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Final Report  
on

STUDY OF IRON-BORATE MATERIALS SYSTEMS PROCESSED IN SPACE

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Owens-Illinois, Inc.  
Materials Research Section  
Toledo, Ohio

Prepared by

G. F. Neilson

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## Abstract

The purpose of this study is to explore the possibility of preparing transparent  $\text{FeBO}_3$  glass-ceramics in space. It is a continuation of a NASA project Contract No. NAS8-31381, DCN 1-5-58-00273(IF). The present study is largely limited to  $\text{Fe}_2\text{O}_3$ - $\text{B}_2\text{O}_3$  compositions containing from 1 to 10 mole %  $\text{Fe}_2\text{O}_3$ , although a few ternary compositions were also examined.

It was calculated that an  $\text{FeBO}_3$ - $\text{B}_2\text{O}_3$  glass-ceramic containing only 1 mole %  $\text{FeBO}_3$  would be equivalent for magneto optic application to a YIG crystal of equal thickness. An  $\text{Fe}_2\text{O}_3$ - $\text{B}_2\text{O}_3$  composition containing 2 mole %  $\text{FeBO}_3$  equivalent (98B) could be converted largely to a dense green, though opaque,  $\text{FeBO}_3$  glass-ceramic through suitable heat treatments. However, phase separation (and segregation) and  $\text{Fe}^{+3}$  reduction could not be entirely avoided with the various procedures that were employed. From light scattering calculations, it was estimated that the  $\text{FeBO}_3$  crystallite size in this 98B composition should be no greater than about 100 Å to allow 90% light transmission through a 1 cm thick sample. However, the actual  $\text{FeBO}_3$  crystallite sizes obtained in 98B were of the order of 1  $\mu\text{m}$  or greater.

It was concluded that further experiments with this system in an earth laboratory to attempt to prepare a transparent glass-ceramic will probably not be fruitful. However, a study of amorphous phase separation in this system under low g conditions may be of value.

## 1. Introduction

In a previous study<sup>1</sup> it was investigated whether it might be possible to prepare useful transparent  $\text{FeBO}_3$  glass-ceramics in space (or on earth). It was envisioned that the desired composition might be prepared initially as a glass, with  $\text{FeBO}_3$  crystallites of suitable size and concentration being formed subsequently by a secondary heat treatment. Based upon glass structural considerations, this study was limited mostly to binary compositions containing from 50 to 90 mole %  $\text{B}_2\text{O}_3$  and the remainder  $\text{Fe}_2\text{O}_3$ . A transparent glass-ceramic material in this composition range could not be prepared, and several problem areas which could prevent being able to prepare them in space were identified. First, phase separation into an iron-rich phase containing roughly 50 mole %  $\text{Fe}_2\text{O}_3$  and an iron-poor phase containing mostly  $\text{B}_2\text{O}_3$  always occurred. Because of the much greater density of the iron-rich phase, its rapid segregation to the bottom of the crucible or mold during cooling or pouring presented tremendous problems and did not allow study of the nature of the separation process itself. Second,  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$  reduction occurred during melting which caused the formed glass or glass-ceramic product to be nonuniform and black. This reduction process could not be adequately suppressed by variation of melting temperature. Clearly, some method to prevent it must be found in order to make space processing feasible. Finally, this study established that the temperature of the secondary heat treatment to promote crystallite formation must not be higher than about  $800^\circ\text{C}$  in order to prevent the formation of a high temperature  $\text{Fe}_3\text{BO}_6$  phase and other unwanted phases.

In the present continuing study it was determined that an  $\text{Fe}_2\text{O}_3\text{-B}_2\text{O}_3$  glass-ceramic containing as little as 0.9 mole %  $\text{FeBO}_3$  would be equivalent to YIG for magneto optic application. Therefore, the present study was limited largely to compositions containing from 1 to 10 mole %  $\text{Fe}_2\text{O}_3$ . It was thought that within this composition range, it should be easier to establish the conditions for minimizing phase separation and  $\text{Fe}^{+3}$  reduction. During this study attempts were also made to reduce the  $\text{FeBO}_3$  crystallite size and/or reduce the refractive index difference between crystallite and matrix by the addition of third components, in order to obtain a transparent glass-ceramic material. It would be very significant if the ability to prepare such a material could be demonstrated, since not only would this establish the criteria regarding required microstructure, but it could also indicate the feasibility of determining suitable conditions for preparation of a useful material on earth as well. In an attempt to achieve this goal and to obtain a uniform material uncontaminated with unwanted phases, a novel approach involving the sintering of  $\text{B}_2\text{O}_3$  with  $\text{FeBO}_3$  crystallites was also unsuccessfully tried. Finally, an evaluation was made of the effectiveness of adding  $\text{TiO}_2$  and  $\text{ZrO}_2$  as nucleating agents for reducing the mean  $\text{FeBO}_3$  crystallite size.

The  $\text{FeBO}$  glass-ceramic compositions discussed in this report will be identified by a code such as 83.3B-2, as in the previous study.<sup>1</sup> The prefix indicates the mole % of  $\text{B}_2\text{O}_3$  (i.e., 83.3B =  $\text{Fe}_2\text{O}_3 \cdot 5\text{B}_2\text{O}_3$ ), and the suffix is the number of the batch prepared if other than the first.

## 2. Minimum iron content needed for magneto optic application

The utility of a magneto optic device is determined by its figure of merit,  $2F/\alpha$ , where  $F$  is the Faraday rotation per unit sample length and  $\alpha$  is the absorption coefficient value at maximum absorption in the visible. The current material used for the magneto optic devices is YIG, for which  $2F/\alpha$  is  $3.2^\circ$ . For the 83.3B and 99.1B  $\text{Fe}_2\text{O}_3$ - $\text{B}_2\text{O}_3$  compositions, the calculated values of  $2F/\alpha$  are  $52^\circ$  and  $3.2^\circ$ , respectively. These values were arrived at by assuming that (a) all the  $\text{Fe}_2\text{O}_3$  content is completely converted to  $\text{FeBO}_3$ , (b) the Faraday rotation is proportional to the amount of  $\text{FeBO}_3$  produced, and (c) the absorption coefficient of the  $\text{FeBO}_3$  is not affected by the  $\text{B}_2\text{O}_3$  matrix. Also these values do not consider scattering losses, as this will be considered in detail in a later section.

However, these calculations do suggest that compositions in the 99B to 90B range may have equal to superior magneto optic capability than YIG. Thus, the present study will concentrate on this composition range, based upon the following advantages: (a) the glass-forming tendency will be increased, since these compositions are located between 83.3B (chain) and 100B (sheet or framework), and (b) the phase separation tendency will be decreased, due to the reduction of iron content.

### 3. Phase separation behavior

#### 3.1. Glass-forming ability

Three compositions; namely, 94B, 98B, and 99.8B, were prepared. They were melted for 2 hrs. and then air quenched to room temperature. The melts were knocked out of the crucibles and examined for the phase separation as indicated in Table 1. These three compositions were found to have less pronounced phase separation than those compositions of higher iron such as 90B which always showed clear demarcation between iron-rich and iron-poor portions. Although a phase separation does exist at the 94B composition, no clear demarcation was found between the two different iron portions. Instead, the iron-rich portion is dispersed through the whole melt, but it tends to gather more at the bottom than the top. A similar situation was found with 98B except that the concentration of the iron-rich portion was much less. At 99.8B, the phase separation is too small to detect by visual examination. However, it should be noted that the 99.8B has a lower iron content than that of the 99.1B which was estimated to have the minimum iron content needed for magneto-optic application.

Since transparency is essential for the magneto-optical application, the above compositions were tested for this property. Each was first melted, after which up to four plates were cast by splat cooling. The melting and transparency data for these melts are listed in Table 2. All the cast splat plates are opaque except one made from 99.8B. Even this one is only translucent. In addition, not all the splat plates from the same melt (1300°C - 2 hrs.) are translucent and in fact the fourth plate is almost opaque. Furthermore, the splat plates prepared from the same

composition of 99.8B but melted at 1100°C for 2 hrs. are opaque. This could suggest an extreme sensitivity of the crystallization processes to small variations in the rate of quenching, but it might also indicate a difference in homogeneity of the melts attained at the two temperatures.

