ARL 73

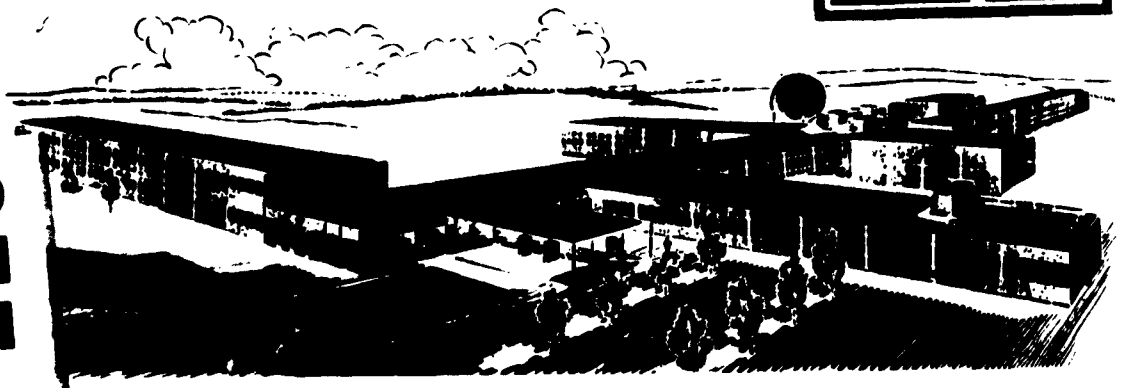
STRUCTURE OF VITREOUS AND LIQUID BORON TRIOXIDE AND SOME SIMPLE BORATES

J. D. MACKENZIE

GENERAL ELECTRIC RESEARCH LABORATORY
SCHENECTADY, NEW YORK

SEPTEMBER 1961

AERONAUTICAL RESEARCH LABORATORY
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE



NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Qualified requesters may obtain copies of this report from the Armed Services Technical Information Agency, (ASTIA), Arlington Hall Station, Arlington 12, Virginia.

This report has been released to the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C. for sale to the general public.

Copies of ARL Technical Reports and Technical Notes should not be returned to Aeronautical Research Laboratory unless return is required by security considerations, contractual obligations, or notices on a specific document.

ARL 73

STRUCTURE OF VITREOUS AND LIQUID BORON TRIOXIDE AND SOME SIMPLE BORATES

J. D. MACKENZIE

GENERAL ELECTRIC RESEARCH LABORATORY
SCHENECTADY, NEW YORK

SEPTEMBER 1961

CONTRACT No. AF 33(616)-5699
PROJECT No. 3048
TASK No. 70321

AERONAUTICAL RESEARCH LABORATORY
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

200 - December 1961 - 15-634 & 635

FOREWORD

This report was prepared for the Aeronautical Research Laboratory, Office of Aerospace Research, by the General Electric Research Laboratory, Schenectady, New York, under Contract No. AF-33(616)-5699, Project 3048, Task 70321, "Structure of Vitreous and Liquid Boron Trioxide and Some Simple Borates." The Air Force scientist responsible for this Task is Dr. William L. Ruigh of the Chemistry Research Branch, ARL. The principal investigator at the General Electric Research Laboratory was J.D. Mackenzie. This report covers work conducted from May 1, 1958 to February 15, 1961.

Those who have collaborated with the principal investigator in various aspects of the work described in this report are Drs. W.F. Claussen, W.E. Kaskan, R.S. McDonald, W.L. Roth, M.B. Webb, and Mr. W.K. Murphy of this Laboratory, and Professor P.J. Bray of Brown University.

Publications arising from the research reported herein include:

1. "Crystallization of B_2O_3 at High Pressures," by W.F. Claussen and J.D. Mackenzie, J. Am. Chem. Soc., 81, 1007 (1959).

2. "The Structure of Liquid Boron Trioxide," by J.D. Mackenzie, J. Phys. Chem., 63, 1875 (1959).

3. "Structure of Some Inorganic Glasses from High Temperature Studies," by J.D. Mackenzie, chapter in book, Modern Aspects of the Vitreous State. I, editor J.D. Mackenzie, Butterworths Scientific Publications, London (1960).

4. "Some Physical Properties and the Structure of Liquid Boron Trioxide," by J.D. Mackenzie, Proc. Propellant Thermodynamics, Spec. Rept. No. 12, Ohio State Univ., 139 (1960).

5. "Crystallization and Phase Relationship of B_2O_3 at High Pressures," by J.D. Mackenzie and W.F. Claussen, J. Am. Ceram. Soc., 44, 79 (1961).

6. "Origin of the Green Bands in the Boron-Oxygen System," by W. E. Kaskan, J.D. Mackenzie, and R.C. Millikan, J. Chem. Phys., 34, 570 (1961).

7. "Infrared Spectroscopy of Melts and Hygroscopic Solids," by J.D. Mackenzie, R.S. McDonald, and W.K. Murphy, Rev. Sci. Instr., 32, 118 (1961).

8. "The Structure of Boron Oxide and Simple Borate," by J.D. Mackenzie, ARL Technical Note 60-130 (October 1960).

ABSTRACT

A broad program of research has been conducted to obtain structural information on the vitreous and liquid B_2O_3 and binary borates. By the use of high-pressure techniques, simple crystals of two forms of B_2O_3 have been prepared for x-ray diffraction studies. The tentative phase diagram for liquid and crystalline B_2O_3 has been constructed up to 1100°C and 90,000 atmospheres. The effects of water on the viscosity, electric conductance, and density of liquid B_2O_3 have been examined. From this, some of the current hypotheses concerning the structure of liquid B_2O_3 can be rejected. Preliminary results on the infrared absorption of solid and liquid B_2O_3 have been obtained. A description is given of other work in progress which includes nuclear magnetic resonance absorption, viscosity measurements of binary borates at temperatures below the liquidus, and single-crystal diffraction on α- and β-B_2O_3.

TABLE OF CONTENTS

LIST OF FIGURES

STRUCTURE OF VITREOUS AND LIQUID BORON TRIOXIDE AND SOME SIMPLE BORATES

J.D. Mackenzie

I. INTRODUCTION

Inorganic oxides and their mixtures form the largest group of glasses commonly encountered. According to the classical theory of the vitreous state,[1] the pure oxide glasses like SiO_2, GeO_2, B_2O_3, and P_2O_5 are made up of disordered three-dimensional continuous networks rigidly held together by the strong M-O bonds. However, other widely divergent hypotheses concerning the structures of these glasses are to be found in the literature. Glassy B_2O_3, for instance, has been considered as a molecular solid composed of B_4O_6 molecules.[2, 3] It is generally agreed that in silica-based glasses containing different amounts of metal oxides, say, from pure SiO_2 to 66 mole per cent alkali oxide, the basic building unit is the SiO_4 tetrahedra. The infinite number of ways these SiO_4 units may be linked together at each composition and their variation with composition have generated the most widely debated problem in the study of glasses. Direct structural techniques such as x-ray diffraction only provide, at best, information on nearest neighbor interactions. In a few instances, structural solutions are possible by a combination of such direct techniques with indirect methods such as transport measurements. However, in general a great deal of uncertainty still exists.

