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THERMAL EXPANSION STUDIES OF BORIC OXIDE GLASS AND OF CRYSTALLINE BORIC OXIDE

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ABSTRACT

The expansion characteristics of a boric oxide (B_2O_3) glass and of a sample of crystalline boric oxide have been studied by the interferometer method. The results obtained are chiefly of qualitative interest, but offer a satisfactory picture of some of the difficulties that must be overcome if true expansion data are to be obtained on these materials.

The characteristics of the expansion curves for boric oxide glass and crystalline boric oxide are very different. The sample of crystalline boric oxide had a melting temperature between 450° and 451° C. Upon being heated to its melting point, this material does not recrystallize on cooling, but remains in a fused state, as indicated by the "critical" and "softening" temperatures shown by its expansion curve.

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I. INTRODUCTION

In a study of the physical properties of experimental glasses of the binary systems SiO_2 - B_2O_3 and Al_2O_3 - B_2O_3 , it became desirable to know the coefficient of linear expansion and other characteristics of the expansion curve for the one-component boric oxide (B_2O_3) glass. Published data on the expansion of this glass are highly conflicting, as shown in the review of the subject by Morey [1].² Furthermore, with a sample of crystalline boric oxide available, it seemed of interest to make a comparison of the expansion characteristics of the vitreous and crystalline forms of this oxide.

II. PREPARATION OF MATERIALS

The boric oxide glass was prepared by C. A. Faick at $1,050^\circ$ C in a platinum crucible from boric acid which had passed the American Chemical Society specification for purity [2]. The sample of crystalline boric oxide was donated by S. R. Scholes, of the New York State College of Ceramics, and had been prepared by the method discovered by L. McCulloch [3].

¹ James J. Donoghue collaborated in this study before he left the National Bureau of Standards in June 1940.

² Figures in brackets indicate the literature references at the end of this paper.

III. EXPERIMENTAL PROCEDURE

The expansion determinations were made by means of the modified Fizeau-Pulfrich interference method [4, 5, 6], using a heating rate of approximately 3°C per minute. The temperature was followed with a Chromel-Alumel thermocouple, calibrated against a small quartz "refraction thermometer" [6, p. 192-194] placed in the position normally occupied by the specimens. This does much to eliminate the temperature error caused by the relatively large gradient between the positions occupied by the thermocouple and that by the specimens, which is so characteristic of a vertical tube furnace [6].

The expansion specimens for the boric oxide glass were drawn from the molten mass by means of a three-tined fork of 1/8-inch Nichrome wire. The glass which adheres to the points when the fork is withdrawn gives small hollow cones which can be shaped into expansion specimens with a minimum amount of grinding and handling [7]. For the crystalline boric oxide, triangular expansion specimens approximately 5 mm high were dry-ground from small pieces broken from the solid mass.

IV. DATA AND RESULTS

1. BORIC OXIDE GLASS

Curve *A* of figure 1 shows the expansion obtained for the initial determination on the drawn specimens of boric oxide glass when heated beyond the annealing temperature, but not to the softening point. This curve has two regions of negative expansion; the one near 150°C is relatively small, while that at the higher temperature is large. Since the specimens were air-quenched from the temperature of the melt, the negative expansion with the minimum near 265°C in the annealing range was to be expected [4, p. 473-475; 8]. Upon cooling these specimens in the furnace from 320°C, which is well above the annealing temperature for this glass, to room temperature, the expansion determination made on the following day showed that the small negative expansion near 150°C still persisted, although altered in position and magnitude, while the large negative expansion of the specimens in the "quenched condition" had been eliminated and in its place was a very large positive expansion, curve *B*, figure 1.

Since anhydrous boric oxide is classified as a dehydrating agent [9], it seemed probable that the irregular negative expansion of the boric oxide glass in the vicinity of 150° C is the result of decomposition of boric acid formed on the surface of the specimens by the reaction of the boric oxide glass with atmospheric moisture. To establish definitely whether this negative expansion was associated with moisture, a series of expansion determinations was made on a set of specimens of the boric oxide glass which had remained in a desiccator over KOH for several weeks. The results are plotted in figure 2 with the segments of the curves near 150° C displaced sufficiently along the ordinates to show the characteristic of each curve. Curve *A* shows a slight rounding off toward a decreasing slope just prior to the negative expansion near 150° C. The data plotted in *B* were obtained by cooling the furnace without disturbing the interferometer set-up of determination *A*, and holding for 1 hour at about 110° C to maintain

a very low relative humidity and to prevent reabsorption of moisture. Upon reheating through 150°C no indication of a negative expansion was found. However, upon cooling to room temperature, again without disturbing the interferometer set-up, and allowing to stand for 24 hours before making another determination, a small negative expansion reappeared (curved *C*). The top curve, *D*, was obtained after placing the specimens in a closed space over water for 24 hours. The resulting