The first splat plates cast from the above compositions were analyzed for iron content and the phase assemblage. These plates were later heat treated at 700°C for 3 days. The crystallized phase assemblage has also been determined. All the results are listed in Table 3. Phase separation is found to persist at an iron content as low as that in 98B. Prior to the heat treatment at 700°C, all the plates contain crystalline  $B_2O_3$  in addition to glass. Also, the untreated plate of 99.8B prepared at 1300°C for 2.5 hrs. was noted to have less crystalline  $B_2O_3$  (thus less scattering) than the plate of the same composition but melted at 1100°C for 2 hrs. This difference in crystalline  $B_2O_3$  may partially explain why the former is more transparent than the latter. Upon crystallization at the temperature of 700°C, the splat plate produced an  $FeBO_2$  phase together with  $B_2O_3$ , residual glass, and sometimes  $Fe_2BO_6$  as indicated in Table 3.

### 3.2. Nature of phase separation process and effect on crystallization

The nature of phase separation was studied by melting a 90B composition at 1300°C for 2, 4, 8, 16, and 32 minutes. The five different melts were then carefully examined for phase separation. The results are listed in Table 4. Based upon this study, it appears that phase separation proceeds as follows. Upon heating,  $B_2O_3$  (the low melting component) melts first and bubbles through the melt. Then,  $B_2O_3$  reacts with  $Fe_2O_3$  to form a uniform and dense material. Finally, the iron-rich portion of the melt originally



distributed uniformly throughout the melt, segregates to form a dense layer at the bottom.

The effect of phase separation on crystallization was studied by heat treating at 700°C for 3 days selected samples melted for the above times. These heat-treated melts were analyzed by x-ray diffraction, and the phase assemblages are listed in Table 5. The degree of phase separation has a great influence on the amount of iron borate formed. Production of iron borate ( $\text{FeBO}_3$ ), which is the ferromagnetic phase, is the main goal of this study. The maximum amount of  $\text{FeBO}_3$  was formed on the 4 minute melt, which had no phase separation. Once the phase separation starts, a portion of the iron remains as  $\text{Fe}_2\text{O}_3$  during heat treatment. This in turn reduces the amount of  $\text{FeBO}_3$  formed.

### 3.3. Temperature dependence of phase separation in an 80B composition

It was noticed that as the melting temperature increases the difference in iron content between the iron-poor and the iron-rich layers decreases. It is estimated by ways of extrapolation that a melting temperature of 1850°C will be needed to completely eliminate the phase separation, as shown in Figure 1. It is of interest that the final estimated iron content (32.5%) at the critical temperature agrees very well with that analyzed for the batch material (33%). However, this approach of eliminating phase separation has three drawbacks; namely, (a) the temperature is too high and is thus beyond the temperature capability of most furnaces, (b) the loss of  $\text{B}_2\text{O}_3$  through evaporation during melting will be very large, and (c) almost all of the iron will reduce to  $\text{Fe}^{2+}$  and will thus make the cast melt very black and nontransparent.

#### 4. Effect of oxygen and melting temperature on Fe<sup>+3</sup> reduction

An ADL furnace (the crystal growing furnace designed by Arthur D. Little, Model MP) was used to test the effect of oxygen on iron reduction. The temperature measuring system for the furnace was a calibrated optical pyrometer. Three batches of composition 90B-2 were melted. One batch was melted at 1300°C for 2 hrs in a pure oxygen atmosphere. The other two batches were melted at 1250°C for 2 hrs., one in pure oxygen and the other in air. These three melts were chemically analyzed for Fe<sup>+2</sup> and Fe<sup>+3</sup> content. The results are listed in Table 6. These data indicate that a pure oxygen atmosphere results in only 27% less iron reduction than with air at a pyrometric temperature of 1250°C

## 5. Heat treatment of batch materials

### 5.1. Reaction of $B_2O_3$ and $Fe_2O_3$

The 94B, 98B, and 99.8 compositions were heat treated at temperatures below the liquidus to determine the nature of the low-temperature phase transformations. To determine if they could crystallize into the  $FeBO_3$  phase without change of shape or melting, the following tests were performed. First, the pelletized batch materials were heat treated at temperatures from  $460^\circ C$  (m.p. of  $B_2O_3$ ) through  $700^\circ C$  (crystallization temperature of 50B). Then, the heat-treated materials were analyzed by x-ray diffraction. The results are listed in Table 7. Almost all pelletized batch materials changed shape when heat treated at  $460^\circ C$  or higher. The lowest temperature for  $FeBO_3$  to crystallize was observed to be  $550^\circ C$ . However, a temperature of about  $700^\circ C$  was needed to crystallize most iron in the material to the  $FeBO_3$  phase. This is not surprising since, as shown in our earlier study,<sup>1</sup> no solid solution can be formed from  $FeBO_3$ .

### 5.2. Reaction of $B_2O_3$ and $FeBO_3$

Another approach of trying to prepare a transparent  $FeBO_3$  glass-ceramic was made based upon the following reasoning.  $B_2O_3$  has a very low melting point of  $460^\circ C$  and can easily be made into a transparent glass. In addition,  $FeBO_3$  crystals can persist up to a temperature of  $800^\circ C$  before transformation or decomposition. Therefore, if  $B_2O_3$  is batched with  $FeBO_3$  crystals instead of  $Fe_2O_3$  and if the mixture of  $B_2O_3$  and  $FeBO_3$  can be melted at  $800^\circ C$  or below,  $B_2O_3$  will melt while  $FeBO_3$  may likely remain intact. The  $FeBO_3$  glass-ceramic thus produced should be transparent, provided (a) a suitable amount of  $FeBO_3$  crystals are used so that the mixture will

melt at 800°C or below, (b) there is no phase segregation between  $\text{FeBO}_3$  and  $\text{B}_2\text{O}_3$ , and very little of the  $\text{FeBO}_3$  will dissolve into the  $\text{B}_2\text{O}_3$  solution, and (c) the  $\text{FeBO}_3$  crystals dispersed through the  $\text{B}_2\text{O}_3$  substrate have a particle size much smaller than the wavelength of light.

A 99.8B composition was prepared by this approach. The cast splat plate was opaque probably because the starting raw material of  $\text{FeBO}_3$  crystals was ground only to a size exceeding 100  $\mu\text{m}$  (200 mesh). However, this material when melted at 800°C for half an hour preserved only about half of the original  $\text{FeBO}_3$ , as shown in Table 8. This indicates that this approach is ineffective for obtaining the maximum  $\text{FeBO}_3$  phase. On the other hand, a 99.8B composition prepared by  $\text{B}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  can produce the maximum amount of  $\text{FeBO}_3$  phase via a short melting and a subsequent heat treatment, as also shown in Table 8. The latter approach will be discussed in detail in the next section.

## 6. Preparation of $\text{FeBO}_3$ glass-ceramics through employment of short heat treatment times

In the experiments to be described next, the object was to investigate the possibility of preparing a transparent, or at least translucent, glass-ceramic material containing  $\text{FeBO}_3$  crystallites by reducing the mean crystallite size, the segregated phase separation, and the  $\text{Fe}^{+3}$  reduction process.

The approach involves a short melting at a relatively low temperature of  $\text{B}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$  composition, followed by a subsequent heat treatment of the hot melt at a lower temperature for the growth of the  $\text{FeBO}_3$  crystals. It was thought that this procedure should avoid the problem of partial or total melting experienced during the heating of the splat plates, and should minimize the phase separation problem experienced during long time melting. Thus, the glass-ceramic is expected to have the same composition as the starting material. Both 94B and 98B compositions were prepared by this approach. They were melted at  $1300^\circ\text{C}$  for 5, 15, and 30 minutes and followed by heat treatment at  $700^\circ\text{C}$  for 69 hrs. or 5.5 days, as shown in Table 9. The glass-ceramic material prepared from 98B which was melted at  $1300^\circ\text{C}$  for 15 minutes and heat treated at  $700^\circ\text{C}$  for 5 days represents the best  $\text{FeBO}_3$  glass-ceramic so far obtained. This material is green and dense but opaque. However, most of the iron was crystallized as  $\text{FeBO}_3$  and very little phase separation was noticed. The material was very uniform throughout and no surface crystallization was noticed as indicated in Table 9 (except that the top surface had a very thin  $\text{B}_2\text{O}_3$  rich layer).

