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on

STUDY OF IRON-BORATE MATERIALS SYSTEMS PROCESSED IN SPACE

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Abstract

The purpose of this study is to explore the possibility of preparing transparent $FeBO_3$ 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 Fe_2O_3-B_2O_3 compositions containing from 1 to 10 mole % Fe_2O_3, although a few ternary compositions were also examined.

It was calculated that an $FeBO_3$-B_2O_3 glass-ceramic containing only 1 mole % $FeBO_3$ would be equivalent for magnetooptic application to a YIG crystal of equal thickness. An Fe_2O_3-B_2O_3 composition containing 2 mole % $FeBO_3$ equivalent (98B) could be converted largely to a dense green, though opaque, $FeBO_3$ glass-ceramic through suitable heat treatments. However, phase separation (and segregation) and Fe^{+3} reduction could not be entirely avoided with the various procedures that were employed. From light scattering calculations, it was estimated that the $FeBO_3$ crystallite size in this 98B composition should be no greater than about 100 Å to allow 90% light transmission though a 1 cm thick sample. However, the actual $FeBO_3$ crystallite sizes obtained in 98B were of the order of 1 μm 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[1] it was investigated whether it might be possible to prepare useful transparent $FeBO_3$ glass-ceramics in space (or on earth). It was envisioned that the desired composition might be prepared initially as a glass, with $FeBO_3$ 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 % B_2O_3 and the remainder Fe_2O_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 % Fe_2O_3 and an iron-poor phase containing mostly B_2O_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, Fe^{+3} to 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°C in order to prevent the formation of a high temperature Fe_3BO_6 phase and other unwanted phases.

In the present continuing study it was determined that an Fe_2O_3-B_2O_3 glass-ceramic containing as little as 0.9 mole % $FeBO_3$ would be equivalent to YIG for magnetooptic application. Therefore, the present study was limited largely to compositions containing from 1 to 10 mole % Fe_2O_3. It was thought that within this composition range, it should be easier to establish the conditions for minimizing phase separation and Fe^{+3} reduction. During this study attempts were also made to reduce the $FeBO_3$ 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 B_2O_3 with $FeBO_3$ crystallites was also unsuccessfully tried. Finally, an evaluation was made of the effectiveness of adding TiO_2 and ZrO_2 as nucleating agents for reducing the mean $FeBO_3$ crystallite size.

The FeBO glass-ceramic compositions discussed in this report will be identified by a code such as 83.3B-2, as in the previous study.[1] The prefix indicates the mole % of B_2O_3 (i.e., 83.3B = $Fe_2O_3 \cdot 5B_2O_3$), and the suffix is the number of the batch prepared if other than the first.

2. Minimum iron content needed for magnetooptic application

The utility of a magnetooptic device is determined by its figure of merit, $2F/\alpha$, where F is the Faraday rotation per unit sample length and α is the absorption coefficient value at maximum absorption in the visible. The current material used for the magnetooptic devices is YIG, for which $2F/\alpha$ is 3.2°. For the 83.3B and 99.1B Fe_2O_3-B_2O_3 compositions, the calculated values of $2F/\alpha$ are 52° and 3.2°, respectively. These values were arrived at by assuming that (a) all the Fe_2O_3 content is completely converted to $FeBO_3$, (b) the Faraday rotation is proportional to the amount of $FeBO_3$ produced, and (c) the absorption coefficient of the $FeBO_3$ is not affected by the B_2O_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 magnetooptic 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 magnetooptic application.

Since transparency is essential for the magnetooptical 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 ($FeBO_3$), which is the ferromagnetic phase, is the main goal of this study. The maximum amount of $FeBO_3$ was formed on the 4 minute melt, which had no phase separation. Once the phase separation starts, a portion of the iron remains as Fe_2O_3 during heat treatment. This in turn reduces the amount of $FeBO_3$ 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 B_2O_3 through evaporation during melting will be very large, and (c) almost all of the iron will reduce to Fe^{2+} and will thus make the cast melt very black and nontransparent.