In addition to such complexity inherent to the liquid-like structures of glasses, the study of liquid and vitreous B_2O_3 and the simple borates is beset with further difficulties not encountered in the case of silica and the silicates. For instance, the only crystal structure study made on B_2O_3 was based on powder diffraction data[4] and as such, involves some degree of uncertainty. Up to most recently, it was not even certain if BO_3 triangles or BO_4 tetrahedra constitute the basic building units in vitreous B_2O_3. There is also evidence that the addition of metal oxides to B_2O_3 results in a change of the coordination number of boron, and that this is probably dependent on both composition and temperature. Compared to the silicates, data which permit structural interpretations for the borates are generally unsatisfactory. In view of the importance of B_2O_3 as a glass former and its relationship to the boron fuels, an urgent need exists, therefore, for further work to clarify the present uncertainty concerning the structure and properties of this oxide and the borates.

Manuscript released June 1961 by the author for publication as an ARL Technical Documentary Report.

The object of the present study is to obtain more structural information on liquid and glassy B_2O_3 and the simple borates. However, as the tardy progress concerning the liquid and the glasses is partly due to the lack of experimental data on crystalline B_2O_3, it was decided that attempts should also be made to prepare single crystals of B_2O_3 for subsequent structure studies.

In this report, the significant findings from work carried out over the entire duration of this contract are presented. Most of the experimental details have been described in a recent publication (ARL Technical Note 60-130, October 1960) and are therefore only discussed briefly in the present report.

II. PREPARATION AND PROPERTIES OF CRYSTALLINE B_2O_3

A. INTRODUCTION

Solid boron trioxide is commonly available only in the vitreous state. The successful preparation of a crystalline phase by the devitrification of glassy B_2O_3 at atmospheric pressure has not been reported. By the conventional method of careful stepwise dehydration of H_3BO_3, microcrystals have been prepared.[5, 6] However, by this technique, Kracek, Morey, and Merwin[6] were only able to prepare crystals having maximum dimensions of 0.05 mm from experiments lasting as long as 8 months. Consequently, the only structural study[4] was based on powder diffraction data. In view of this, and of the possibility of incomplete dehydration which, for instance, had led to earlier erroneous structural conclusions,[7] the preparation of single crystals by other methods is highly desirable.

In the initial phases of the present contract, microcrystals obtained from the dehydration of H_3BO_3 were immersed in supercooled liquid B_2O_3 in an attempt to induce crystallization. However, experiments carried out at various temperatures of undercooling up to a duration of 1 week were unsuccessful. Devitrification was also not observed in samples of glassy B_2O_3 which were first melted with common nucleating agents such as platinum or Sb_2O_3 and then heat treated at temperatures between 300° and 450°C. Hydrothermal treatment of powdered B_2O_3 glass at 400°C and 3000 atmospheres, however, resulted in partial devitrification after 12 hours. This prompted the use of higher pressure which was remarkably successful in the rapid preparation of microcrystals. Such techniques have been recently reported by Dachille and Roy[8] and the preliminary aspect of the present work was described by Claussen and Mackenzie.[9] In this section, the high-pressure preparation of relatively large single crystals of two modifications of B_2O_3 and studies of some of their properties are described. A tentative phase diagram up to 1100°C and 90,000 atm has also been constructed.

B. EXPERIMENTAL

Most of the details concerning the preparation of the charge,[10] the high-pressure apparatus,[11] and the technique[12] have been described in ARL Technical Note 60-130. Briefly, glassy B_2O_3 in the form of cylindrical rods of diameter 2 mm and height 5 mm were wrapped in platinum foil and subjected to high pressures

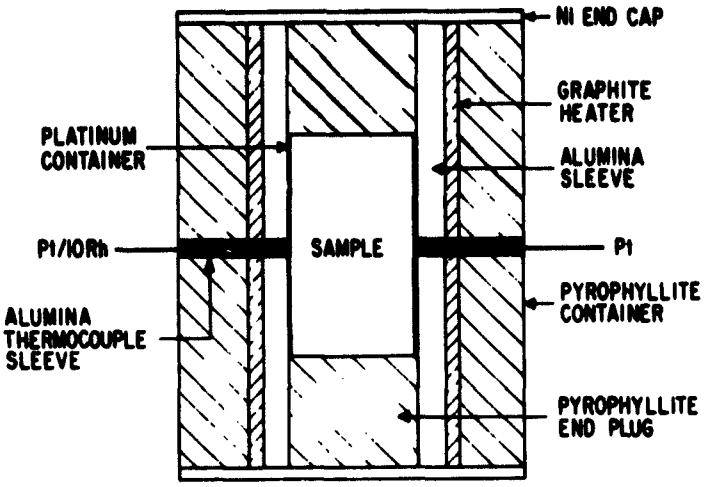


Fig. 1 High-pressure cell for the crystallization of B_2O_3.

in the cell shown in Fig. 1. The duration of the experiments varied from 2 minutes to 3 days, the temperatures, 25° to 1100°C, and the pressures, 10,000 to 90,000 atm. The phase relationships at high pressures were partially confirmed by a differential thermal conductivity analysis method.[13]

C. RESULTS AND DISCUSSION

1. Crystallization

Microcrystals of both the ordinary hexagonal and a dense modification of B_2O_3 were easily prepared from the glass at elevated temperatures and pressures. (For purpose of brevity, it is presently suggested that these two forms be denoted as α-B_2O_3 and β-B_2O_3, respectively.) Thus, for example, at 40,000 atm, devitrification was complete after only 2 minutes at 600°C. Even at room temperature, some crystallization in the order of 5 to 10 per cent had occurred after the sample was compressed at 40,000 atm for 1 day. However, by such simple single-step compaction of vitreous B_2O_3, only microcrystals could be obtained. Two special techniques were subsequently developed for the preparation of single crystals having dimensions up to about 0.3 mm. It was found that at elevated pressures, if the charge was first heated to temperatures above the melting point to destroy the nuclei present, and then subsequently cooled slowly to the stability region of the crystalline phase and maintained here for a period of about 1 hour, growth occurred via the surface inwards. The formation of relatively large crystals by this method is illustrated in Fig. 2. Crystals of comparable dimensions were also prepared by a "cycling" technique. A temperature gradient was established in the high-pressure cell by the use of dissimilar end plugs (Fig. 1). The compacted charge was then alternately heated and cooled at temperatures in the vicinity of the melting point. This thus favored crystal growth at the colder end of the cell. The duration of a typical successful experiment is in the order of 2 hours.

Fig. 2 Section of compacted charge showing the growth of β-B_2O_3 (dense) crystals in glass. 100X

2. X-ray Diffraction and Properties

The x-ray powder diffraction data for both α- and β-B_2O_3, obtained from Debye-Scherrer and spectrometer methods, are presented in Table I. Although the powder data for β-B_2O_3 are similar to those reported by Dachille and Roy[8] for their dense form of B_2O_3, some of the properties appear to be different. Thus, our β-B_2O_3 single crystals are only very slowly attacked by water and dilute hydrofluoric acid, whereas Dachille and Roy reported that their "new variety is attacked readily by atmospheric moisture." Single crystals were carefully separated from a compressed charge and studied by the Buerger Precession method. Results obtained for the two forms and some of their properties are listed in Table II.