Thus the question of greatest concern is whether a transparent or translucent material can be prepared. Therefore, efforts were made to

optimize the composition and to some degree the melting temperature and time in order to control or reduce the crystal size. Three different compositions, 90B, 94B and 98B, were melted at 1300°C for different short periods of time followed by a heat treatment at 700°C, as shown in Table 10. The 98B seems to be the best composition based upon the following observed advantages:

- (a) It achieves a complete melting and thus can produce a dense material.
- (b) There is little or no phase separation so that a uniform composition can be assured.
- (c)  $\text{FeBO}_3$  is the predominant phase and there is no other Fe-phases such as  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{BO}_6$ , and  $\text{Fe}^{2+}$  compounds.

A melting temperature of 1300°C was used to test and compare the three different compositions. Since the 98B was found to be the best composition, as indicated above, the effect of melting temperature on 98B glass-ceramic formation was examined as follows. The melting temperature was reduced from 1300 to 1200°C while other melting and heat treating conditions were kept the same, as shown also in Table 10. At 1200°C the melting was found to be incomplete and the melt product was porous. In addition, much of the  $\text{Fe}_2\text{O}_3$  was left unreacted. Thus, the optimum melting temperature may be somewhere between 1200 and 1300°C.

Scanning electron microscopy (SEM) was used to determine the  $\text{FeBO}_3$  crystal sizes for the above 98B compositions which were melted at 1300°C for 5 through 15 minutes (Table 10). The 5 minute melt produced a crystal size of 4 to 5  $\mu\text{m}$ , and voids were in evidence. For the 10 and 15 minute melts, the crystal sizes were found to be about 1  $\mu\text{m}$ , although

fewer crystals were formed than with the 5 minute melt. Thus the optimum melting conditions to produce the maximum number of crystals of smallest size would appear to be near a 1300°C melting temperature for a time somewhere between 5 and 15 minutes.

Next an attempt was made to optimize the heat treatment (crystallization) time which was often run for 5 days at 700°C. Two 98B compositions were melted at 1300°C for 10 minutes, followed by heat treatment at 700°C for 5 and 24 hrs., respectively. The 24 hr. heat treatment showed green color while the 5 hr. one had very little green color. This indicates that the former has produced more  $\text{FeBO}_3$  than the latter, as shown in Table 11. However, the amount of  $\text{FeBO}_3$  produced by the one-day heat treatment is smaller than that of the five-day heat treatment run previously at the same temperature of 700°C. The  $\text{FeBO}_3$  crystal size is 7  $\mu$  for 24 hrs. treatment, but only 3.5  $\mu$  for 5 hrs. treatment. It is noted that although the 24 hrs. or longer heat treatment in general produces the desired phase assemblage of  $\text{FeBO}_3$  plus glass or  $\text{B}_2\text{O}_3$ , the 5 hrs. heat treatment produces many additional unwanted phases such as  $\text{FeO}\cdot\text{B}_2\text{O}_3$ ,  $\text{Fe}_2\text{FeBO}_5$ , and  $\text{Fe}_2\text{O}_3$ .

It would appear from the above results that the extraneous crystal phases from either during the melting process or during the cooling to the  $\text{FeBO}_3$  crystallization temperature. To confirm that these processes do not occur during the latter heat treatment, part of the material given the 5 hr. heat treatment (Table 11) was heat treated for an additional five days at 700°C. All of the extraneous phases did indeed convert to the desired  $\text{FeBO}_3$  phase during this heat treatment, as is also indicated in Table 11. This result suggests that it may be possible to eliminate the  $\text{Fe}^{+2}$  that causes the glass-ceramic to be black by a suitable crystallization heat treatment. It also indicates that the opaqueness of the green

FeBO<sub>3</sub> glass-ceramic is probably due to internal scattering by the FeBO<sub>3</sub> crystallites.

In an effort to reduce the FeBO<sub>3</sub> particle size to obtain a more transparent material, the above melting and crystallization heating conditions were altered, as indicated in the bottom two rows of Table 11. The SEM photos of the smaller crucible amount (1/8 full) in Table 11 showed a high concentration (greater than 10%) of particles having diameters in excess of about 3 μm, with the appearance of a sintered material. However, this and the other sample appeared to undergo complete melting, and the final products appeared to be dense and non-porous, though they were all opaque. These conditions did produce the highest concentration of FeBO<sub>3</sub>, as indicated in the table. It should be noted that the black layer which has been attributed to Fe<sup>+2</sup> phases appeared to have formed at the melt-crucible interface, which suggests that these reactions may not occur under containerless conditions.



## 7. Preparation of FeBO<sub>3</sub> glass-ceramics containing third components

### 7.1. Effect of TiO<sub>2</sub> and ZrO<sub>2</sub>

It will be shown in the following section that the lack of transparency of the green 98B glass-ceramics discussed previously is probably due to the large FeBO<sub>3</sub> crystallite size and/or the large refractive index difference between the FeBO<sub>3</sub> crystallites and the B<sub>2</sub>O<sub>3</sub> matrix. Thus TiO<sub>2</sub> or ZrO<sub>2</sub> was added to several B<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> compositions in an attempt to improve the transparency after conversion to the glass-ceramics. Since TiO<sub>2</sub> and ZrO<sub>2</sub> have much higher refractive indices than B<sub>2</sub>O<sub>3</sub>, they will increase the refractive index of the matrix, and thus decrease the refractive index difference, if they remain dissolved. Also they might act as nucleating agents and promote the formation of a larger number of FeBO<sub>3</sub> crystallites of smaller size.

Thus 0.5, 2, and 4 weight % of either TiO<sub>2</sub> or ZrO<sub>2</sub> were added to the 98B composition, after which they were given the respective melting and crystallization heat treatments indicated in Table 12. In addition, 12.2% wt.% TiO<sub>2</sub> was added to the 60B composition, and the batch given a similar heat treatment schedule. The phase assemblages of these seven materials were analyzed by x-ray diffraction, and the results are also shown in Table 12. With the exception of the material containing 0.5% ZrO<sub>2</sub>, crystalline phases containing Ti or Zr always were present after the heat treatment. This suggests that they are ineffective in increasing the refractive index of the matrix. In addition, the amount of FeBO<sub>3</sub> crystallized was found to decrease with increasing amount of nucleating agent in the 98B composition, indicating that they are also ineffective in this capacity. Finally, the

ZrO<sub>2</sub> and TiO<sub>2</sub> imparted pronounced color to the heat-treated products.

SEM photographs of the sample containing 0.5% ZrO<sub>2</sub> showed a much greater number density of particles having less than one-half of the mean size of the particles seen in the other samples. These smaller particles are probably B<sub>2</sub>O<sub>3</sub> crystallites, as evidenced by the higher concentration in the diffraction pattern for this material as indicated in the table. Since no ZrO<sub>2</sub> phase was detected in this material, it is possible that it reacts with the B<sub>2</sub>O<sub>3</sub> to form the phase observed. However, there was no indication that ZrO<sub>2</sub> or TiO<sub>2</sub> may be beneficial to transparency in any of the materials prepared.