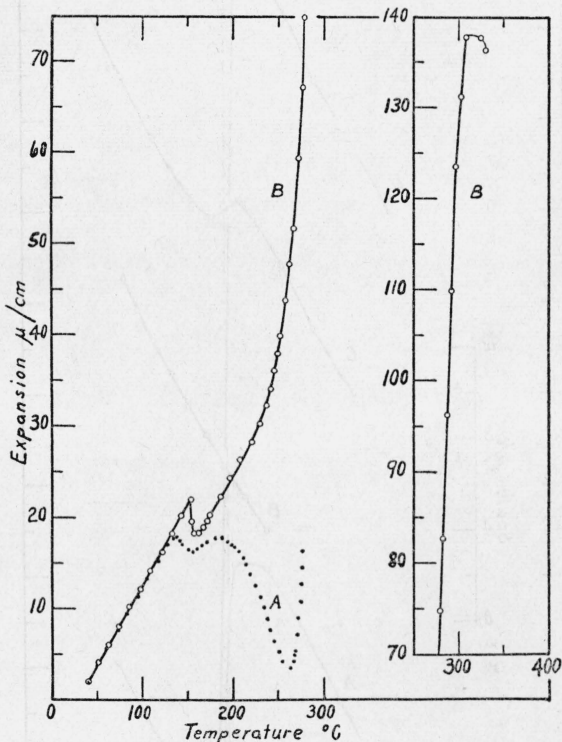


FIGURE 1.—Expansion curves *A* and *B* of fused B_2O_3 , with the glass in the quenched and annealed conditions, respectively, both determinations exhibiting a negative expansion near 150°C .

negative expansion was very large. After following the dimensional change for more than 43 microns per centimeter, the passage of the bands became so rapid that no further counts could be made.

The fact that curve *B* passed through the temperature region near 150°C without deflection leads one to believe that a curve closely approximating the true expansion of boric oxide glass could be obtained. However, in light of the knowledge of the tenacity with which boric oxide holds to the final fraction of water, one should hesitate to accept the data as giving the true expansion for B_2O_3 glass.

The two examples of negative expansion shown in figure 1 probably account for most of the discrepancies in the published data. In obtaining a true expansion for boric oxide glass, the negative expansion near 150°C presents a more difficult problem to surmount

than does the annealing, because exposure to moisture of the atmosphere while preparing the specimens and making the interferometer set-up must necessarily give rise to some surface contamination. This contaminated surface does not give up all of its water below red

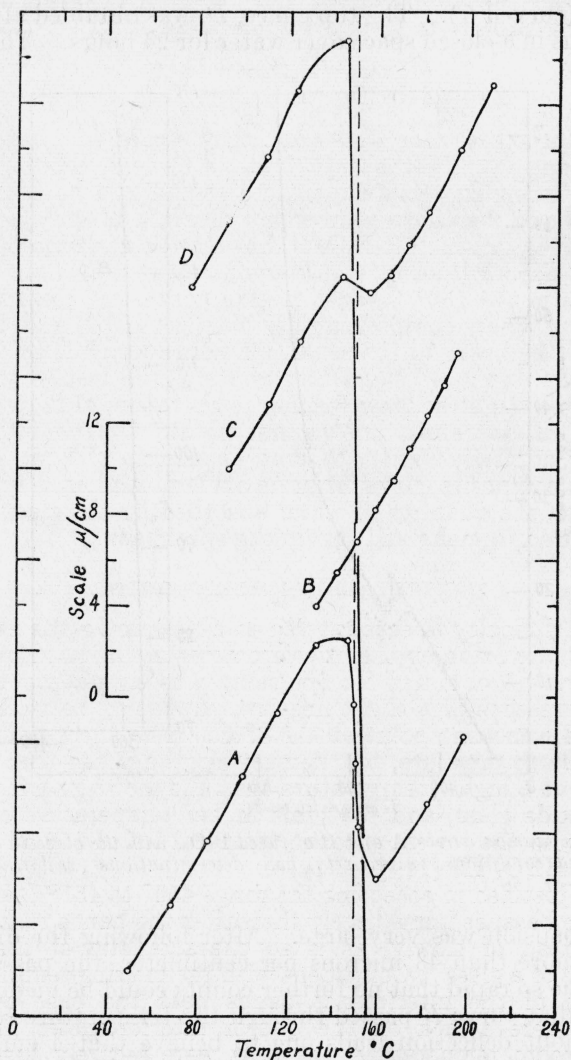


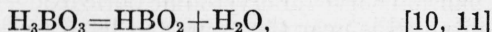
FIGURE 2.—Expansion determinations of B_2O_3 glass, showing the effect of moisture on the expansion curve near $150^\circ C$.

