量の増大とともに単調に低下したが、粒度が極端に細かいときは、かさ密度には極小値が測定された。

(3) シラス含有率 70% 以上のバッチに対し、平均粒径 $30\mu\text{m}$ のシリコンカーバイドを 0.75% 添加した実験では、シラス含有率 70~90% のバッチから、かさ密度 1.0Mg/m^3 以下の泡ガラスが得られた。これら泡ガラス中には空洞等の異常組織がなく、製品歩留まりが高いこと、シラス含有量の高いこと、などのため、所期の目的であるコスト低下に有力な手掛かりを得た。

(4) 泡ガラスの特性値間の相関関係について言えば、かさ密度の小さい泡ガラスの熱伝導率、曲げ強さは小さく、気泡直径は大きかった。ただしかさ密度と気泡直径を直接関係付けるのには無理があった。

(5) 特定の試料について凍害試験を行った。試料は 15 回の繰り返し実験に耐えた。

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論 文・Paper

Arrangements and Fractions of BO_3 and RBO_4 Units in Alkali Borate Crystals

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As an aid for interpreting the boron oxide anomaly, the structure of several alkali borate crystals was studied. It was found that the five kinds of BO_3 units such as B_3 (3B_3), B_3 ($2\text{B}_3, \text{B}_4$), B_3 ($\text{B}_3, 2\text{B}_4$), B_3 (3B_4) and B_R and two kinds of RBO_4 units such as B_4 (4B_3) and B_4 ($3\text{B}_3, \text{B}_4$) are the basic constituents of the crystals in the range $0 \leq x \leq 1.0$, where x represents the molar ratio $\text{R}_2\text{O}/\text{B}_2\text{O}_3$. The variation of the fractions of those units with x shows the two tendencies. (1) The number of B_4 units to which a B_3 or a B_4 unit is bonded increases gradually with x . (2) The fraction of each kind of B_4 or B_3 unit becomes maximum in one of the crystals, in which the unit is the single kind of constituent B_4 or B_3 unit. These tendencies suggest that four kinds of B_4 units bonded with more than one B_4 units appear in the range $0.5 < x \leq 1.0$ if the fraction of the B_4 units is assumed to increase linearly with x in this range. A relation of the relative stability between the real and hypothetical units is derived from the viewpoint of the energy of the units, defined as, for example, a sum of the bond energies.

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アルカリホウ酸塩結晶中の BO_3 及び RBO_4 単位の配置と分率

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ホウ酸異常を解明するための一助として幾つかのアルカリホウ酸塩結晶の構造を調べた。その結果 $0 \leq x \leq 1.0$ の領域 (x はモル比 $\text{R}_2\text{O}/\text{B}_2\text{O}_3$ を表す) の結晶は基本的には 5 種類の BO_3 単位,

すなわち B_3 ($3 B_3$), B_3 ($2 B_3, B_4$), B_3 ($B_3, 2 B_4$), B_3 ($3 B_4$) 及び B_R 並びに 2 種類の RBO_4 単位, すなわち B_4 ($4 B_3$) 及び B_4 ($3 B_3, B_4$) から構成されていることが分った. これらの単位の分率の x に対する変化の様子からは二つの傾向が見て取れる. (1) 一つの B_3 又は B_4 単位に結合する B_4 単位の数は x とともに徐々に増加する. (2) 各々の B_4 又は B_3 単位はある一つの結晶においてその分率が最大となり, またそれがこの結晶を構成する唯一の B_4 又は B_3 単位である. これらの傾向は, B_4 単位の分率が $0.5 \leq x \leq 1.0$ の領域で x に対し直線的に増加すると仮定するならば, この領域では 2 個以上の B_4 単位に結合する 4 種の仮想的な B_4 単位が現れることを示唆する. これら現実の, 及び仮想的な単位のエネルギーとして, 例えば結合エネルギーの和を定義すれば, エネルギーの面からそれらの単位の相対的な安定度の関係が導かれる.