### 7.2. Effect of BaO

In still another effort to produce transparent FeBO<sub>3</sub> glass-ceramic, the approach of adding another third component to the binary compound of Fe<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> was considered. It was reported that a ferromagnetic material could be obtained by adding Ba (40BaO·20Fe<sub>2</sub>O<sub>3</sub>·40B<sub>2</sub>O<sub>3</sub>, Russian Patent 550,352 from 1977) to Fe<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>. The Russian claimed that (a) a lowered Fe<sub>2</sub>O<sub>3</sub> content from 30% to 20% mole would reduce crystallization so that amorphous material could be obtained by quenching melt in water, and (b) the use of Ba(NO<sub>3</sub>)<sub>2</sub> rather than BaO would help to prevent the formation of Fe<sup>2+</sup>. A comparison between the Ba-compound and the basic binary composition of B<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> is shown as follows:

|   | <u>33Fe<sub>2</sub>O<sub>3</sub>·67B<sub>2</sub>O<sub>3</sub></u> | <u>40BaO·20Fe<sub>2</sub>O<sub>3</sub>·40B<sub>2</sub>O<sub>3</sub></u> |
|---|---|---|
| Melting temp., °C                                   | 1300  | 1250-1300   |
| Crystallization temp., °C                           | 700   | 680-800   |
| Phase   | FeBO <sub>3</sub>   | Ba-hexaferrite  |
| Specific magnetization,<br>Gauss-cm <sup>3</sup> /g | 26.7  | 13-62   |

In order to check the effect of Ba on glass-ceramic formation, two Ba-containing compositions cited in the Russian patent were prepared, as shown in Table 13. The materials were melted at 1300°C for 2 hrs. and then cast by splat cooling. All the cast plates were found to be amorphous but also black, as shown in Table 14. Upon crystallization at 700°C for 2 days, the phase assemblages contain  $BaO \cdot B_2O_3$  and  $BaO \cdot 6Fe_2O_3$ , but no  $FeBO_3$  phase is present. Therefore, incorporation of 40 mol % Ba does not improve the possibility of producing a transparent glass-ceramic.

### 8. Effect of internal scattering on transparency

We shall consider an  $\text{FeBO}_3$  glass-ceramic in which small  $\text{FeBO}_3$  crystallites are randomly and uniformly distributed within a matrix of pure  $\text{B}_2\text{O}_3$  glass. Differences in physical properties between  $\text{FeBO}_3$  and  $\text{B}_2\text{O}_3$  are indicated below.

|                     | <u><math>\text{FeBO}_3</math></u> | <u><math>\text{B}_2\text{O}_3</math></u> |         |
|---------------------|-----------------------------------|--|---------|
| Form                | Crystal                           | Glass                                    | Crystal |
| Index of Refraction | 2.10                              | 1.49                                     | 1.63    |
| Density, g/cc       | 4.30                              | 1.81                                     | 2.46    |
| M.P. °C             | 800 (transformation)              | 450                                      | 460     |

Due to the large difference in refractive index between  $\text{FeBO}_3$  and  $\text{B}_2\text{O}_3$ , internal scattering poses a serious problem, which may greatly decrease the transparency of an  $\text{FeBO}_3$  glass-ceramic material. The extent of the effect of scattering on transparency was evaluated by a method outlined by Van De Hulst.<sup>2</sup> The method employed is applicable to the Mie scattering region, and, therefore, the results obtained from it should be at least approximately valid for the index difference of concern here. Following Van De Hulst, we employ the equation

$$I/I_0 = \exp(-\gamma \ell) ,$$

for the fraction of light transmitted, where  $\ell$  is the sample thickness and  $\gamma$  is the extinction coefficient defined by

$$\gamma = N\pi(d/2)^2 Q_{\text{ext}} ,$$

where  $N$  is the number of particles per cubic micron,  $d$  is the particle

diameter in microns, and  $Q_{\text{ext}}$  is defined by

$$Q_{\text{ext}} = Q_{\text{abs}} + Q_{\text{scat}} .$$

Assuming no absorption,  $Q_{\text{abs}} = 0$ , whence

$$Q_{\text{ext}} = x^2 \left( \frac{8}{3} \right) \left( \frac{m^2 - 1}{m^2 + 2} \right)^2 ,$$

where  $x = \pi d/\lambda$  with  $\lambda$  being the wavelength of the light, and  $m = n_1/n_2$  is the reduced index with  $n_1$  being the refractive index of the particle and  $n_2$  that of the matrix.

The number of  $\text{FeBO}_3$  crystalline particles per unit volume of glass-ceramic at size 1/10 and 1/100  $\mu$  was estimated for various compositions from 99.8B through 50B, as shown in Table 15. The effect of scattering on transparency of  $\text{FeBO}_3$  glass-ceramic was then evaluated and the results are listed in Tables 16 and 17. For  $n = 2.10/1.49 = 1.41$  of present concern, only 98B or those compositions of lower iron content could be transparent ( $I/I_0 = 0.916$ ) at a sample thickness of  $10^4 \mu$  (1 cm) and a particle size of 1/100  $\mu$ . Thus for a 1 cm thick sample of the 98B glass-ceramic material in which all of the  $\text{Fe}_2\text{O}_3$  has been converted to  $\text{FeBO}_3$ , a spherical crystallite diameter of 100  $\text{\AA}$  would be required to insure 90% light transmission according to these calculations.

From Table 16 it may be noted also that as the  $\text{Fe}_2\text{O}_3$  content increases above the 98B concentration, the light transmission rapidly decreases, with the sample being essentially opaque ( $I/I_0 = 0.04$ ) for the 50B composition even with a crystallite size of 100  $\text{\AA}$ . As would be anticipated, the calculated transmission also decreases with increasing particle size and sample thickness, as indicated in Table 17. It may be noted that if  $n$  can

be made smaller than 1:41 by adding a third component of high index so as to increase the  $n_2$  of the matrix, then the allowable crystallite size can be much larger than 100 Å and/or the  $\text{FeBO}_3$  concentration can be greater than in the 98B composition.

## 9. Conclusions

(1) An  $\text{Fe}_2\text{O}_3\text{-B}_2\text{O}_3$  glass-ceramic containing only 1 mole %  $\text{FeBO}_3$  could be equivalent to pure single crystal YIG for magneto optic application.

(2) Phase separation during melting cannot be avoided in  $\text{Fe}_2\text{O}_3\text{-B}_2\text{O}_3$  compositions containing as little as 2 mole %  $\text{FeBO}_3$  under earth conditions.

(3) Useful transparent  $\text{FeBO}_3$  glass-ceramics cannot be prepared on earth due to (a)  $\text{Fe}^{+3}$  reduction, (b) phase separation and segregation, and (c) formation of large crystallites of  $\text{FeBO}_3$  and other species which cause prohibitively high internal scattering.

(4) The  $\text{Fe}^{+3}$  reduction during melting in a platinum crucible cannot be adequately suppressed through control of atmosphere. However, it might be possible to reconvert the  $\text{Fe}^{+2}$  compounds to  $\text{FeBO}_3$  by a suitable crystallization heat treatment in the vicinity of  $700^\circ\text{C}$ .

(5) No evidence was found that  $\text{TiO}_2$  or  $\text{ZrO}_2$  might be beneficial to the transparency of an  $\text{FeBO}_3$  glass-ceramic, either by serving as a useful nucleating agent or by increasing the refractive index of the matrix.

(6) Incorporation of 40 mole %  $\text{BaO}$  to the 67B composition is not beneficial for producing an  $\text{FeBO}_3$  glass-ceramic.

(7) Based upon light scattering calculations, it is estimated that the  $\text{FeBO}_3$  crystallite size cannot exceed about  $100 \text{ \AA}$  in the 98B composition in order to allow a light transmission of at least 90%.

## 10. Recommendations

(1) It does not appear warranted to conduct further experiments on earth to attempt to prepare a transparent material, since it is unlikely that phase separation and segregation can be avoided and that sufficiently small  $\text{FeBO}_3$  crystallite size can be achieved.

(2) Further studies to determine the nature of the  $\text{Fe}^{+3}$  reduction mechanism are needed. In particular, it should be determined if this process occurs exclusively at the container walls.

(3) It does not appear likely that an  $\text{FeBO}_3$  crystallite size as small as would be required for a useful transparent glass-ceramic (approximately 100 Å) can be obtained by direct crystallite nucleation and growth. However, it is possible that the desired crystalline microstructure could be obtained through an initial amorphous phase separation process in which one of the amorphous phases has approximately the  $\text{FeBO}_3$  composition, as is the case found for the  $\text{Fe}_2\text{O}_3$ - $\text{B}_2\text{O}_3$  system. Thus, if segregation of phases can be avoided in space, it is possible that a composition range can be found where spinodal decomposition occurs at the obtainable cooling rates. Without the segregation of the high density phase that always occurs under 1 g conditions, this could lead to an interconnected microstructure on about the scale required for transparency. Crystallization of the iron-rich phase would then be a secondary process occurring at a lower temperature. Thus, it is recommended that a study of the amorphous phase separation process in this system be made under containerless and low g conditions, with particular attention given to the variation of microstructure with composition, temperature and cooling rate.



