely broken line, showing a bending at $x=0.5$. In the potassium system, however, a bending is seen at $x=0.5$ in Fig. 1, while $\Delta H_s(\text{KBO}_2(\text{c}))$ adopted in JANAF has been obtained by the extrapolation of the ΔH_s data in the range $0.25 < x < 0.5$ to $x=1$. The correct value of $\Delta H_s(\text{KBO}_2(\text{c}))$ is -14.1 kcal/mol according to Fig. 1, which results in $\Delta H_f(\text{KBO}_2(\text{c})) = -235.6$ kcal/mol. $\Delta H_s(\text{K}_2\text{O} \cdot 3.8 \text{B}_2\text{O}_3(\text{c}))$ has been interpolated from the ΔH_s data in the range $0.25 < x < 0.5$. **Table 2** summarizes the ΔH_s and ΔH_f data of some alkali borate crystals.

3. Discussion

3.1 Stability of the RBO_4 units relative to the ROBO_2 units

Three borate units BO_3 , RBO_4 and ROBO_2 (later denoted as B_3 , RB_4 and B_R units, respectively) compose the alkali borate crystals. The molar enthalpy of a crystal is assumed to be a sum of the partial molar enthalpy of each component unit. Kawazoe et al.⁵⁾ have reported that the delocalization of the planar π electrons of a B_3 unit is restricted by the adjacent RB_4 units. This effect may change the energy of the B_3 unit. As a first order approximation, however, it is assumed

Table 2. The heats of solution and formation data for several alkali borate crystals.

Crystals	ΔH_s^a (kcal/mol)	ΔH_f (kcal/mol)
B_2O_3	-3.6	-304.0 ^c
$\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$	-10.2	-806.9 ^b -803.6 ^c
$\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$	-4.5	-1403.5 ^b
$\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$	-15.1	-782.8 ^b -783.2 ^c
$\text{K}_2\text{O} \cdot 4\text{B}_2\text{O}_3$	0.4	-1423.7 ^b -1420.9 ^c
$\text{K}_2\text{O} \cdot 3.8\text{B}_2\text{O}_3$	1.1	-1362.8 ^b
$\text{K}_2\text{O} \cdot 2\text{B}_2\text{O}_3$	-8.2	-799.3 ^b -796.9 ^c

a] heats of solution in 2N-HNO₃ aqueous solution; ref. 1.

b] this work

c] JANAF; ref. 3.

here that the partial molar enthalpies such as ΔH_f and ΔH_s of the B_3 units in any crystals are equivalent to those in $\text{B}_2\text{O}_3(\text{c})$. The stabilization energy H_{stab} of the RB_4 unit relative to the B_R unit is defined as the heat of decomposition,

and is the difference in the partial molar heats of formation of the two units. Since the difference in the heats of solution is equivalent to the difference in the heats of formation, the stabilization energy is expressed as

$$H_{\text{stab}} = -\Delta h_s(\text{B}_R) + \Delta h_s(\text{RB}_4) \quad (2)$$

For instance, lithium diborate $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3(\text{c})$ consists of two B_3 units and two LiB_4 units, then,

$$\Delta H_s(\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3(\text{c})) = 2\Delta h_s(\text{B}_3) + 2\Delta h_s(\text{LiB}_4)$$

Application of $\Delta h_s(\text{B}_3) = -1.8$ kcal/mol and $\Delta H_s(\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3(\text{c})) = -10.2$ kcal/mol gives $\Delta h_s(\text{LiB}_4) = -3.3$ kcal/mol. Since $\Delta H_s(\text{LiBO}_2(\text{c})) = \Delta h_s(\text{BL}_4) = -10.8$ kcal/mol as indicated in Table 1, H_{stab} of the LiB_4 unit is 7.5 kcal/mol according to Eq. (2). In this way the values of H_{stab} are obtained and shown in **Table 3** for several crystals.

Furthermore, the heats of formation of $\text{RBO}_2(\text{c})$ and the gaseous atoms $\text{R}(\text{g})$, $\text{B}(\text{g})$

Table 3. The stabilization energy H_{stab} and the B-O bond energy of the RBO_4 units in some alkali borate crystals.

Crystals	H_{stab}^a	$D(\text{RBO}_2(\text{c}))^b$	$D(\text{RBO}_4)^b$	$E(\text{B}^4-\text{O})^c$
$\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$	7.5	534.3	541.8	135
$\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$	15.0	511.2	526.2	132
$\text{K}_2\text{O} \cdot 3.8\text{B}_2\text{O}_3$	19.7		528.7	132
$\text{K}_2\text{O} \cdot 2\text{B}_2\text{O}_3$	11.8	508.9	520.7	130

* data in kcal/mol

a] defined as the heat of reaction: $\text{RBO}_{4/2} \rightarrow \text{ROBO}_{2/2} + H_{\text{stab}}$ b] dissociation (atomization) energies of $\text{RBO}_2(\text{c})$ and the RBO_4 unitsc] bond energies of the RBO_4 units; $E(\text{B}-\text{O}) = 1/4D(\text{RBO}_4)$

and $O(g)^{3)}$ derive the dissociation energy D of the crystal as follows.

The dissociation energy D of an RB_4 unit in a crystal can be defined as the heat absorbed in the reaction,

and is related to D' ,

$$D = D' + H_{\text{stab}} \quad (3)$$

The dissociation energy divided by the oxygen coordination number of the cation has been called the bond energy of the cation-oxygen bond^{(6)~(8)}. Although the energies due to the alkali ion such as $R^+-BO_4^-$ interaction and heat of formation of $R(g)$ take part in D of the RB_4 unit, a quarter of D is assigned here to the B-O bond energy of the RB_4 units, shown in Table 3, which can be compared with the reported Si-O, P-O and Ge-O bond energies⁹⁾.