3. Phase Relationships

From the present observations and the results of a limited number of differential thermal conductivity analyses, the tentative phase diagram constructed is presented in Fig. 3. The variation of the melting temperature

TABLE I

X-ray Powder Diffraction Data for α-B_2O_3 and β-B_2O_3 (CrKa, λ = 2.2896 A)

α-B_2O_3		β-B_2O_3	
d_o (A)	I	d_o (A)	I
3.424	S	3.968	MS
2.792	VS	3.900	S
2.236	S	2.860	VS
2.166	W	2.305	W
2.098	S	2.264	M
1.932	S	2.065	M
1.826	W	2.013	WM
1.712	S	1.985	M
1.556	M	1.949	W
1.525	M	1.823	VW
1.419	M	1.788	M
1.399	S	1.538	VW
1.396	VW	1.527	VW
1.342	M	1.510	VVW
1.322	M	1.477	VW
1.306	M	1.430	VVW
1.266	M	1.417	W
1.251	MS	1.401	VW
1.249	W	1.392	VW
1.238	W	1.324	W
1.193	MS	1.301	VW
1.191	VW	1.208	VVW
1.173	MS	1.202	VW
1.171	VW	1.182	M
1.140	M	1.176	M
1.130	M	1.153	VW

TABLE II

Unit-Cell Dimensions, Density, and Refractive Indices of α-B_2O_3 and β-B_2O_3

	α-B_2O_3*	β-B_2O_3†
System	Hexagonal	Monoclinic
a_0 (A)	4.334	4.52
c_0 (A)	8.334	4.64
b_0 (A)		4.14
β		120° 25'
N (molecules/unit cell)	3	2
ρ x-ray (g cm^{-3})	2.56	3.05
ρ obs. (g cm^{-3})	2.44	2.95
Refractive indices	1.64, 1.61	1.69, 1.70

*Data from Refs. 4 and 6. †Crystallographic data not yet refined.

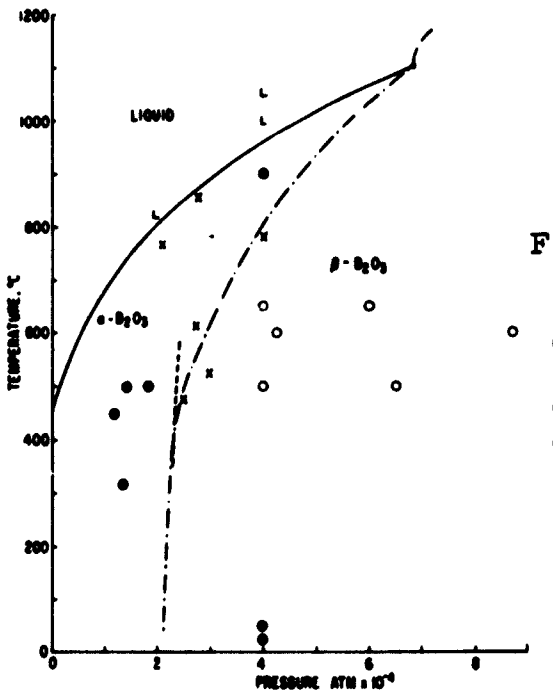


Fig. 3 Tentative temperature-pressure relationship for B_2O_3: L, liquid; ●, α-B_2O_3; o, β-B_2O_3; ⊙, incomplete conversion to β-B_2O_3; X, approximate transition point from differential thermal conductivity analysis;——best curve from Simon equation; ------, Dachille and Roy.[8]

with pressure for a large number of solids such as metals,[14] van der Waals solids,[15] and alkali halides[16] is satisfactorily described by the semi-empirical Simon equation[15]

$$P-P_0 = \alpha\,[(T/T_0)^c - 1] \qquad (1)$$

where α and c are constants for a particular solid, and T_0 is the melting temperature at pressure P_0. According to Eq. (1), the initial slope of the melting curve is given by $(dP/dT) = \alpha c/T_0$. From the Clausius-Clapeyron relationship, $(dP/dT) = L_f/T_0\,(V_L - V_c)$. Therefore, αc is given by $L_f/(V_L - V_c)$, which, from published values of L_f = 5.27 kcal/mole,[17] V_L = 41 cc[18] and V_c = 29 cc,[19] is 1.81×10^4. Values of c found for other solids vary between 1.5 and 6. By the systematic choice of c over this range, the most satisfactory melting curve in Fig. 3 was obtained with c = 4.5 and α = 4020 atm. Assuming that $(V_\alpha - V_\beta)$ decreases slightly with increasing pressure,[20] the approximate heat of the β-α transformation from room temperature to 400°C is about 2 kcal/mole. The triple point is approximately located at 1100°C and 70,000 atm.

From x-ray examinations of compacted B_2O_3, Dachille and Roy[8] had found yet a third phase present at pressures between 18,000 and 35,000 atm and at temperatures below about 350°C, which was referred to as the metastable phase. That this is not a polymorph of B_2O_3 but a hydrated compound was considered possible by these workers. This metastable phase was not observed in the present work with the carefully dehydrated glass. However, the d values of the four main x-ray lines reported for this modification are similar to those presently found in a sample of H_3BO_3 which has been compacted for 1 hour at 300°C and 25,000 atm. It is thus likely that this so-called metastable phase is a dense modification of either H_3BO_3 or HBO_2.

Both room and elevated temperature experiments indicated that the transformation sequence is vitreous $B_2O_3 \rightarrow \alpha \rightarrow \beta$. The α-β transformation is extremely sluggish. At room temperature, for instance, a small amount of α-B_2O_3 is found in the glass after compaction for 1 hour at 40,000 atm, but no β-B_2O_3 is formed. However, after 1 day both forms are present. Although the β-modification is considered to be the thermodynamically metastable phase at room temperature and atmospheric pressure, it is surprisingly stable even on prolonged heating. High-temperature x-ray diffraction experiments indicated that at atmospheric pressure, no β-α transformation occurs up to the melting temperature of α-B_2O_3. Even after 4 days at 445°C, assuming the melting point of α-B_2O_3 to be 450°C, the β-α transition is still not observed.