## References

1. C. T. Li, "Processing FeBO<sub>3</sub> Glass-Ceramics in Space," Contract NAS8-31381, DCN 1-5-58-00273(IF), (NASA, Marshall Space Flight Center, Alabama, October 15, 1976) Annual Report.
2. H. C. Van De Hulst, "Light Scattering by Small Particles," (John Wiley and Sons, New York, 1957).

Table 1

Melts Prepared for Phase Separation Examination

| Ident.<br>Code | wt. %*                            |                                    | Melting<br>°C-Hr. | Melting <sup>+</sup><br>Loss<br>% | <u>Melts (air quench)</u>                                   |  |
|----------------|-----------------------------------|------------------------------------|-------------------|-----------------------------------|---|--|
|                | <u>B<sub>2</sub>O<sub>3</sub></u> | <u>Fe<sub>2</sub>O<sub>3</sub></u> |                   |                                   | <u>Evidence<br/>B<sub>2</sub>O<sub>3</sub><br/>Bubbling</u> | <u>Phase Separation</u>  |
| 94B            | 87.06                             | 12.94                              | 1100-2            | 1.2                               | Yes   | Yes, no clear demarcation iron-rich phase dispersed through bulk, but more at bottom than top. |
| 98B            | 95.46                             | 4.54                               | 1100-2            | 1.4                               | No  | Yes, similar to 94B but much less iron-rich phase.   |
| 99.8B          | 99.54                             | 0.46                               | 1000-2            | 3.2                               | No  | No, almost identical appearance throughout the whole melt.                                     |

+With lid.

\*Based upon the raw materials of 99.5% B<sub>2</sub>O<sub>3</sub> and 98% Fe<sub>2</sub>O<sub>3</sub>.

Table 2

A Summary of Cast Splat Plates

| <u>Composition Code</u> | <u>Melting Condition</u> |               |               | <u>Fe<sub>2</sub>O<sub>3</sub> % (Target)</u> | <u>Cast Plates</u> |                       |
|-------------------------|--------------------------|---------------|---------------|---|--------------------|-----------------------|
|                         | <u>T, °C</u>             | <u>t, hr.</u> | <u>Loss %</u> |   | <u>Cast No.</u>    | <u>Appearance</u>     |
| 94B                     | 1300                     | 3             |               | 12.94   | 1st<br>3rd         | Opaque<br>"           |
| 98B                     | 1300                     | 3             | 1.5           | 4.54  | 1st<br>4th         | Opaque                |
| 99.8B                   | 1300                     | 2.5           | 3.2           | 0.46  | 1st<br>4th         | Translucent<br>Opaque |
| 99.8B                   | 1100                     | 2             | 2.2           | 0.46  | 1st<br>3rd         | Opaque<br>"           |

Table 3

Characterization of The First Splat Plates

| Composition | Melting Condition<br>°C - Hrs. | Fe <sub>2</sub> O <sub>3</sub> % |          | Phase Assemblage     |  |
|-------------|--------------------------------|----------------------------------|----------|----------------------|--|
|             |                                | Target                           | Analysis | Heat Treatment       | Phase in Decreasing Order  |
| 94B         | 1300 - 3                       | 12.94                            | 4.3      | --<br>700°C - 3 days | B <sub>2</sub> O <sub>3</sub> , glass<br>B <sub>2</sub> O <sub>3</sub> , FeBO <sub>3</sub> , Fe <sub>3</sub> BO <sub>6</sub> , glass |
| 98B         | 1300 - 3                       | 4.54                             | 3.1      | --<br>700°C - 3 days | B <sub>2</sub> O <sub>3</sub> , glass<br>FeBO <sub>3</sub> , B <sub>2</sub> O <sub>3</sub> , Fe <sub>3</sub> BO <sub>6</sub> , glass |
| 99.8B       | 1300 - 2.5                     | 0.46                             | 1.8*     | --<br>700°C - 3 days | B <sub>2</sub> O <sub>3</sub> , glass<br>FeBO <sub>2</sub> , B <sub>2</sub> O <sub>3</sub> , glass                                   |
| 99.8B       | 1100 - 2                       | 0.46                             | 1.5*     | --<br>700°C - 3 days | B <sub>2</sub> O <sub>3</sub> , glass<br>FeBO <sub>3</sub> , B <sub>2</sub> O <sub>3</sub> , glass                                   |

\*Difficulties were encountered in the determination of the low iron content.

Table 4

Results of Phase Separation Study

| <u>Composition</u> | <u>Melting<br/>Condition<br/>°C - Min.</u> | <u>Phase<br/>Separation</u> | <u>Appearance of Melt<br/>(after cooling)</u>   |
|--------------------|--|-----------------------------|---|
| 90B                | 1300 - 2                                   | No                          | Honeycomb structures  |
| 90B                | 1300 - 4                                   | No                          | Honeycomb structure, but top surface<br>has started to condense   |
| 90B                | 1300 - 8                                   | Start                       | Melt very dense with very few cavities,<br>iron-rich phase appears but dispersed<br>throughout the whole melt |
| 90B                | 1300 - 16                                  | Complete                    | Iron-rich layer at bottom   |
| 90B                | 1300 - 32                                  | Complete                    | Iron-rich layer at bottom   |

Table 5

Effect of Phase Separation on Crystallization

| Composition<br>90E3<br>Portion of Melt | Melting<br>Condition<br>°C-Min. | Phase<br>Separation | Heat<br>Treatment<br>°C-Days | Phase Assemblages Arranged in Decreasing<br>Order (Relative Magnitude in Parenthesis)* |
|--|---------------------------------|---------------------|------------------------------|--|
| Bulk                                   | 1300-4                          | No                  | 700-3                        | FeBO <sub>3</sub> (50), glass (4)  |
| Bulk                                   | 1300-8                          | Start               | 700-3                        | Fe <sub>2</sub> O <sub>3</sub> (23), FeBO <sub>3</sub> (15)                            |
| Top                                    | 1300-16                         | Complete            | 700-3                        | FeBO <sub>3</sub> (23), glass (18)   |
| Bottom                                 | 1300-16                         | Complete            | 700-3                        | Fe <sub>2</sub> O <sub>3</sub> (22), FeBO <sub>3</sub> (15)                            |

\*In this and in the following tables where the relative magnitudes of various phases are given, they are estimated by a pre-selected x-ray peak height. This provides a relative comparison of the same phase among the different crystallized materials for a given stoichiometric composition. However, these values are unreliable for comparing amounts of a given phase between compositions of very different Fe<sub>2</sub>O<sub>3</sub> content.

Table 6

Effect of Oxygen on Iron Reduction on Composition 90B

| <u>Atmosphere</u> | <u>Sample</u>                | <u>Melting</u> |              | <u>Sample Location in Melt</u> | <u>% of Total Wt.</u>  |                        | <u>% Reduction Fe<sup>3+</sup> + Fe<sup>2+</sup></u> |
|-------------------|------------------------------|----------------|--------------|--------------------------------|------------------------|------------------------|--|
|                   | <u>Fe<sup>3+</sup> % (T)</u> | <u>T, °C</u>   | <u>t, Hr</u> |                                | <u>Fe<sup>2+</sup></u> | <u>Fe<sup>3+</sup></u> |  |
| Oxy.<br>(25 psi)  | 14.38                        | 1300           | 2            | Top                            | 1.01                   | 2.70                   | 27.2   |
| Oxy.<br>(25 psi)  | 14.38                        | 1250           | 2            | Top                            | 0.86                   | 3.55                   | 19.4   |
| Air<br>(1 atm.)   | 14.38                        | 1250           | 2            | Top                            | 0.93                   | 2.57                   | 26.6   |

Note: ADL: Furnace designed by ADL (Arthur D. Little).