A, Initial set-up; B, after preheating above $170^\circ C$ and cooling to $110^\circ C$; C, after cooling to room temperature and allowing to stand in the furnace 24 hours; D, effect of exposing specimens to high humidity for 24 hours.

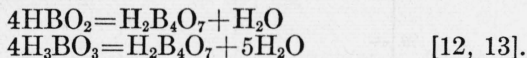
heat, which is several hundred degrees above the softening temperature of the boric oxide glass. Thus, the specimens cannot be completely freed of moisture without destroying the interferometer set-up.

The difficulty may be better appreciated by following what happens to the boric acid upon heating. According to the older reports,

H_3BO_3 gives up water gradually between 80° and 108° C, presumably according to the equation



while between the temperatures 140° to 160° C HBO_2 and H_3BO_3 give up water rapidly to form tetraboric acid.



If these three reactions were true, they would adequately account for the expansion curve near 150° C. However, a truer picture of what is occurring in this temperature region can be obtained by a careful study of the phase-equilibrium diagram of the system water-boric oxide [14], in which $H_2B_4O_7$ is shown to be nonexistent. In their publication Kracek, Morey, and Merwin report that, upon raising the temperature above 150° C, dehydration continues, yielding a highly viscous liquid whose composition lies between HBO_2 and B_2O_3 . This gives rise to the break in the expansion curve which is so conspicuous between 145° and 160° C. Unfortunately, the last of the water is not given up until after the softening temperature of boric oxide glass is reached. As a result, one cannot obtain by the interferometer method (as normally used) the true expansion of boric oxide glass alone, but a composite curve for boric oxide plus an indefinite mixture depending on the quantity of water absorbed by the glass during the period required to make and set up the specimens.

2. CRYSTALLINE BORIC OXIDE

A similar difficulty is encountered in determining the expansion of crystalline boric oxide by the interferometer method. The expansion curve in figure 3 obtained for the sample of crystalline boric oxide shows the presence of a slight negative expansion between 155° and 161° C. and a melting point at 450.8° C. The effect near 160° C is probably due to moisture, but it must also be noted that this is unmistakably at a higher temperature than the moisture effect given by the boric oxide glass, and that this higher temperature corresponds very closely to the lowest eutectic temperature of 158.5° C between H_3BO_3 and HBO_2 III [14, p. 171].

One feels justified in accepting the range 450° to 451° C as a melting temperature because immediately thereafter the bands rushed by very rapidly instead of slowly, as is so characteristic of the softening temperature of a glass. Coincident with the melting temperature, the deformation of the interference bands near the base of the pegs indicated severe attack on the quartz interferometer flats. After cooling to room temperature, the pegs were securely fused to both the upper and lower plates. The value of 450.8° C obtained for the melting temperature of the crystalline boric oxide, although in good agreement with the value of $450^\circ \pm 2^\circ$ C reported by Kracek, Morey, and Merwin [14], may be somewhat low because of the possible presence of water, fused B_2O_3 , or HBO_2 III as an impurity. That some impurity is present is indicated by a "bulge" in the expansion curve (fig. 4) for peg specimens which had been preheated well above 150° C to eliminate moisture. This bulge, which persisted after three passages through this temperature range, reached a maximum at 200° C. Furthermore, petrographic inspection by H. Insley of the original

sample revealed that not all of the specimen was in the crystalline state. Therefore, the curve in figure 4 must not be considered the true expansion curve for crystalline boric oxide. However, the melting point obtained is near that reported by Kracek, Morey, and Merwin,