4. Effect of oxygen and melting temperature on Fe^{+3} 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^{+2} and Fe^{+3} 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°C (m.p. of B_2O_3) through 700°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°C or higher. The lowest temperature for $FeBO_3$ to crystallize was observed to be 550°C. However, a temperature of about 700°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,[1] 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°C and can easily be made into a transparent glass. In addition, $FeBO_3$ crystals can persist up to a temperature of 800°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°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 $FeBO_3$ and B_2O_3, and very little of the $FeBO_3$ will dissolve into the B_2O_3 solution, and (c) the $FeBO_3$ crystals dispersed through the B_2O_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 $FeBO_3$ crystals was ground only to a size exceeding 100 μm (200 mesh). However, this material when melted at 800°C for half an hour preserved only about half of the original $FeBO_3$, as shown in Table 8. This indicates that this approach is ineffective for obtaining the maximum $FeBO_3$ phase. On the other hand, a 99.8B composition prepared by B_2O_3 and Fe_2O_3 can produce the maximum amount of $FeBO_3$ 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 $FeBO_3$ 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 $FeBO_3$ crystallites by reducing the mean crystallite size, the segregated phase separation, and the Fe^{+3} reduction process.

The approach involves a short melting at a relatively low temperature of B_2O_3-Fe_2O_3 composition, followed by a subsequent heat treatment of the hot melt at a lower temperature for the growth of the $FeBO_3$ 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°C for 5, 15, and 30 minutes and followed by heat treatment at 700°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°C for 15 minutes and heat treated at 700°C for 5 days represents the best $FeBO_3$ glass-ceramic so far obtained. This material is green and dense but opaque. However, most of the iron was crystallized as $FeBO_3$ 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 B_2O_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) $FeBO_3$ is the predominant phase and there is no other Fe-phases such as Fe_2O_3, Fe_3BO_6, and 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 Fe_2O_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 $FeBO_3$ 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 μm, and voids were in evidence. For the 10 and 15 minute melts, the crystal sizes were found to be about 1 μm, 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 $FeBO_3$ than the latter, as shown in Table 11. However, the amount of $FeBO_3$ 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 $FeBO_3$ crystal size is 7 μ for 24 hrs. treatment, but only 3.5 μ for 5 hrs. treatment. It is noted that although the 24 hrs. or longer heat treatment in general produces the desired phase assemblage of $FeBO_3$ plus glass or B_2O_3, the 5 hrs. heat treatment produces many additional unwanted phases such as $FeO \cdot B_2O_3$, Fe_2FeBO_5, and Fe_2O_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 $FeBO_3$ 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 $FeBO_3$ phase during this heat treatment, as is also indicated in Table 11. This result suggests that it may be possible to eliminate the 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

$FeBO_3$ glass-ceramic is probably due to internal scattering by the $FeBO_3$ crystallites.

In an effort to reduce the $FeBO_3$ 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 $FeBO_3$, as indicated in the table. It should be noted that the black layer which has been attributed to Fe^{+2} phases appeared to have formed at the melt-crucible interface, which suggests that these reactions may not occur under containerless conditions.

7. Preparation of $FeBO_3$ glass-ceramics containing third components

7.1. Effect of TiO_2 and ZrO_2

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 $FeBO_3$ crystallite size and/or the large refractive index difference between the $FeBO_3$ crystallites and the B_2O_3 matrix. Thus TiO_2 or ZrO_2 was added to several B_2O_3-Fe_2O_3 compositions in an attempt to improve the transparency after conversion to the glass-ceramics. Since TiO_2 and ZrO_2 have much higher refractive indices than B_2O_3, 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 $FeBO_3$ crystallites of smaller size.

Thus 0.5, 2, and 4 weight % of either TiO_2 or ZrO_2 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_2 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_2 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 $FeBO_3$ 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_2 and TiO_2 imparted pronounced color to the heat-treated products.

SEM photographs of the sample containing 0.5% ZrO_2 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_2O_3 crystallites, as evidenced by the higher concentration in the diffraction pattern for this material as indicated in the table. Since no ZrO_2 phase was detected in this material, it is possible that it reacts with the B_2O_3 to form the phase observed. However, there was no indication that ZrO_2 or TiO_2 may be beneficial to transparency in any of the materials prepared.