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Key-words Alkali borate, Crystal, Glass, Boron oxide anomaly, Units, Energy, Bond, Stability

1. Introduction

The properties of alkali borate and borosilicate glasses change abruptly at specific compositions which vary in the range $0.2 \leq x \leq 0.25$ depending on the properties and the alkali species, where x represents the molar ratio R_2O/B_2O_3 ¹⁾. The phenomenon, the boron oxide anomaly, has not thoroughly been clarified yet. The other change of the properties at about $x=0.5$ which can be called the second boron oxide anomaly has been attributed to the fact that the fraction N_4 of the four-coordinated boron atoms becomes maximum near $x=0.5$ ^{2), 3)}. However, the reason why N_4 could not continue increasing in the range $0.5 < x$ has not been explained.

In order to approach the anomalies, it seems important to know the arrangements of the $BO_{3/2}$, $RBO_{4/2}$ and $ROBO_{2/2}$ units (later denoted as B_3 , B_4 and B_R units, respectively) in the glasses, that is, to know the kinds and numbers of the units in the first neighbor of the relevant unit. The arrangements may govern the stability of these units in the sense of energy as they affect the orbital energies of the oxygens⁴⁾. Whereas it is very difficult to know every detail of the glass constitutions, some of the borate groups found in the borate crystals, such as boroxol and diborate groups, are proposed to be present in the borate and borosilicate glasses¹⁾, suggesting the similarity of the arrangements of the B_3 and B_4 units in the glasses to those in the crystals to some extent. Therefore, it is useful in the interpretation of the boron oxide anomalies in the glasses to study the arrangements of those units in the alkali borate crystals.

borate crystals

Figure 1 shows the arrangements of the B_3 , B_4 and B_R units in several crystals⁵⁾ found in the phase diagrams of the systems $R_2O-B_2O_3$ ⁶⁾. Their molar ratio's $R_2O : B_2O_3$ are 1 : 9 (crystal I), 1 : 5 (J), 1 : 4 (K), 1 : 3.8 (K'), 1 : 3 (L), 1 : 2 (M) and 1 : 1 (N). B_2O_3 crystal is represented by H. Crystals J, L and M are built of the single borate groups known as a pentaborate group, a triborate group and a diborate group, respectively. A triborate group and a pentaborate group are connected to be a tetraborate group which constructs the network of sodium tetraborate crystal (K). The procedure to know the arrangements of the borate units is shown for crystal K as the example in the following. In Fig. 1 the asterisked B_3 unit shares an extra-annular

Fig. 1 The arrangements of the BO_3 and RBO_4 units in the alkali borate crystals H through N. The closed and open circles represent the boron and oxygen atoms, respectively.

2. Constitutions of the alkali

Fig. 2 The kinds and the fractions of the basic borate units found in the alkali borate crystals H through N, plotted as a function of x (=molar ratio R_2O/B_2O_3).

oxygen with a B_4 unit which is a member of the triborate part belonging to the other tetraborate group. The B_3 unit, thus, is bonded with one B_3 unit and two B_4 units. Consequently, the B_3 unit is represented as B_3 ($B_3, 2B_4$) in order to indicate the kinds and numbers of the units in the neighborhood. Therefore, crystal K is built of B_3 ($2B_3, B_4$), B_3 ($B_3, 2B_4$) and B_4 ($4B_3$) units, whose fractions are 0.5, 0.25 and 0.25, respectively. In the same way, the arrangements of the borate units are examined for all crystals H through N. It has been found that, besides B_R unit in crystal N, four kinds of B_3 units such as B_3 ($3B_3$), B_3 ($2B_3, B_4$), B_3 ($B_3, 2B_4$) and B_3 ($3B_4$) and two kinds of B_4 units such as B_4 ($4B_3$) and B_4 ($3B_3, B_4$) construct the alkali borate crystals H through M. Their fractions are plotted in **Fig. 2** as a function of x . The ordinates OP and N'N represent the total fractions of the three- and four-coordinated boron atoms, N_3 and N_4 , respectively. N_3 decreases along the fragment of line PR in the range $x \leq 0.5$ and increases along RN' in the range $0.5 \leq x$ due to the decomposition of the B_4 units to the B_R units: $RBO_{4/2} \rightarrow ROBO_{2/2}$. In the figure crystal K' represents $K_2O \cdot 3.8 B_2O_3$ ⁷⁾. Potassium diborate⁸⁾ and high-temperature modification of sodium triborate⁹⁾ have the same arrangements of the borate units as lithium diborate (M) and lithium triborate (L), respectively, though they are constructed by the different borate groups from those constructing the lithium crystals. However, sodium diborate¹⁰⁾, having B_R units, and low-temperature modification of sodium triborate¹¹⁾ are different in the arrangements of the borate units from the lithium crystals