4. Fusion at Atmospheric Pressure

It is not generally realized that certain oxides may be easily superheated to temperatures far beyond their melting points. Thus arsenolite-As_4O_6 (mp 278°C) may be heated to 310°C with as slow a heating rate as 5° to 8°/hr.[21] With higher rates of heating, it may be superheated to 330°C. Similarly, quartz-SiO_2

(mp ~1450°C) may be superheated to 1600°C for 1 hour with only a small observable degree of fusion.[22] The accurate determination of the melting point of these oxides by direct means is thus extremely difficult. For α-B_2O_3, with heating rates of 1° to 4°C/min, fusion is first observed at about 490°C. However, after the crystals have been kept at 475°C for 3 days in dry N_2, some 75 per cent of the vitreous B_2O_3 was present. No glass was observed after 4 days at 455°C. The correct melting point of α-B_2O_3 is therefore probably between 455° and 475°C. A value of 450.8°C was reported by Donoghue and Hubbard[19] for a sample which contained small amounts of H_3BO_3 and glass. With the higher heating rates of 1° to 4°C/min, β-B_2O_3 may be heated to 520°C before fusion occurs. The refractive index of the quenched glass is similar to that from a sample of α-B_2O_3 heated to the same temperature. After a sample of β-B_2O_3 had been heated at 445°C for 4 days, neither α-B_2O_3 nor glass was observed. However, for a similar period at 475°C, approximately 50 per cent of glass was present but no α-B_2O_3 was found. This suggests that the sequence of fusion is probably $\beta \rightarrow \alpha \rightarrow$ liquid, the rate of the latter step being in excess of that of the first.

5. Infrared Absorption

It is well known that both vitreous and the crystalline α-B_2O_3 are rapidly attacked by moisture, especially when these are in a finely divided state. In the conventional KBr pellet technique, the concentration of sample is in the order of 0.1 to 0.5 per cent. In the formation of the KBr pellet, most of the B_2O_3 may thus be easily transformed into H_3BO_3 since the complete dehydration of the KBr or the total exclusion of moisture during the processing is difficult. Simon[23] has pointed out that the use of this method by various workers[8, 24] for studying the infrared spectra of both vitreous and crystalline B_2O_3 could lead to erroneous results, the spectra observed being in fact totally or partly that of H_3BO_3. The present work has confirmed Simon's suggestions in that the spectra of α-B_2O_3, vitreous B_2O_3 and H_3BO_3 were indeed similar if the KBr disk technique was employed. The Nujol mull method was tried but was also unsatisfactory. It was thus not possible to correlate the structures of the different forms of solid B_2O_3 from infrared studies alone.

6. Nuclear Magnetic Resonance Absorption

Preliminary experiments were carried out on both the α- and the β-B_2O_3. In the case of α-B_2O_3 which is supposedly made up of BO_4 tetrahedra,[4] 4-coordinated boron similar to that found in the binary borate glasses was not detectable. However, at least some of the borons in β-B_2O_3 are 4-coordinated. For the purpose of experimental confirmation, experiments were also made with BPO_4 and $BAsO_4$, all the boron atoms in both of which being 4-coordinated. Absorption maxima were observed in both samples similar to those attributed to 4-coordinated boron in the binary glasses. This work on the crystalline B_2O_3 will be useful as a guide for their structural determination by x-ray diffraction.

III. STRUCTURE OF LIQUID AND VITREOUS B_2O_3

A. INTRODUCTION

The structures of liquid and glassy B_2O_3 have long been a subject of much controversy. In the case of liquid B_2O_3, early concepts range from that of a molecular liquid consisting of B_4O_6 molecules,[2] an ionic melt involving complex boron-oxygen ions,[24] to that of a highly associated network of interlinking BO_3 triangles similar to the structure of liquid SiO_2. Recently, it was pointed out that although the energy of the B-O and Si-O bonds are similar in magnitude, the flow parameters of liquid SiO_2 and B_2O_3 are grossly different.[25, 26] A so-called random network structure identical to that of liquid SiO_2 is therefore incompatible with the observed flow data. At temperatures between 450° and 1000°C, studies of viscosity, density, and electric conductivity suggested that the structure of liquid B_2O_3 is temperature dependent but that ionic dissociation is negligible.[18] At higher temperatures, however, 1200° to 1600°C, it has been postulated that extensive ionic dissociation does occur.[27] Electric conductivity data are not available at these elevated temperatures. From a consideration of the thermal expansion of the glass and the liquid, Fajans and Barber[2] have further indicated that some drastic structural variation must occur at around 300°C. It is clear from the above brief summary that more work is necessary to clarify the situation concerning liquid B_2O_3 before correlations can be made between the structures of the liquid and the solid glass. In this section, a summary is presented of the results of measurements of different properties of both liquid and glassy B_2O_3 as a function of temperature.

B. VISCOSITY

Although the degree of association in liquid B_2O_3 is less extensive than that in liquid SiO_2 at temperatures near their respective melting points,[25, 26] viscosity data, though empirical, are not compatible with the concept of a molecular liquid involving B_4O_6 molecules and weak van der Waals forces. A comparison of the flow parameters of five liquid "types" in Table III indicates that B_2O_3 is essentially a network of polymeric liquid.[28]

In the present work, viscosity measurements have been made at temperatures between 800° and 1350°C on liquid B_2O_3 containing approximately 0.2 and 0.1 per cent H_2O.[10] The effects of these concentrations of H_2O are minor. Even at 1350°C, the viscosity is as high as 30 poise and the structure of the melt is thus still polymeric (Table IV). The activation energy for viscous flow decreases from 40 kcal/mole at 450°C to about 10 kcal/mole at 1350°C. This is clearly indicative of a decreasing degree of association with increasing temperature.

C. ELECTRIC CONDUCTANCE

In order to examine the validity of the idea that liquid B_2O_3 undergoes extensive dissociation to give oxygen ions at high temperatures, measurements of

TABLE III

Viscosity and Energy of Activation for Flow of Different Liquids at the Melting Temperature[28]

Substance	Liquid Type	T_m(°C)	Viscosity (poise)	E_η (kcal/mole)	Ref.
Benzene	Molecular	5.5	0.01	2.3	26
Naphthalene	Molecular	80	.01		26
Octadecane	Molecular	28	.04	4.0	27
Sulfur	Molecular	120	.1	7.0	28
Water	Hydroxylic	0	.2	5.1	26
Methanol	Hydroxylic	-98	.1	2.5	26
Glycerol	Hydroxylic	18	15	13	26
Stearic acid	Hydroxylic	69	.1		26
Sodium	Metallic	98	.1	1.5	29
Zinc	Metallic	420	.03	3.1	29
Iron	Metallic	1535	.07	6.8	30
LiCl	Ionic	6.3	.02	8.8	31
CdBr	Ionic	567	.03	4.5	32
Al_2O_3	Ionic	2050	.6	~30	33
As_2O_3	Network	309	10^6	23	21
B_2O_3	Network	450	10^5	40	10
GeO_2	Network	1115	10^7	180	34
SiO_2	Network	1710	10^7	180	35
BeF_2	Network	540	$> 10^6$	> 100	36

TABLE IV

Viscosity, Electric Conductivity, and Density
of Liquid B_2O_3 Containing Approximately 0.1 Per Cent H_2O

Temp (°C)	Viscosity (poise)	Sp. Conductivity x 10^6 ohm^{-1} cm^{-1}	Density (g cm^{-3})
800	363*		1.540*
850	257	0.19	1.533
900	182	.35	1.525
950	133	.53	1.517
1000	103	.80	1.510
1050	82.2	1.19	1.505
1100	66.4	1.70	1.500
1150	54.7	2.34	1.496
1200	46.2	3.16	1.493
1250	40.1	4.17	1.491
1300	35.1	5.37	1.489
1350	31.0*	7.05	