7.2. Effect of BaO

In still another effort to produce transparent $FeBO_3$ glass-ceramic, the approach of adding another third component to the binary compound of Fe_2O_3-B_2O_3 was considered. It was reported that a ferromagnetic material could be obtained by adding Ba ($40BaO \cdot 20Fe_2O_3 \cdot 40B_2O_3$, Russian Patent 550,352 from 1977) to Fe_2O_3-B_2O_3. The Russian claimed that (a) a lowered Fe_2O_3 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 $Ba(NO_3)_2$ rather than BaO would help to prevent the formation of Fe^{2+}. A comparison between the Ba-compound and the basic binary composition of B_2O_3-Fe_2O_3 is shown as follows:

	$33Fe_2O_3 \cdot 67B_2O_3$	$40BaO \cdot 20Fe_2O_3 \cdot 40B_2O_3$
Melting temp., °C	1300	1250-1300
Crystallization temp., °C	700	680-800
Phase	$FeBO_3$	Ba-hexaferrite
Specific magnetization, Gauss-cm^3/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 molt % Ba does not improve the possibility of producing a transparent glass-ceramic.

8. Effect of internal scattering on transparency

We shall consider an $FeBO_3$ glass-ceramic in which small $FeBO_3$ crystallites are randomly and uniformly distributed within a matrix of pure B_2O_3 glass. Differences in physical properties between $FeBO_3$ and B_2O_3 are indicated below.

	$FeBO_3$	B_2O_3	
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 $FeBO_3$ and B_2O_3, internal scattering poses a serious problem, which may greatly decrease the transparency of an $FeBO_3$ glass-ceramic material. The extent of the effect of scattering on scattering was evaluated by a method outlined by Van De Hulst.[2] 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

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

for the fraction of light transmitted, where ℓ is the sample thickness and γ is the extinction coefficient defined by

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

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

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

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

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

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

where $x = \pi d/\lambda$ with λ 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 $FeBO_3$ crystalline particles per unit volume of glass-ceramic at size 1/10 and 1/100 μ was estimated for various compositions from 99.8B through 50B, as shown in Table 15. The effect of scattering on transparency of $FeBO_3$ 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_o = 0.916) at a sample thickness of 10^4 μ (1 cm) and a particle size of 1/100 μ. Thus for a 1 cm thick sample of the 98B glass-ceramic material in which all of the Fe_2O_3 has been converted to $FeBO_3$, a spherical crystallite diameter of 100 Å would be required to insure 90% light transmission according to these calculations.

From Table 16 it may be noted also that as the Fe_2O_3 content increases above the 98B concentration, the light transmission rapidly decreases, with the sample being essentially opaque (I/I_o = 0.04) for the 50B composition even with a crystallite size of 100 Å. 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 $FeBO_3$ concentration can be greater than in the 98B composition.

9. Conclusions

(1) An Fe_2O_3-B_2O_3 glass-ceramic containing only 1 mole % $FeBO_3$ could be equivalent to pure single crystal YIG for magnetooptic application.

(2) Phase separation during melting cannot be avoided in Fe_2O_3-B_2O_3 compositions containing as little as 2 mole % $FeBO_3$ under earth conditions.

(3) Useful transparent $FeBO_3$ glass-ceramics cannot be prepared on earth due to (a) Fe^{+3} reduction, (b) phase separation and segregation, and (c) formation of large crystallites of $FeBO_3$ and other species which cause prohibitively high internal scattering.

(4) The 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 Fe^{+2} compounds to $FeBO_3$ by a suitable crystallization heat treatment in the vicinity of 700°C.

(5) No evidence was found that TiO_2 or ZrO_2 might be beneficial to the transparency of an $FeBO_3$ glass-ceramic, either by serving as a useful nucleating agent or by increasing the refractive index of the matrix.

(6) Incorporation of 40 mole % BaO to the 67B composition is not beneficial for producing an $FeBO_3$ glass-ceramic.

(7) Based upon light scattering calculations, it is estimated that the $FeBO_3$ crystallite size cannot exceed about 100 Å 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 $FeBO_3$ crystallite size can be achieved.

(2) Further studies to determine the nature of the 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 $FeBO_3$ 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 $FeBO_3$ composition, as is the case found for the Fe_2O_3-B_2O_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 interconncected 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 $FeBO_3$ 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. Code	wt. %* B_2O_3	wt. %* Fe_2O_3	Melting °C-Hr.	Melting+ Loss %	Melts (air quench) Evidence B_2O_3 Bubbling	Melts (air quench) Phase Separation
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.
99.5B	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_2O_3 and 98% Fe_2O_3.