(T): Target composition of batch material.

Table 7  
Heat Treatment of Batch Materials

| Composition | Fe <sub>2</sub> O <sub>3</sub><br>wt. % | Sample<br>Form | Heat Treatment | Shape<br>Change | Phase Assemblage<br>(in order of decreasing<br>intensity)  |
|-------------|---|----------------|----------------|-----------------|--|
| 99.8B       | 0.46                                    | Pellet         | 460°C-1 hr.    | Yes             | B <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub>   |
| "           | "                                       | "              | 500°C-2.5 days | "               | B <sub>2</sub> O <sub>3</sub>  |
| "           | "                                       | "              | 550°C-1 day    | "               | B <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub>   |
| "           | "                                       | "              | 650°C-1 day    | "               | B <sub>2</sub> O <sub>3</sub>  |
| "           | "                                       | "              | 700°C-62 hrs.  | "               | B <sub>2</sub> O <sub>3</sub> , FeBO <sub>3</sub>  |
| 98B         | 4.54                                    | "              | 460°C-1 hr.    | "               | Fe <sub>2</sub> O <sub>3</sub> , B <sub>2</sub> O <sub>3</sub>   |
| "           | "                                       | "              | 500°C-2.5 day  | "               | B <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub>   |
| "           | "                                       | "              | 550°C-1 day    | "               | B <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , FeBO <sub>3</sub>                                   |
| "           | "                                       | "              | 650°C-1 day    | "               | B <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , FeBO <sub>3</sub>                                   |
| "           | "                                       | "              | 700°C-62 hrs.  | "               | FeBO <sub>3</sub> , B <sub>2</sub> O <sub>3</sub>  |
| 94B         | 12.94                                   | "              | 460°C-1 hr.    | No              | B <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub>   |
| "           | "                                       | "              | 500°C-2.5 days | Yes             | Fe <sub>2</sub> O <sub>3</sub> , B <sub>2</sub> O <sub>3</sub>   |
| "           | "                                       | "              | 550°C-1 day    | "               | Fe <sub>2</sub> O <sub>3</sub> , B <sub>2</sub> O <sub>3</sub>   |
| "           | "                                       | "              | 650°C-1 day    | "               | B <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , FeBO <sub>3</sub> , Fe <sub>3</sub> BO <sub>6</sub> |
| "           | "                                       | "              | 700°C-62 hrs.  | "               | FeBO <sub>3</sub> , B <sub>2</sub> O <sub>3</sub>  |
| 90B2        | 20.56                                   | "              | 700°C-62 hrs.  | "               | FeBO <sub>3</sub>  |



Table 8

Preparation of  $\text{FeBO}_3$  Glass-Ceramics by  $\text{B}_2\text{O}_3$  and  $\text{FeBO}_3$ 

| Composition | Raw Material  | Melting Condition | Heat Treatment | Appearance | Phase Assemblage (relative magnitude)                            |
|-------------|---|-------------------|----------------|------------|--|
| 99.8B       | $\text{B}_2\text{O}_3 + \text{FeBO}_3$<br>(unmelted batch material) | --                | --             | Opaque     | $\text{B}_2\text{O}_3$ (44), $\text{FeBO}_3$ (10)                |
| 99.8B       | $\text{B}_2\text{O}_3 + \text{FeBO}_3$                              | 300°C-1/2 hr      | --             | Opaque     | $\text{B}_2\text{O}_3$ (10), $\text{FeBO}_3$ (5),<br>glass (20)  |
| 99.8B       | $\text{B}_2\text{O}_3 + \text{Fe}_2\text{O}_3$                      | 1300°C-5 min      | 700°C-69 hr    | Opaque     | $\text{B}_2\text{O}_3$ (11), $\text{FeBO}_3$ (10),<br>glass (26) |

Table 9

Preparation by Short Melting and Subsequent  
Heat Treatment from Batched  $B_2O_3$ - $Fe_2O_3$

| Composition   | Raw Material         | Melting Condition | Heat Treatment | Appearance     | Phase Assemblage (relative magnitude)                  |
|---------------|----------------------|-------------------|----------------|----------------|--|
| 94B (Bottom)  | $B_2O_3$ , $Fe_2O_3$ | 1300°C-5 min      | 700°C-69 hr    | Yellow & Black | $Fe_2O_3$ (21), $FeBO_3$ (18), $B_2O_3$ (4), glass (5) |
| 94B (Bulk)    | $B_2O_3$ , $Fe_2O_3$ | 1300°C-15 min     | 700°C-5 days   | Green & Black  | $FeBO_3$ (17), $B_2O_3$ (4), glass (19)                |
| 94B (Bottom)  | $B_2O_3$ , $Fe_2O_3$ | 1300°C-15 min     | 700°C-5 days   | Green & Black  | $Fe_2O_3$ (17), $FeBO_3$ (15), $B_2O_3$ (4)            |
| 94B (Bulk)    | $B_2O_3$ , $Fe_2O_3$ | 1300°C-30 min     | 700°C-5 days   | Green & Black  | $FeBO_3$ (14), $B_2O_3$ (5), glass (19)                |
| 98B (Bulk)    | $B_2O_3$ , $Fe_2O_3$ | 1300°C-5 min      | 700°C-69 hr    | Yellow & Black | $FeBO_3$ (14), $B_2O_3$ (8), glass (20)                |
| 98B (Bulk)    | $B_2O_3$ , $Fe_2O_3$ | 1300°C-15 min     | 700°C-5 days   | Green & Black  | $FeBO_3$ (17), glass (22)                              |
| 98B (Surface) | $B_2O_3$ , $Fe_2O_3$ | 1300°C-15 min     | 700°C-5 days   | Green & Black  | $FeBO_3$ (15), $B_2O_3$ (12), glass (22)               |
| 98B (Bulk)    | $B_2O_3$ , $Fe_2O_3$ | 1300°C-30 min     | 700°C-5 days   | Green & Black  | $FeBO_3$ (15), glass (24)                              |
| 98B (Bottom)  | $B_2O_3$ , $Fe_2O_3$ | 1300°C-30 min     | 700°C-5 days   | Green & Black  | $FeBO_3$ (11)  |

Table 10  
A Search for Optimum Conditions for Producing FeO<sub>3</sub> Glass-Ceramic Material

| <u>Composition</u> | <u>Melting &amp; Subsequent Heat Treatment</u> | <u>Complete Melting</u> | <u>Phase Separation</u> | <u>Appearance</u> | <u>Phase Assemblage (relative magnitude)</u>  |
|--------------------|--|-------------------------|-------------------------|-------------------|---|
| 90C3               | 1300°C-4 min + 700°C - 51.5 hr                 | No                      | No                      | Porous            | FeBO <sub>3</sub> (30), Fe <sub>2</sub> O <sub>3</sub> (27), B <sub>2</sub> O <sub>3</sub> (6)  |
| 90B3               | 1300°C-8 min + 700°C - 51.5 hr                 | No                      | Start                   | Porous            | Fe <sub>2</sub> O <sub>3</sub> (46), FeBO <sub>3</sub> (17)   |
| 90E3, Top          | 1300°C-16 min + 700°C - 51.5 hr                | Yes                     | Yes                     | Dense             | FeBO <sub>3</sub> (21), Fe <sub>2</sub> O <sub>3</sub> (13), B <sub>2</sub> O <sub>3</sub> (10), FeO·B <sub>2</sub> O <sub>3</sub> (10) |
| 90B3, Bottom       | 1300°C-16 min + 700°C - 51.5 hr                | Yes                     | Yes                     | Dense             | Fe <sub>2</sub> O <sub>3</sub> (20), FeO·B <sub>2</sub> O <sub>3</sub> (13), FeBO <sub>3</sub> (9)                                      |
| 90B3               | 1300°C-12 min + 700°C - 6 hr                   | Almost                  | Yes                     | S. porous         | Fe <sub>2</sub> O <sub>3</sub> (26), FeO·B <sub>2</sub> O <sub>3</sub> (12), B <sub>2</sub> O <sub>3</sub> (9)                          |
| 90B3               | 1300°C 16 min + 700°C - 6 hr                   | Yes                     | Yes                     | Dense             | Fe <sub>2</sub> O <sub>3</sub> (20), FeO·B <sub>2</sub> O <sub>3</sub> (15)   |
| 94E                | 1300°C-5 min + 700 - 5 days                    | Almost                  | Start                   | S. porous         | Fe <sub>2</sub> O <sub>3</sub> (30), FeBO <sub>3</sub> (20)   |
| 94E, Top           | 1300°C-10 min + 700°C - 5 days                 | Yes                     | Yes                     | Dense             | FeBO <sub>3</sub> (22)  |
| 96D2               | 1300°C-5 min + 700°C - 5 days                  | Yes                     | No                      | Dense             | FeBO <sub>3</sub> (13), B <sub>2</sub> O <sub>3</sub> (7)   |
| 96D2               | 1300°C-10 min + 700°C - 5 days                 | Yes                     | Slightly                | Dense             | FeBO <sub>3</sub> (9), B <sub>2</sub> O <sub>3</sub> (9)  |
| 96B1               | 1300°C-15 min + 700°C - 5 days                 | Yes                     | Slightly                | Dense             | FeBO <sub>3</sub> (17)  |
| 96B2               | 1200°C-5 min + 700°C - 5 days                  | No                      | No                      | Porous            | FeBO <sub>3</sub> (38), Fe <sub>2</sub> O <sub>3</sub> (30)   |