*Extrapolated values.

electric conductivity have been made between 800° and 1350°C.[10] The effects of small amounts of H_2O have also been examined. A combination of the present and past results[18] showed that between 450° and 1350°C, the empirical relation

$$K = A_K \exp(-E_K/RT) \qquad (2)$$

is obeyed. The activation energy, E_K, was 25 ± 2 kcal/mole over the entire temperature range. This is different from the energy of activation for viscous flow which is temperature dependent. For the melt containing about 0.1 per cent H_2O, the specific conductivity, K, was only 7×10^{-6} ohm^{-1} cm^{-1} at 1350°C (Table IV). These facts indicated that ionic dissociation is probably negligible even up to 1350°C, although viscosity data showed that the degree of association is temperature dependent. The present work has shown that specific conductance is very sensitive to the water content of the melt. In Fig. 4, a summary is presented of the results of various workers. The similarity of E_K in all cases supports the idea that the difference of the observed K values is primarily due to the residual H_2O contents in the different experiments.

D. DENSITY

The relation between density and temperature is nonlinear over the temperature range 800° to 1350°C. This is contrary to the behavior of most liquids and confirms the viscosity results that the structure of the melt is temperature

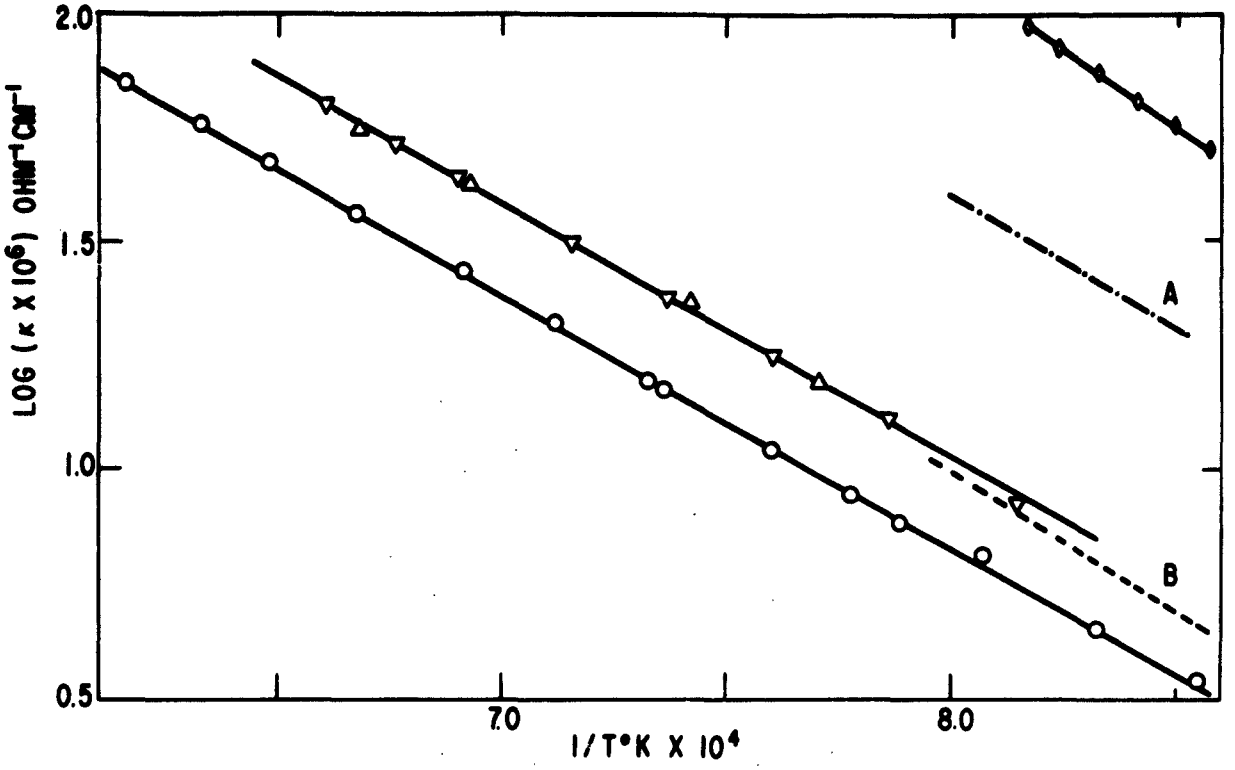


Fig. 4 Relation between log specific conductivity and 1/T for liquid B_2O_3: o, containing about 0.1 per cent H_2O; △, ▽, containing about 0.2 per cent H_2O; ◇, Shartsis[29] and Mackenzie;[18] A, Arndt and Gessler;[30] B, Phelps and Grace.[31]

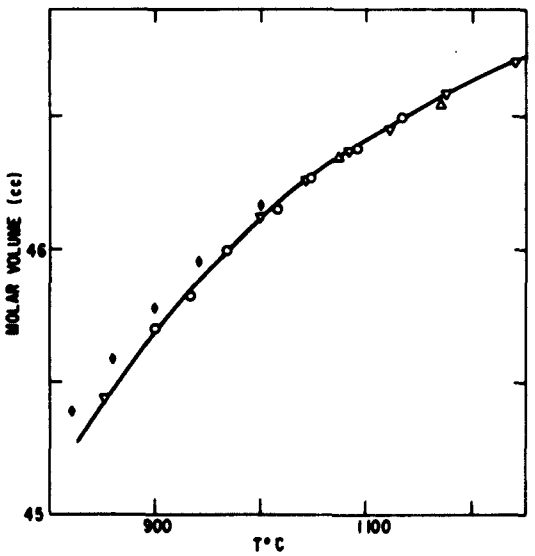


Fig. 5 Relation between molar volume and temperature for liquid B_2O_3. Notations as for Fig. 4.

dependent. Another significant feature is that the molar volume deviates negatively from linearity with increasing temperature (Fig. 5).

E. NUCLEAR MAGNETIC RESONANCE ABSORPTION

It has been suggested that for liquids having "directional forces," the coordination increases with increasing temperature.[32] Since the structure of liquid B_2O_3 is temperature dependent, it is possible then that the coordination number of boron will vary with temperature. Recently, Silver and Bray[33] were able to demonstrate by NMR techniques that the BO_3 triangle is the basic building unit in glassy boron oxide. It thus seemed desirable to study the NMR absorption of B_2O_3 as a function of temperature.

Preliminary experiments were carried out on solid samples quenched from temperatures as high as 1300°C. However, no 4-coordinated boron was detected in these samples. (The lower limit of detectability of 4-coordinated boron is estimated to be 2 per cent.) Subsequently, experiments were carried out on liquid B_2O_3 up to 500°C, but the results were still negative. It thus appeared that the structural variation of liquid B_2O_3 with temperature is not the result of a boron coordination change from 3 to 4.