Table 2

A Summary of Cast Splat Plates

Composition Code	Melting Condition			Fe_2O_3 % (Target)	Cast Plates	
	T, °C	t, hr.	Loss %		Cast No.	Appearance
94B	1300	3		12.94	1st	Opaque
					3rd	"
98B	1300	3	1.5	4.54	1st	Opaque
					4th	
99.8B	1300	2.5	3.2	0.46	1st	Translucent
					4th	Opaque
99.8B	1100	2	2.2	0.46	1st	Opaque
					3rd	"

Table 3

Characterization of The First Splat Plates

Composition	Melting Condition °C - Hrs.	Fe_2O_3 %		Phase Assemblage	
		Target	Analysis	Heat Treatment	Phase in Decreasing Order
94B	1300 - 3	12.94	4.3	--	B_2O_3, glass
				700°C - 3 days	B_2O_3, $FeBO_3$, Fe_3BO_6, glass
98B	1300 - 3	4.54	3.1	--	B_2O_3, glass
				700°C - 3 days	$FeBO_3$, B_2O_3, Fe_3BO_6, glass
99.8B	1300 - 2.5	0.46	1.8*	--	B_2O_3, glass
				700°C - 3 days	$FeBO_2$, B_2O_3, glass
99.8B	1100 - 2	0.46	1.5*	--	B_2O_3, glass
				700°C - 3 days	$FeBO_3$, B_2O_3, glass

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

Table 4

Results of Phase Separation Study

Composition	Melting Condition °C - Min.	Phase Separation	Appearance of Melt (after cooling)
90B	1300 - 2	No	Honeycomb structures
90B	1300 - 4	No	Honeycomb structure, but top surface has started to condense
90B	1300 - 8	Start	Melt very dense with very few cavities, iron-rich phase appears but dispersed 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 90B$_2$O$_3$ Portion of Melt	Melting Condition °C-Min.	Phase Separation	Heat Treatment °C-Days	Phase Assemblages Arranged in Decreasing Order (Relative Magnitude in Parenthesis)*
Bulk	1300-4	No	700-3	$FeBO_3$ (50), glass (4)
Bulk	1300-8	Start	700-3	Fe_2O_3 (23), $FeBO_3$ (15)
Top	1300-16	Complete	700-3	$FeBO_3$ (23), glass (18)
Bottom	1300-16	Complete	700-3	Fe_2O_3 (22), $FeBO_3$ (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_2O_3 content.

Table 6

Effect of Oxygen on Iron Reduction on Composition 90B

Atmosphere	Sample Fe^{3+} % (T)	Melting T, °C	Melting t, Hr	Sample Location in Melt	% of Total Wt. Fe^{2+}	% of Total Wt. Fe^{3+}	% Reduction $Fe^{3+} \rightarrow Fe^{2+}$
Oxy. (25 psi)	14.38	1300	2	Top	1.01	2.70	27.2
Oxy. (25 psi)	14.38	1250	2	Top	0.86	3.55	19.4
Air (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_2O_3 wt. %	Sample Form	Heat Treatment	Shape Change	Phase Assemblage (in order of decreasing intensity)
99.8B	0.46	Pellet	460°C-1 hr.	Yes	B_2O_3, Fe_2O_3
"	"	"	500°C-2.5 days	"	B_2O_3
"	"	"	550°C-1 day	"	B_2O_3, Fe_2O_3
"	"	"	650°C-1 day	"	B_2O_3
"	"	"	700°C-62 hrs.	"	B_2O_3, $FeBO_3$
98B	4.54	"	460°C-1 hr.	"	Fe_2O_3, B_2O_3
"	"	"	500°C-2.5 day	"	B_2O_3, Fe_2O_3
"	"	"	550°C-1 day	"	B_2O_3, Fe_2O_3, $FeBO_3$
"	"	"	650°C-1 day	"	B_2O_3, Fe_2O_3, $FeBO_3$
"	"	"	700°C-62 hrs.	"	$FeBO_3$, B_2O_3
94B	12.94	"	460°C-1 hr.	No	B_2O_3, Fe_2O_3
"	"	"	500°C-2.5 days	Yes	Fe_2O_3, B_2O_3
"	"	"	550°C-1 day	"	Fe_2O_3, B_2O_3
"	"	"	650°C-1 day	"	B_2O_3, Fe_2O_3, $FeBO_3$, Fe_3BO_6
"	"	"	700°C-62 hrs.	"	$FeBO_3$, B_2O_3
90B2	20.56	"	700°C-62 hrs.	"	$FeBO_3$