Fig. 3 The fraction N_4 of the four-coordinated boron atoms in the alkali borate crystals and glasses, plotted as a function of x (=molar ratio R_2O/B_2O_3).

L and M, respectively. The behaviors of the last two sodium crystals cannot be represented in **Fig. 2** nor be explained at present.

Furthermore, N_4 of the alkali borate crystals is plotted in **Fig. 3** along with that of the alkali borate glasses^{11, 12)}. Here, crystal G represents sodium diborate having $N_4 = 3/8$. Therefore, N_4 of the lithium and potassium crystals varies along the fragments of lines HM and MN, and that of the sodium crystals along HL, LG and GN. The broken lines LM, LG and GN indicate the presence of the crystals of unknown structure in the phase diagrams such as $2Li_2O \cdot 5B_2O_3$, $2Na_2O \cdot 5B_2O_3$ and $2Na_2O \cdot 3B_2O_3$. N_4 of the alkali borate glasses in the range $x \leq 0.5$ varies along the fragment of line HM, while it decreases very slowly with x in the range $0.5 < x$ and becomes null at $x = 2.5$ ¹²⁾. Such difference in the variation of N_4 between the crystals and glasses indicates the difference in their constitutions in the range $0.5 < x$.

3. Discussion

It has been found that the arrangements of the borate units and N_4 vs x relations of the sodium crystals are different from those of the lithium and potassium crystals. Such behavior of the sodium crystals will be discussed later when more knowledges are available, and the discussion here is focused on the lithium and potassium crystals.

The following two tendencies can be found from **Fig. 2** in the lithium and potassium crystals in the range $0 \leq x \leq 0.5$.

(1) The number n of the B_4 units in the neighbor of a B_3 or a B_4 unit increases gradually with x ; for example, B_4 ($4B_3$) ($n =$

0, in crystals I, J, K, K' and L) $\rightarrow$ B₄ (3 B₃, B₄) ($n=1$, in crystal M).

(2) The fraction of a B₃ or a B₄ unit becomes maximum in one of the crystals, in which the unit is the single constituent B₃ or B₄ unit. For example, the fraction of the B₄ (3 B₃, B₄) unit is maximum in crystal M and the unit is the single kind of B₄ constituent unit of the crystal.

Therefore, when it is assumed that a change of the B₃ units to the B₄ units occurs instead of formation of the B_R units in the range $0.5 < x$, three kinds of hypothetical B₄ units such as B₄ (2 B₃, 2 B₄), B₄ (B₃, 3 B₄) and B₄ (4 B₄) with $n=2, 3$ and 4 will appear one after another. Since neither of those B₄ units nor the crystals containing them are present actually, these units are unstable and are decomposed immediately to the B_R units. Moreover, the tendencies can be interpreted as showing that a B₄-B₄ bond is obliged to be formed when N_4 exceeds some threshold value. Thus, it can be suggested that a B₄-B₄ bond is less stable than a B₃-B₄ bond and that a B₄-B₄-B₄ bond is much less stable. Therefore, the energy of the borate units defined as, e.g., a sum of the bond energies with the neighboring units decreases in the order of increasing number n of the B₄ units bonded to them.

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論文・Paper

Glass Transition Temperature of Na₂O·3 SiO₂ Glasses with High Water Content

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Na₂O·3 SiO₂ glasses with various water contents (up to ~8 wt%) were prepared under high pressure, hydrothermal conditions and their glass transition temperatures (T_g) were measured by DTA. Exsolution of dissolved water occurs at temperature above T_g , and is accompanied by foaming. Both the glass transition temperature and the foaming tempera-