Table 11

Effect of Heat Treatment Time on Crystallization in 98B2 Composition

| <u>Melting Condition</u>          | <u>Heat Treatment</u>     | <u>Appearance</u>  | <u>Phase Assemblage (relative magnitude)</u>   |
|-----------------------------------|---------------------------|--|--|
| 1300°C-10 min                     | 700°C-24 hrs              | Green, brown and black   | Glass (20), FeBO <sub>3</sub> (9), B <sub>2</sub> O <sub>3</sub> (9)   |
| 1300°C-10 min                     | 700°C-5 hrs               | Red, brown and black   | Glass (21), FeBO <sub>3</sub> (6), B <sub>2</sub> O <sub>3</sub> (3); other Fe <sup>3+</sup> phase: Fe <sub>2</sub> O <sub>5</sub> (5), Fe <sub>3</sub> B <sub>6</sub> (2); Fe <sup>2+</sup> phases: FeO·B <sub>2</sub> O <sub>3</sub> (4), Fe <sub>2</sub> FeB <sub>5</sub> (1) |
| 1300°C-10 min                     | 700°C-5 hrs +700°C-5 days | Green majority and black spots                                     | Glass (17), FeBO <sub>3</sub> (15), B <sub>2</sub> O <sub>3</sub> (19)   |
| 1250°C-10 min (crucible 1/8 full) | 700°C-10 days             | Pure green interior and black layer at surface contacting crucible | Glass (15), FeBO <sub>3</sub> (20), B <sub>2</sub> O <sub>3</sub> (14), Fe <sub>2</sub> O <sub>3</sub> (12)  |
| 1250°C-10 min (crucible 1/2 full) | 700°C-10 days             | Green majority and black spots                                     |  |

Table 12

Phase Assemblages in 98B2 Base Compositions

| <u>Composition</u>                  | <u>Melting Condition</u> | <u>Heat Treatment</u> | <u>Appearance</u>              | <u>Phase Assemblage (relative magnitude)</u>   |
|-------------------------------------|--------------------------|-----------------------|--------------------------------|--|
| 98B                                 | 1300°C-10 min            | 700°C-5 hrs + 5 days  | Green majority & black spots   | FeB <sub>3</sub> (15), B <sub>2</sub> O <sub>3</sub> (19), glass (17)  |
| 98B2 + 0.5% TiO <sub>2</sub>        | 1250°C-10 min            | 700°C-10 days         | Gray                           | Glass (20), FeB <sub>3</sub> (18), B <sub>2</sub> O <sub>3</sub> (15), TiO <sub>2</sub> (~ 6)  |
| 98B2 + 0.5% ZrO <sub>2</sub>        | 1250°C-10 min            | 700°C-10 days         | Brown gray with orange streaks | Glass (20), FeB <sub>3</sub> (16), B <sub>2</sub> O <sub>3</sub> (49), ZrO <sub>2</sub> (0)  |
| 98B + 2% TiO <sub>2</sub>           | 1300°C-10 min            | 700°C-5 days          | Gray                           | FeB <sub>3</sub> (11), TiO <sub>2</sub> (11), glass (12)   |
| 98B + 4% TiO <sub>2</sub>           | 1300°C-10 min            | 700°C-5 days          | Brown & black                  | TiO <sub>2</sub> (15), glass (15)  |
| 98B + 2% ZrO <sub>2</sub>           | 1300°C-10 min            | 700°C-5 days          | Light gray & brown             | FeB <sub>3</sub> (9), ZrO <sub>2</sub> (4), glass (21)   |
| 98B + 4% ZrO <sub>2</sub>           | 1300°C-10 min            | 700°C-5 days          | Gray & brown                   | FeB <sub>3</sub> (11), ZrO <sub>2</sub> (9), glass (17)  |
| 60B Top + 12.2% TiO <sub>2</sub>    | 1300°C-10 min            | 700°C-5 days          | Yellow                         | TiO <sub>2</sub> (16), B <sub>2</sub> O <sub>3</sub> (14), glass (10)  |
| 60B Bottom + 12.2% TiO <sub>2</sub> | 1300°C-10 min            | 700°C-5 days          | Gray                           | Fe <sub>2</sub> O <sub>3</sub> (17), FeB <sub>3</sub> (15), TiO <sub>2</sub> (12), Fe <sub>0.2</sub> B <sub>2</sub> O <sub>3</sub> (5), Fe <sub>2</sub> FeB <sub>5</sub> (3), Fe <sub>3</sub> B <sub>6</sub> (4) |

Table 13

Preparation of Ba-containing compositions

| Composition  | Fe <sub>2</sub> O <sub>3</sub> | BaO   | B <sub>2</sub> O <sub>3</sub> | Bi <sub>2</sub> O <sub>3</sub> | Total | % B <sub>2</sub> O <sub>3</sub> /(B <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> ) |
|--|--------------------------------|-------|-------------------------------|--------------------------------|-------|--|
| 67B + 40% BaO  | Mole %                         | 20.12 | 40.55                         | 39.33                          | 100   | 66.6   |
|  | wt %                           | 26.4  | 51.1                          | 22.5                           | 100   |  |
| 67B + 39% BaO +<br>2% Bi <sub>2</sub> O <sub>3</sub> | Mole %                         | 19.68 | 39.15                         | 39.25                          | 100.0 | 66.6   |
|  | wt %                           | 24.6  | 47                            | 21.4                           | 100.0 |  |

Table 14

Phase assemblages of Ba-containing compounds

| <u>Composition</u>  | <u>Melting Condition</u> | <u>Heat Treatment</u> | <u>Appearance</u> | <u>Phase Assemblage</u>   |
|---|--------------------------|-----------------------|-------------------|---|
| 67B + 40% BaO<br>2nd plate  | 1300°C-2 hrs             | --                    | Black             | Glass only  |
| 67B + 40% BaO<br>2nd plate  | 1300°C-2 hrs             | 700°C-2 days          | Black             | BaO·B <sub>2</sub> O <sub>3</sub> , BaO·6Fe <sub>2</sub> O <sub>3</sub>   |
| 67B + 37% BaO<br>+ 2% Bi <sub>2</sub> O <sub>3</sub><br>2nd plate | 1300°C-2 hrs             | --                    | Black             | Glass only  |
| 67B + 39 BaO<br>+ 2% Bi <sub>2</sub> O <sub>3</sub><br>2nd plate  | 1300°C-2 hrs             | 700°C-2 days          | Black             | BaO·B <sub>2</sub> O <sub>3</sub> (same as above)<br>BaO·6Fe <sub>2</sub> O <sub>3</sub> (much larger than above) |