Table 8

Preparation of $FeBO_3$ Glass-Ceramics by B_2O_3 and $FeBO_3$

Composition	Raw Material	Melting Condition	Heat Treatment	Appearance	Phase Assemblage (relative magnitude)
99.8B	B_2O_3 + $FeBO_3$ (unmelted batch material)	--	--	Opaque	B_2O_3 (44), $FeBO_3$ (10)
99.8B	B_2O_3 + $FeBO_3$	800°C-1/2 hr	--	Opaque	B_2O_3 (10), $FeBO_3$ (5), glass (20)
99.8B	B_2O_3 + Fe_2O_3	1300°C-5 min	700°C-69 hr	Opaque	B_2O_3 (11), $FeBO_3$ (10), 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 $FeBO_3$ Glass-Ceramic Material

Composition	Melting & Subsequent Heat Treatment	Complete Melting	Phase Separation	Appearance	Phase Assemblage (relative magnitude)
90B3	1300°C-4 min + 700°C - 51.5 hr	No	No	Porous	$FeBO_3$ (30), Fe_2O_3 (27), B_2O_3 (6)
90B3	1300°C-8 min + 700°C - 51.5 hr	No	Start	Porous	Fe_2O_3 (46), $FeBO_3$ (17)
90B3, Top	1300°C-16 min + 700°C - 51.5 hr	Yes	Yes	Dense	$FeBO_3$ (21), Fe_2O_3 (13, B_2O_3 (10), $FeO{\cdot}B_2O_3$ (10)
90B3, Bottom	1300°C-16 min + 700°C - 51.5 hr	Yes	Yes	Dense	Fe_2O_3 (20), $FeO{\cdot}B_2O_3$ (13), $FeBO_3$ (9)
90B3	1300°C-12 min + 700°C - 6 hr	Almost	Yes	S. porous	Fe_2O_3 (28), $FeO{\cdot}B_2O_3$ (12) B_2O_3 (9)
90B3	1300°C 16 min + 700°C - 6 hr	Yes	Yes	Dense	Fe_2O_3 (20), $FeO{\cdot}B_2O_3$ (15)
94B	1300°C-5 min + 700 - 5 days	Almost	Start	S. porous	Fe_2O_3 (30), $FeBO_3$ (20)
94B, Top	1300°C-10 min + 700°C - 5 days	Yes	Yes	Dense	$FeBO_3$ (22)
98B2	1300°C-5 min + 700°C - 5 days	Yes	No	Dense	$FeBO_3$ (13), B_2O_3 (7)
98B2	1300°C-10 min + 700°C - 5 days	Yes	Slightly	Dense	$FeBO_3$ (9), B_2O_3 (9)
98B1	1300°C-15 min + 700°C - 5 days	Yes	Slightly	Dense	$FeBO_3$ (17)
98B2	1200°C-5 min + 700°C - 5 days	No	No	Porous	$FeBO_3$ (38), Fe_2O_3 (30)

Table 11

Effect of Heat Treatment Time on Crystallization in 98B2 Composition

Melting Condition	Heat Treatment	Appearance	Phase Assemblage (relative magnitude)
1300°C-10 min	700°C-24 hrs	Green, brown and black	Glass (20), $FeBO_3$ (9), B_2O_3 (9)
1300°C-10 min	700°C-5 hrs	Red, brown and black	Glass (21), $FeBO_3$ (6), B_2O_3 (3); other Fe^{3+} phase: Fe_2O_5 (5), Fe_3BO_6 (2); Fe^{2+} phases: $FeO \cdot B_2O_3$ (4), Fe_2FeBO_5 (1)
1300°C-10 min	700°C-5 hrs +700°C-5 days	Green majority and black spots	Glass (17), $FeBO_3$ (15), B_2O_3 (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), $FeBO_3$ (20), B_2O_3 (14), Fe_2O_3 (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