F. INFRARED ABSORPTION

Among the various hypotheses made to account for the structural variation of liquid B_2O_3 with temperature is one which involves the formation of -B=O in the melt.[10] In order to examine this and other models, two high-temperature infrared apparatus have been developed in the present work to study both glassy and liquid B_2O_3. The experimental details have been described in ARL Technical Note 60-130. Briefly, thin films of the glass or liquid were examined as a function of temperature by the use of a vertical technique (Fig. 6) and a horizontal technique (Fig. 7). Films were examined from room temperature to about 1000°C and showed no drastic variation in their absorption with increasing temperature. In gaseous B_2O_3 the infrared band at 2040 cm^{-1} has been ascribed to B=O stretchings. In glassy B_2O_3, a small absorption band is observed at about 2060 cm^{-1}. If -B=O does form as the temperature is increased, it should be observable at about this wave number. However, in Fig. 8, it is seen that even if -B=O groups are present in the melt, their concentration must be exceedingly small. The dissociation of liquid B_2O_3 at high temperatures is therefore not explicable by this mechanism.

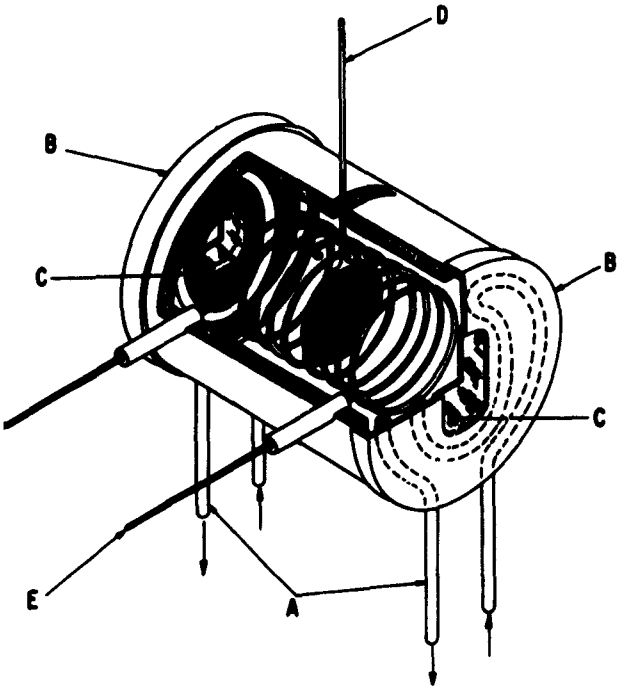


Fig. 6 Vertical micro-furnace, 2-inch diameter, 29/16-inch length, for high-temperature infrared studies of liquid films: (A) 1/8-inch OD water-cooling copper coils; (B) detachable end-plates; (C) 1/32-inch-thick single-crystal MgO windows; (D) platinum wire sample holder with loop of 3/4-inch diameter; (E) Kanthal heater.

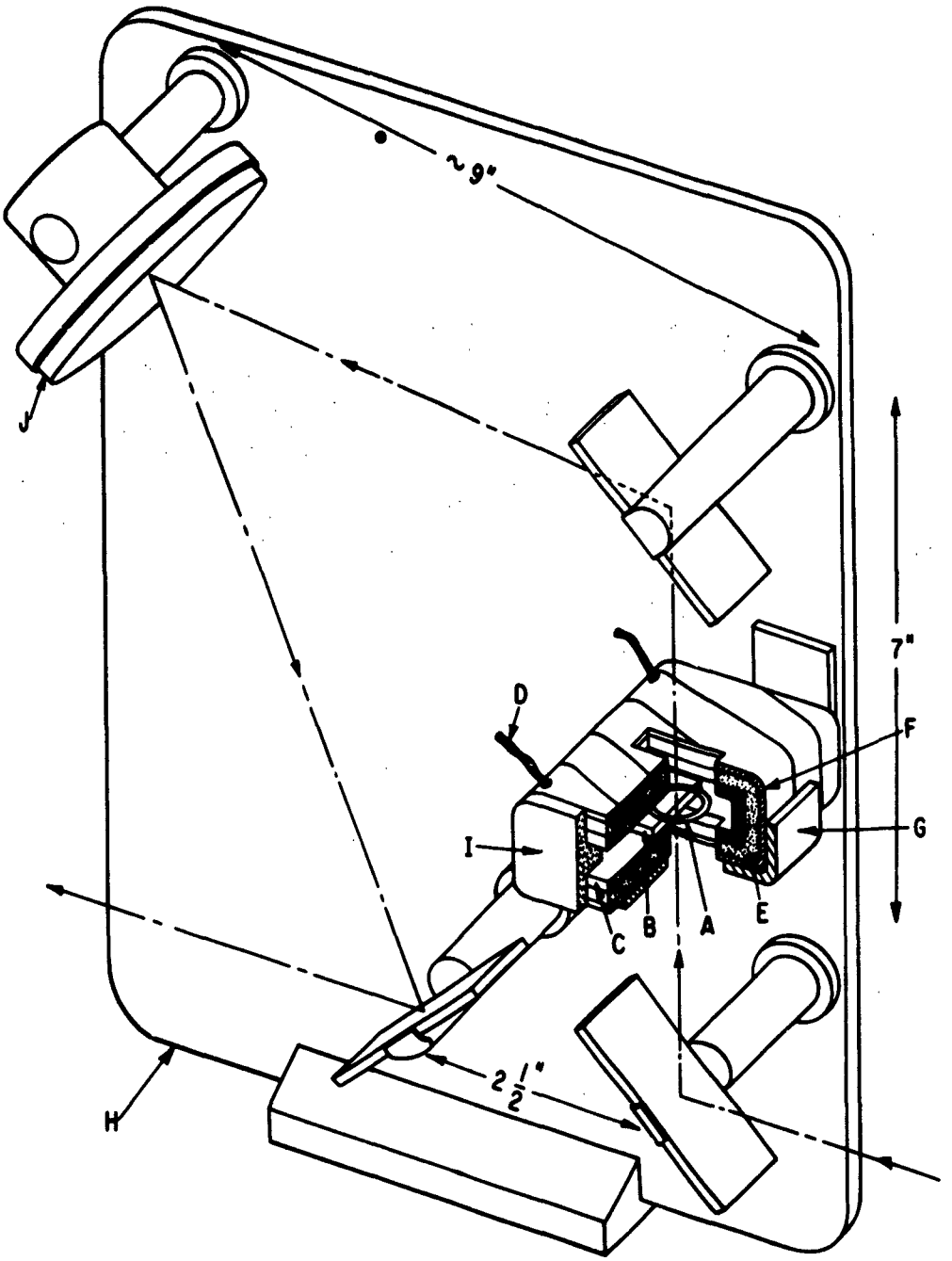


Fig. 7 Horizontal micro-furnace and mirror system for high-temperature infrared studies of liquids: (A) 3/4-inch-diameter platinum loop sample container; (B) 1/32-inch-thick single-crystal MgO supporting plate; (C) rectangular alumina furnace tube; (D) Pt-20 per cent Rh wire; (E) alumina cement; (F) sheet asbestos cover; (G) aluminum furnace holder; (H) rigid wooden mount; (I) alumina plug; (J) convex mirror.