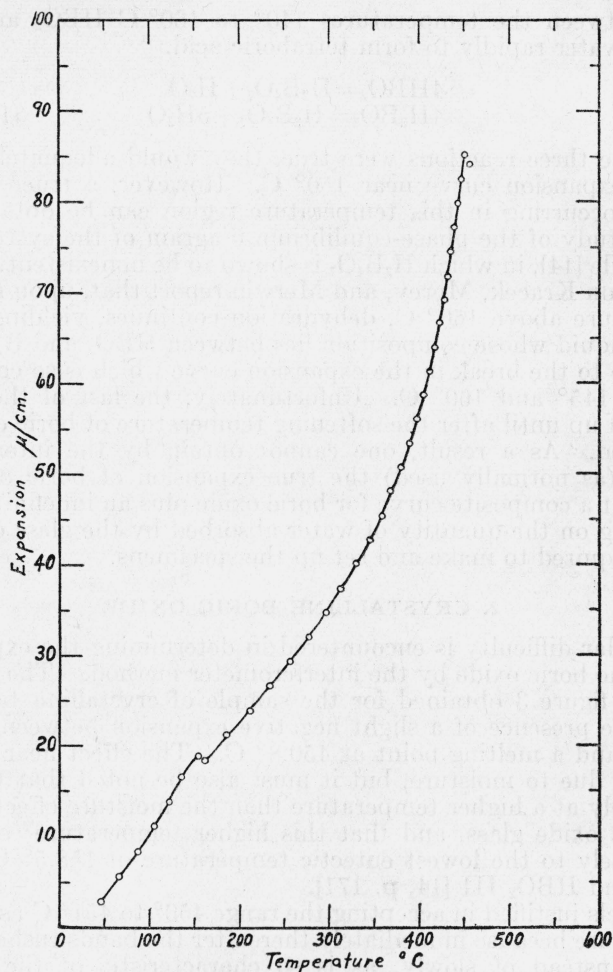


FIGURE 3.—Expansion curve for a sample of crystalline B_2O_3 , showing a small negative expansion between 155° and 161° C.

but appreciably lower than the lower limit of the range 460° to 470° C reported by L. McCulloch [3].

The melting point of the crystalline material prepared by Scholes is not to be associated with the temperature of 294° C reported for supposedly crystalline B_2O_3 by Cole and Taylor [15]. Disregarding all other possibilities, the value of 294° C, obtained with the differential thermocouple, can be adequately accounted for by the large heat absorption which must accompany the large volume change indicated by the long neck of the expansion curve of boric oxide glass (B, fig. 1). Since the region of maximum volume change should be the temperature of maximum heat absorption, the temperature obtained by the differ-

ential thermocouple should be that indicated by the first derivative of the expansion curve. Plotting $\Delta E/\Delta T$ of the data for figure 1 against T , one obtains a curve which has a complete reversal between 285° and 295° C, with a sudden decline beginning at 293° to 294° C (fig. 5).

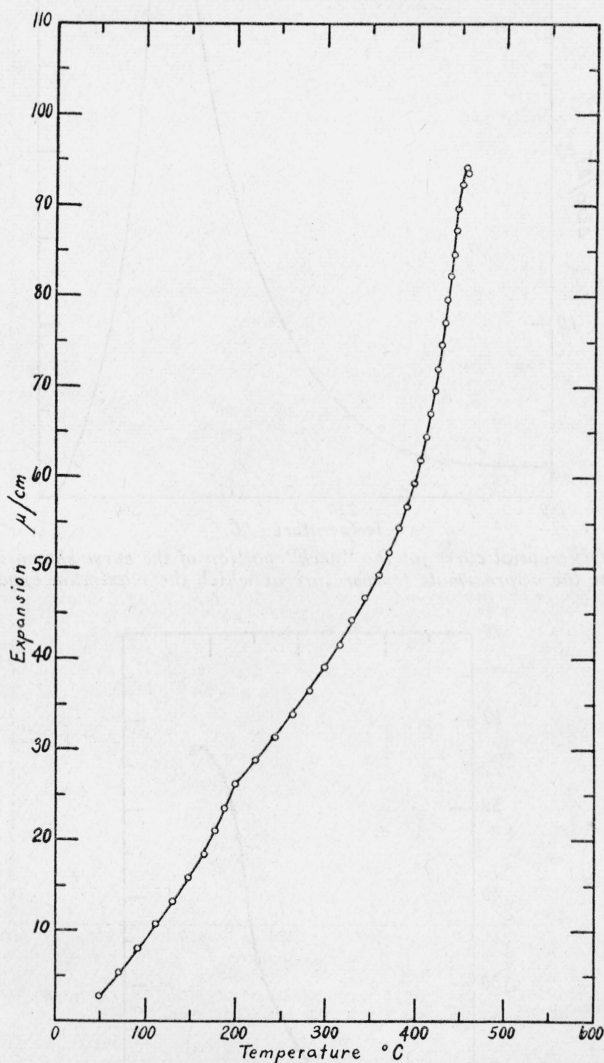


FIGURE 4.—Expansion curve for crystalline B_2O_3 after preheating above 150° C to remove moisture.