Table 15

Determination of No.  $\text{FeB}_2\text{O}_7$  Particles Per Unit Volume of Glass-Ceramic

| Composition | Mole %                                       |   | Volume ( $\mu^3$ )     |                          | Total                   | Size, d<br>$\mu$ | Spheric Particle       |                        |                            |
|-------------|--|---|------------------------|--------------------------|-------------------------|------------------|------------------------|------------------------|----------------------------|
|             | $\text{B}_2\text{O}_3/\text{Fe}_2\text{O}_3$ | $\text{B}_2\text{O}_3/\text{FeB}_2\text{O}_7$ | $\text{B}_2\text{O}_3$ | $\text{FeB}_2\text{O}_7$ |                         |                  | Vol ( $\mu^3$ )        | No. Particle           | Part./ $\mu^3$ , $\bar{n}$ |
| 99.8B       | 99.8/0.2                                     | 99.6/0.4                                      | $38.31 \times 10^{12}$ | $0.107 \times 10^{12}$   | $38.417 \times 10^{12}$ | 1/10 $\mu$       | $0.524 \times 10^{-3}$ | $.204 \times 10^{15}$  | 5.32                       |
| 98B         | 98/2   | 96/4  | $36.93 \times 10^{12}$ | $1.07 \times 10^{12}$    | $38.0 \times 10^{12}$   | 1/100 $\mu$      | $0.524 \times 10^{-6}$ | $.204 \times 10^{18}$  | $5.32 \times 10^3$         |
| 90B         | 90/10  | 80/20   | $30.77 \times 10^{12}$ | $5.33 \times 10^{12}$    | $36.10 \times 10^{12}$  | 1/10 $\mu$       | $0.524 \times 10^{-3}$ | $2.04 \times 10^{15}$  | 53.64                      |
| 80B         | 80/20  | 60/40   | $23.08 \times 10^{12}$ | $10.67 \times 10^{12}$   | $33.75 \times 10^{12}$  | 1/100 $\mu$      | $0.524 \times 10^{-6}$ | $2.04 \times 10^{18}$  | $5.36 \times 10^4$         |
| 50B         | 50/50  | 0/100   | --                     | $26.66 \times 10^{12}$   | $26.66 \times 10^{12}$  | 1/10 $\mu$       | $0.524 \times 10^{-3}$ | $50.92 \times 10^{15}$ | $1.91 \times 10^3$         |
|             |  |   |                        |                          |                         | 1/100 $\mu$      | $0.524 \times 10^{-6}$ | $50.92 \times 10^{18}$ | $1.91 \times 10^6$         |

Note:  $\mu$  = micron. This calculation is based upon one mole of  $\text{Fe}_2\text{O}_3 \cdot n\text{B}_2\text{O}_3$ .



Table 16

Effect of Scattering on Light Transmission for Various Iron Borate Compositions (50-99.88)

| Composition | $\frac{d}{(\mu)}$ | $x$    | $Q_{ext}$              | $N$<br>(Part./ $\mu^3$ ) | $Y$                    | $I/I_0$ for<br>$k = 1 \text{ cm} = 10^4 \mu$ |
|-------------|-------------------|--------|------------------------|--------------------------|------------------------|--|
| 99.88       | 1/10              | 0.598  | $2.088 \times 10^{-2}$ | 5.32                     | $8.724 \times 10^{-4}$ | .0002  |
| 98B         | "                 | "      | "                      | 53.64                    | $8.796 \times 10^{-3}$ | 0  |
| 90B         | "                 | "      | "                      | 282.1                    | $4.626 \times 10^{-2}$ | -0   |
| 80B         | "                 | "      | "                      | 603.6                    | $9.898 \times 10^{-2}$ | 0  |
| 50B         | "                 | "      | "                      | 1,909.8                  | $3.132 \times 10^{-1}$ | 0  |
| <hr/>       |                   |        |                        |                          |                        |  |
| 99.88       | 1/100             | 0.0598 | $2.088 \times 10^{-6}$ | $5.32 \times 10^3$       | $8.724 \times 10^{-7}$ | 0.391  |
| 98B         | "                 | "      | "                      | $5.364 \times 10^4$      | $8.796 \times 10^{-6}$ | 0.916  |
| 90B         | "                 | "      | "                      | $2.821 \times 10^5$      | $4.626 \times 10^{-5}$ | 0.530  |
| 80B         | "                 | "      | "                      | $6.036 \times 10^5$      | $9.898 \times 10^{-5}$ | 0.372  |
| 50B         | "                 | "      | "                      | $1.91 \times 10^6$       | $3.132 \times 10^{-4}$ | 0.044  |

Table 17

Effect of Particle Size, Sample Thickness, and Refractive Index Ratio on Transparency of Iron Borate Composition 98B

| Composition | Size<br>$d$ | $m^*$<br>$n_1/n_2$ | $N_2$<br>Matrix | $\left(\frac{m^2-1}{m^2+2}\right)^2$ | N<br>Part./u <sup>3</sup> | Y                     |                       | I/I <sub>0</sub> for  |            |
|-------------|-------------|--------------------|-----------------|--------------------------------------|---------------------------|-----------------------|-----------------------|-----------------------|------------|
|             |             |                    |                 |                                      |                           | 0                     | 0                     | $z = 10^4 \mu$        | $z = 10^5$ |
| 98B         | 1/10 $\mu$  | 1.0                | 2.1             | 0                                    | 53.64                     | 0                     | 0                     | 1.0                   | 1.0        |
| "           | "           | 1.05               | 2.0             | $1.09 \times 10^{-3}$                | "                         | $3.72 \times 10^{-4}$ | $1.57 \times 10^{-4}$ | 0.21                  | 0.992      |
| "           | "           | 1.1                | 1.91            | $4.28 \times 10^{-3}$                | "                         | $1.46 \times 10^{-3}$ | $6.15 \times 10^{-4}$ | 0.002                 | 0.994      |
| "           | "           | 1.2                | 1.75            | $1.64 \times 10^{-2}$                | "                         | $5.58 \times 10^{-3}$ | $2.35 \times 10^{-3}$ | $1 \times 10^{-10}$   | 0.977      |
| "           | "           | 1.3                | 1.62            | $3.50 \times 10^{-2}$                | "                         | $1.19 \times 10^{-2}$ | $5.02 \times 10^{-3}$ | $1.6 \times 10^{-22}$ | 0.951      |
| "           | "           | 1.409              | 1.49            | $6.12 \times 10^{-2}$                | "                         | $2.09 \times 10^{-2}$ | $8.79 \times 10^{-3}$ | $6.3 \times 10^{-39}$ | 0.916      |
| "           | 1/100 $\mu$ | 1.0                | 2.1             | 0                                    | $53.64 \times 10^3$       | 0                     | 0                     | 1.0                   | 1.0        |
| "           | "           | 1.05               | 2.0             | $1.09 \times 10^{-3}$                | "                         | $3.72 \times 10^{-8}$ | $1.57 \times 10^{-7}$ | 0.998                 | 1.0        |
| "           | "           | 1.1                | 1.91            | $4.28 \times 10^{-3}$                | "                         | $1.46 \times 10^{-7}$ | $6.15 \times 10^{-7}$ | 0.994                 | 1.0        |
| "           | "           | 1.2                | 1.75            | $1.64 \times 10^{-2}$                | "                         | $5.58 \times 10^{-7}$ | $2.35 \times 10^{-6}$ | 0.977                 | 1.0        |
| "           | "           | 1.3                | 1.62            | $3.50 \times 10^{-2}$                | "                         | $1.19 \times 10^{-6}$ | $5.02 \times 10^{-6}$ | 0.951                 | 1.0        |
| "           | "           | 1.409              | 1.49            | $6.12 \times 10^{-2}$                | "                         | $2.09 \times 10^{-6}$ | $8.79 \times 10^{-6}$ | 0.916                 | 1.0        |

\*The 98 composition is valid only for  $m = 1.409$ . As  $m$  decreases by adding a third component, the original 98 composition will only apply for the binary system of  $B_2O_3$  and  $Fe_2O_3$ .

FIGURE 1 - Estimation of Melting Temperature  
of 80B Composition