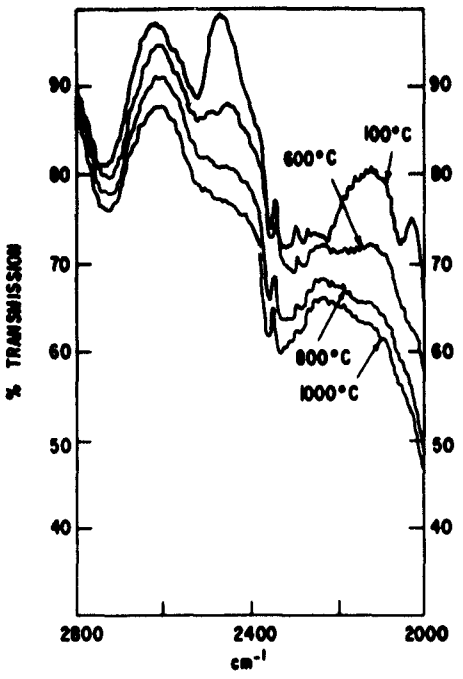
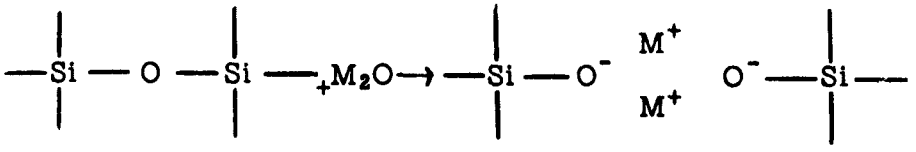


Fig. 8 Infrared absorption spectra of liquid and vitreous B_2O_3 over the region 2000 to 2800 cm^{-1} up to 1000°C. Single-beam apparatus.

IV. BINARY BORATES

It appears conclusive that from the measurements of a number of physical properties the coordination number of boron in a binary borate glass such as the alkali borate is dependent on its composition. Early work by Shartsis et al.[29] also indicated that the structures of the liquid binary borates are temperature dependent. Correlation between the structures of the melt and the solidified glass is further complicated by the fact that, at some temperature range between the glass transition and the liquid regions, a maximum thermal expansivity is observed.[34,35] This would indicate that a significant change in the structure of the supercooled liquid has occurred. In general, the data available on the borates are scattered, and hence structural interpretations are difficult. The initial objective of the present work is to gain an understanding of the structural variations of the liquid borates with composition and temperature before attempts are made on studying the solidified glass.

Since a large amount of data are available on the liquid silicates from which much structural information has been obtained,[36] it appeared desirable to compare the properties of borate and silicate melts. In general, it is accepted that when a metal oxide is added to vitreous SiO_2, the resultant reaction may be formally represented by a bond rupture of the type:



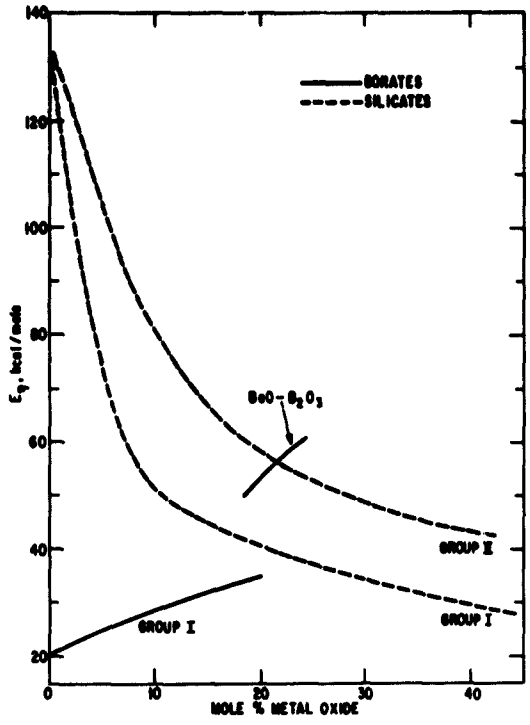


Fig. 9 Relationship between the energies of activation for viscous flow of molten silicates and borates with composition. Silicates, 1750°C; borates, 950°C.

The degree of breakdown of the three-dimensional silicon-oxygen network is thus directly proportional to the concentration of metal oxide. Hence the viscosity and electrical resistance of the melt will decrease with increasing amount of metal oxide. In the present work, a critical review of the literature has been made and revealed some remarkable differences between the silicates and the borates. For instance, in Fig. 9, the energies of activation for viscous flow of these two liquids are compared as a function of composition. The widely different variations of the two melts are evident. The electrical conductance and expansivity are also dissimilar.[28] It may be concluded that the type of structural treatment which was successful in the case of the silicates is not applicable to borates.

One of the interesting observations made in the present review is concerned with the variation of viscosity of binary liquid borates with composition at constant temperature. The occurrence of maxima and minima in these viscosity isotherms has been reported by various workers[29, 37] who, however, have made no mention of the fact that measurements were often made at temperatures far below the liquidus. It is therefore possible that the observed maxima and minima may be the result of phase separation occurring in the supercooled melt. In the present work, very careful experiments have been carried out on the system Na_2O-B_2O_3 as a function of supercooling and confirmed that these anomalies cannot be due to phase separations.

Studies of the physical properties-structure relationships of PbO-B_2O_3 and SiO_2-B_2O_3 have been initiated and are still in progress.

REFERENCES

1. W.H. Zachariasen, J. Am. Chem. Soc., 54, 3841 (1932).
2. K. Fajans and S.W. Barber, ibid., 74, 2761 (1952).
3. E.P. Markin and N.N. Sobolev, Izvest. Akad. Nauk SSSR, Ser. Fiz., 22, 1097 (1958).
4. S.V. Berger, Acta Chem. Scand., 7, 611 (1953).
5. L. McCulloch, J. Am. Chem. Soc., 59, 2650 (1937).
6. F.C. Kracek, G.W. Morey, and H.E. Merwin, Am. J. Sci., 35A, 14 (1938).
7. S.S. Cole and N.W. Taylor, J. Am. Ceram. Soc., 18, 55 (1935).
8. F. Dachille and R. Roy, ibid., 42, 78 (1959).
9. W.F. Claussen and J.D. Mackenzie, J. Am. Chem. Soc., 81, 1007 (1959).
10. J.D. Mackenzie, J. Phys. Chem., 63, 1875 (1959).
11. H.T. Hall, Rev. Sci. Instr., 31, 125 (1960).
12. J.D. Mackenzie and W.F. Claussen, J. Am. Ceram. Soc., 44, 79 (1961).
13. W.F. Claussen, Rev. Sci. Instr., 31, 878 (1960).
14. F.E. Simon, Nature, 172, 746 (1953).
15. F. Simon and G. Glatzel, Z. anorg. Chem., 178, 309 (1929).
16. S.P. Clark, Jr., J. Chem. Phys., 31, 1526 (1959).
17. J.C. Southard, J. Am. Chem. Soc., 63, 3147 (1941).
18. J.D. Mackenzie, Trans. Faraday Soc., 52, 1564 (1956).
19. J.J. Donoghue and D. Hubbard, J. Res. Natl. Bur. Standards, 27, 371 (1941).
20. P.W. Bridgman, The Physics of High Pressure, G. Bell and Sons, Ltd., London (1949).
21. I. Karutz and I.N. Stranski, Z. anorg. Chem., 292, 330 (1957).
22. J.D. Mackenzie, J. Am. Ceram. Soc., 43, 615 (1960).