3.2 Application H_{stab} to interpreting the variation of the fraction of the RB_4 units, N_4

The free energy of formation ΔG_f of the borate crystals, $xR_2O \cdot B_2O_3$, calculated from the entropy data of JANAF, are plotted in Fig. 2 as a function of x together with ΔH_f and $T\Delta S_f$ at $T=298\text{ K}$ (25°C). The ratio's $T\Delta S_f/\Delta G_f$ and $T\Delta S_f/\Delta H_f$ are respectively about

Fig. 2. The $-\Delta H_f$, $-\Delta G_f$ and $-T\Delta S_f$ data at $T=298\text{ K}$ (25°C) for the alkali borate crystals, $xR_2O \cdot B_2O_3$, plotted as a function of x . The entropy data were cited from Ref. 3.

0.06 and 0.05 irrespective of the compositions or the kinds of alkali of the crystals. It can also be shown that the entropy changes accompanied by the formation reactions of the crystals from $R_2O(c)$ and $B_2O_3(c)$ are substantially negligible. Therefore, the heats of formation or solution of the borate units can be utilized for predicting the kinds of borate units produced at the reaction $R_2O(c) + B_2O_3(c)$, thus, H_{stab} is useful for this purpose.

The large positive values of H_{stab} in the range $x < 0.5$ shown in Table 3 indicate $\Delta h_f(RB_4) < \Delta h_f(B_R)$, and that the formation of the RB_4 unit is preferred to that of the B_R unit. Thus an increase in the fraction of the RB_4 units has been interpreted thermochemically in the range $x < 0.5$. However, the value of H_{stab} are smaller in the diborate crystal than in the tetraborate crystal, as suggested previously⁴⁾. Therefore, the formation of the RB_4 units is getting less preferred and, contrarily, that of B_R units becomes preferred gradually. If the B_3 units are assumed to be changed continuously to the RB_4 units due to the addition of R_2O in the range $0.5 < x$, the RB_4 units connected to more than one RB_4 units will appear⁴⁾. They are $B_4(2B_3, 2B_4)$, $B_4(B_3, 3B_4)$ and $B_4(4B_4)$ and can be denoted in a simplified manner as $B_4(n=2)$, $B_4(n=3)$ and $B_4(n=4)$, respectively, where n represents the number of the RB_4 units connected to the relevant RB_4 unit. It can be seen that hypothetical crystals $S(x=0.6)$, $T(x=0.75)$ and $U(x=1.0)$ are constructed by $B_4(n=2)$ and B_3 , $B_4(n=3)$ and B_3 , and $B_4(n=4)$, respectively. Since such units are not present in the actual crystals, H_{stab} 's of them are smaller than those of the $B_4(n=0)$ and $B_4(n=1)$ units present in tetra and diborate crystals, respectively. If H_{stab} is assumed to be decreased linearly with n , H_{stab} of the $B_4(n=2)$ unit of S is 3.9 kcal/mol in the potassium system where H_{stab} 's for $n=0$ and $n=1$ are available in Table 3. In the actual borate systems in the range $0.5 < x$ the diborate and metaborate crystals are aggregated, while in the hypothetical case the system is an aggregate of the diborate and S in the range $0.5 < x < 0.6$, that of S and T in $0.6 < x < 0.75$ and that of T and U in $0.75 < x < 1.0$. In order to interpret the stability of the both cases in the range $x > 0.5$ from thermo-

chemical view point, it is sufficient to compare ΔH_s 's of S and the actual crystal aggregate C with $x=0.6$, because H_{stab} 's of the RB_4 units in T and U are smaller than that in S.

The difference δ in ΔH_s 's of C and S containing 2.5 mol of B_2O_3 is given by

$$\delta = -3 \Delta h_s(B_4(n=2)) + 2 \Delta h_s(B_4(n=1)) + \Delta h_s(B_R)$$

Application of Eq. (2) reduces to

$$\begin{aligned} \delta &= 3 H_{stab}(B_4(n=1)) \\ &\quad - 2 H_{stab}(B_4(n=2)) \\ \delta &= 11.9 \text{ kcal/mol} \end{aligned}$$

The positive value of δ indicates $\Delta H_f(C) < \Delta H_f(S)$. Therefore, it has been shown that no more B_3 units can be changed to the RB_4 units in the range $0.5 < x$. This is equivalent to the fact that N_4 becomes maximum at diborate composition in the potassium borate system. The same conclusion might be derived for the lithium and sodium systems if H_{stab} 's could be obtained for all n . Although the above discussions are based on the heats of formation and solution, the bond energies

of the metal-oxygen bonds can also stand the discussions since they are the sum of the heats of formation of the borate units and the component gaseous atoms.

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ノート・Note

Diffusion Joining of Silicon Nitride Ceramics

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常圧焼結窒化ケイ素セラミックスの拡散接合

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Considerable attention has been given to the joining of engineering ceramics such as silicon nitride or silicon carbide, because of their practical importance for use as high-temperature structural materials. Some attempts have

been carried out for the joining of $SiC^{1) \sim 4)}$ and $Si_3N_4^{5) \sim 6)}$ ceramics, with the use of joining agent between the joining couple.

In the present study, an attempt was made to join sintered silicon nitride ceramics without