The "bulge" can probably be accredited to the presence of some noncrystalline B_2O_3 .

The correspondence is sufficiently close to leave little or no doubt that the temperature recorded by Cole and Taylor as the melting point of their supposedly crystalline boric oxide, and obtained by the differential thermocouple, is the region of the endothermic reaction accompanying the rapid expansion of fused boric oxide.

Another interesting observation is, that after crystalline boric oxide has once been heated to the melting point, additional deter-

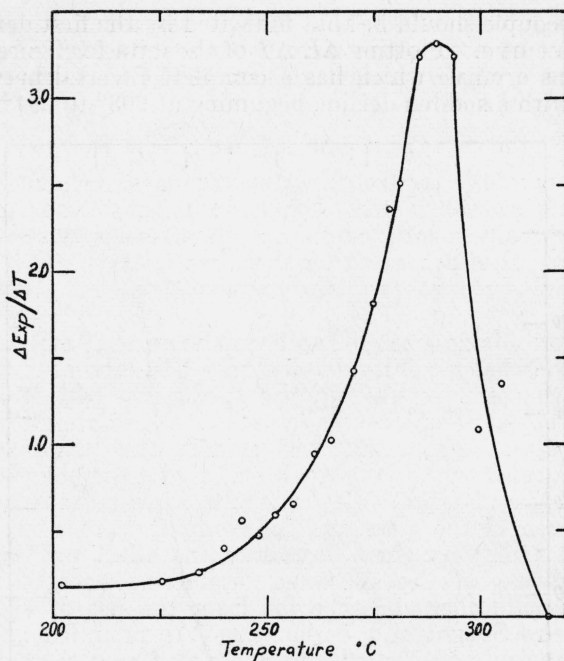


FIGURE 5.—Differential curve for the "neck" portion of the curve shown in figure 1, to determine the approximate temperature at which the maximum expansion rate occurs.

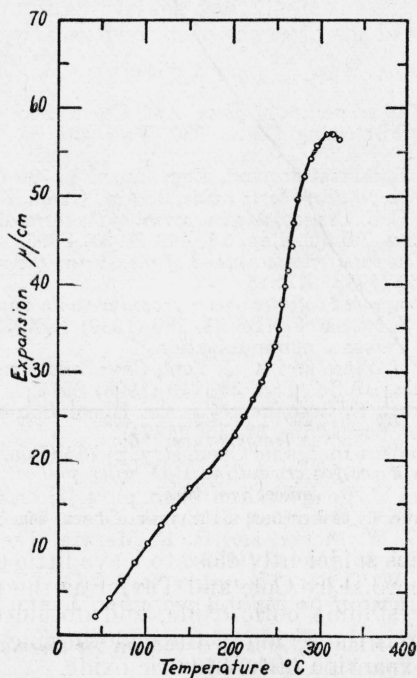


FIGURE 6.—Expansion curve obtained after specimens of crystalline B_2O_3 had been heated to the melting temperature.

minations of its expansion show that it has taken on some of the characteristics of boric oxide glass, with a softening temperature at 315° C and a critical temperature near 235° C. (Compare curve in fig. 6 with curve B of fig. 1.)

V. CONCLUSIONS

Although carefully controlled expansion measurements have been made by the interferometer method on a boric oxide glass and a sample of crystalline boric oxide, no quantitative values are offered for the coefficient of expansion for these materials, because the results indicate definitely that the true expansion curves have not been obtained.

For the boric oxide glass it has been shown that moisture vitiates the results and that moisture, having once been absorbed by the glass while preparing and setting up the specimens, cannot be entirely removed except at temperatures far above the softening point of the boric oxide glass. From this it is evident that the interferometer method as normally used is incapable of giving correct values for the expansion of this material. Better results could be expected by using a bar specimen of the glass and following the procedure of Souder and Hidnert [16]. By their procedure the effect produced by the surface condition of the specimen would be greatly minimized. Also, good results might be expected from the use of a liquid dilatometer of the Spaght and Parks type [17], provided one could be designed that could be heated and exhausted at a temperature near 1,000° C.

In the case of the crystalline boric oxide it is believed that the curves obtained represent significant deviations from those of the true expansions because of the presence of impurities as well as of moisture.

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