23. I. Simon, Modern Aspects of the Vitreous State, ed. J.D. Mackenzie, Butterworths Scientific Pub., London (1960), Chap. 6.

24. S. Anderson, R.L. Bohon, and D.D. Kimpton, J. Am. Ceram. Soc., 38, 370 (1955).

25. J.D. Mackenzie, J. Chem. Phys., 25, 187 (1956).

26. J.D. Mackenzie, ibid., 24, 925 (1956).

27. J. Zarzycki, Proc. IV Intern Conf. on Glass, Paris, VI, 323 (1956).

28. J.D. Mackenzie, Modern Aspects of the Vitreous State, ed. J.D. Mackenzie, Butterworths Scientific Pub., London (1960), Chap. 8.

29. L. Shartsis, W. Capps, and S. Spinner, J. Am. Ceram. Soc., 36, 319 (1953).

30. K. Arndt and A. Gessler, Z. Elektrochem., 14, 662 (1908).

31. W.C. Phelps, Jr. and R.E. Grace, J. Metals, 9, 1447 (1957).

32. J.D. Bernal, Trans. Faraday Soc., 33, 27 (1937).

33. A.H. Silver and P.J. Bray, J. Chem. Phys., 29, 984 (1958).

34. L. Shartsis and H.F. Shermer, J. Am. Ceram. Soc., 37, 544 (1954).

35. L. Shartsis, W. Capps, and S. Spinner, ibid., 36, 35 (1953).

36. J.D. Mackenzie, Chem. Revs., 56, 455 (1956).

37. M.P. Volarovitch and D.M. Tolstoi, Bull. Acad. Sci. USSR, classe sci. phys.-math., 897 (1930).

GENERAL ELECTRIC RESEARCH LABORATORY, Schenectady, N. Y., STRUCTURE OF VITREOUS BORON TRIOXIDE AND SOME SIMPLE BORATES, by J. D. Mackenzie, September 1961. 18 p. incl figs. and tables. (Project 3048) (Task 70321) (Contract AF 33(616)-5699)
Unclassified report

A broad program of research has been conducted to obtain structural information on the vitreous and liquid B_2O_3 and binary borates. By the use of high-pressure techniques, simple crystals of two forms of B_2O_3 have been prepared for x-ray diffraction studies. The tentative phase diagram for liquid and crystalline B_2O_3 has been constructed up to 1100°C and 90,000 atmospheres.

(over)

UNCLASSIFIED

GENERAL ELECTRIC RESEARCH LABORATORY, Schenectady, N. Y., STRUCTURE OF VITREOUS BORON TRIOXIDE AND SOME SIMPLE BORATES, by J. D. Mackenzie, September 1961. 18 p. incl figs. and tables. (Project 3048) (Task 70321) (Contract AF 33(616)-5699)
Unclassified report

A broad program of research has been conducted to obtain structural information on the vitreous and liquid B_2O_3 and binary borates. By the use of high-pressure techniques, simple crystals of two forms of B_2O_3 have been prepared for x-ray diffraction studies. The tentative phase diagram for liquid and crystalline B_2O_3 has been constructed up to 1100°C and 90,000 atmospheres.

(over)

UNCLASSIFIED

The effects of water on the viscosity, electric conductance, and density of liquid B_2O_3 have been examined. From this, some of the current hypotheses concerning the structure of liquid B_2O_3 can be rejected. Preliminary results on the infrared absorption of solid and liquid B_2O_3 have been obtained. A description is given of other work in progress which includes nuclear magnetic resonance absorption, viscosity measurements of binary borates at temperatures below the liquidus, and single-crystal diffraction on α- and β-B_2O_3.

UNCLASSIFIED

The effects of water on the viscosity, electric conductance, and density of liquid B_2O_3 have been examined. From this, some of the current hypotheses concerning the structure of liquid B_2O_3 can be rejected. Preliminary results on the infrared absorption of solid and liquid B_2O_3 have been obtained. A description is given of other work in progress which includes nuclear magnetic resonance absorption, viscosity measurements of binary borates at temperatures below the liquidus, and single-crystal diffraction on α- and β-B_2O_3.

UNCLASSIFIED

GENERAL ELECTRIC RESEARCH LABORATORY, Schenectady, N. Y., STRUCTURE OF VITREOUS BORON TRIOXIDE AND SOME SIMPLE BORATES, by J. D. Mackenzie, September 1961, 18 p. incl figs. and tables. (Project 3048) (Task 70321) (Contract AF 33(616)-5699)
Unclassified report

A broad program of research has been conducted to obtain structural information on the vitreous and liquid B_2O_3 and binary borates. By the use of high-pressure techniques, simple crystals of two forms of B_2O_3 have been prepared for x-ray diffraction studies. The tentative phase diagram for liquid and crystalline B_2O_3 has been constructed up to 1100°C and 90,000 atmospheres.

(over)

UNCLASSIFIED

The effects of water on the viscosity, electric conductance, and density of liquid B_2O_3 have been examined. From this, some of the current hypotheses concerning the structure of liquid B_2O_3 can be rejected. Preliminary results on the infrared absorption of solid and liquid B_2O_3 have been obtained. A description is given of other work in progress which includes nuclear magnetic resonance absorption, viscosity measurements of binary borates at temperatures below the liquidus, and single-crystal diffraction on α- and β-B_2O_3.

UNCLASSIFIED

UNCLASSIFIED

GENERAL ELECTRIC RESEARCH LABORATORY, Schenectady, N. Y., STRUCTURE OF VITREOUS BORON TRIOXIDE AND SOME SIMPLE BORATES, by J. D. Mackenzie, September 1961, 18 p. incl figs. and tables. (Project 3048) (Task 70321) (Contract AF 33(616)-5699)
Unclassified report

A broad program of research has been conducted to obtain structural information on the vitreous and liquid B_2O_3 and binary borates. By the use of high-pressure techniques, simple crystals of two forms of B_2O_3 have been prepared for x-ray diffraction studies. The tentative phase diagram for liquid and crystalline B_2O_3 has been constructed up to 1100°C and 90,000 atmospheres.

(over)

UNCLASSIFIED

UNCLASSIFIED

The effects of water on the viscosity, electric conductance, and density of liquid B_2O_3 have been examined. From this, some of the current hypotheses concerning the structure of liquid B_2O_3 can be rejected. Preliminary results on the infrared absorption of solid and liquid B_2O_3 have been obtained. A description is given of other work in progress which includes nuclear magnetic resonance absorption, viscosity measurements of binary borates at temperatures below the liquidus, and single-crystal diffraction on α- and β-B_2O_3.

UNCLASSIFIED