Composition	Melting Condition	Heat Treatment	Appearance	Phase Assemblage (relative magnitude)
98B	1300°C-10 min	700°C-5 hrs + 5 days	Green majority & black spots	$FeBO_3$ (15), B_2O_3 (19), glass (17)
98B2 +0.5% TiO_2	1250°C-10 min	700°C-10 days	Gray	Glass (20), $FeBO_3$ (18), B_2O_3 (15), TiO_2 (~ 6)
98B2 +0.5% ZrO_2	1250°C-10 min	700°C-10 days	Brown gray with orange streaks	Glass (20), $FeBO_3$ (16), B_2O_3 (49), ZrO_2 (0)
98B + 2% TiO_2	1300°C-10 min	700°C-5 days	Gray	$FeBO_3$ (11), TiO_2 (11), glass (12)
98B + 4% TiO_2	1300°C-10 min	700°-5 days	Brown & black	TiO_2 (15), glass (15)
98B + + 2% ZrO_2	1300°C-10 min	700°-5 days	Light gray & brown	$FeBO_3$ (9), ZrO_2 (4), glass (21)
98B + 4% ZrO_2	1300°C-10 min	700°-5 days	Gray & brown	$FeBO_3$ (11), ZrO_2 (9), glass (17)
60B + 12.2% TiO_2 Top	1300°C-10 min	700°-5 days	Yellow	TiO_2 (16), B_2O_3 (14), glass (10)
60B + 12.2% TiO_2 Bottom	1300°C-10 min	700°-5 days	Gray	Fe_2O_3 (17), $FeBO_3$ (15), TiO_2 (12), $FeO \cdot 2B_2O_3$ (5), Fe_2FeBO_5 (3), Fe_3BO_6 (4)

Table 13

Preparation of Be-containing compositions

Composition		Fe_2O_3	BaO	B_2O_3	Bi_2O_3	Total	% $B_2O_3/(B_2O_3 + Fe_2O_3)$
67B + 40% BaO	Mole %	20.12	40.55	39.33	--	100	66.6
	wt %	26.4	51.1	22.5	--	100	
67B + 39% BaO + 2% Bi_2O_3	Mole %	19.68	39.15	39.25	1.92	100.0	66.6
	wt %	24.6	47	21.4	7	100.0	

Table 14

Phase assemblages of Ba-containing compounds

Composition	Melting Condition	Heat Treatment	Appearance	Phase Assemblage
67B + 40% BaO 2nd plate	1300°C-2 hrs	--	Black	Glass only
67B + 40% BaO 2nd plate	1300°C-2 hrs	700°C-2 days	Black	$BaO \cdot B_2O_3$, $BaO \cdot 6Fe_2O_3$
67B + 37% BaO + 2% Bi_2O_3 2nd plate	1300°C-2 hrs	--	Black	Glass only
67B + 39 BaO + 2% Bi_2O_3 2nd plate	1300°C-2 hrs	700°C-2 days	Black	$BaO \cdot B_2O_3$ (same as above) $BaO \cdot 6Fe_2O_3$ (much larger than above)

Table 15

Determination of No. $FeBO_3$ Particles Per Unit Volume of Glass-Ceramic

Composition	Mole %		Volume (u^3)			Spheric Particle			
	B_2O_3/Fe_2O_3	$B_2O_3/FeBO_3$	B_2O_3	$FeBO_3$	Total	Size, d	Vol (u^3)	No. Particle	Part./u^3, N
99.8B	99.8/0.2	99.6/0.4	38.31×10^{12}	0.107×10^{12}	38.417×10^{12}	1/10 u	0.524×10^{-3}	$.204 \times 10^{15}$	5.32
						1/100 u	0.524×10^{-6}	$.204 \times 10^{18}$	5.32×10^3
98B	98/2	96/4	36.93×10^{12}	1.07×10^{12}	38.0×10^{12}	1/10 u	0.524×10^{-3}	2.04×10^{15}	53.64
						1/100 u	0.524×10^{-6}	2.04×10^{18}	5.36×10^4
90B	90/10	80/20	30.77×10^{12}	5.33×10^{12}	36.10×10^{12}	1/10 u	0.524×10^{-3}	10.19×10^{15}	2.82×10^2
						1/100 u	0.524×10^{-6}	10.19×10^{18}	2.82×10^5
80B	80/20	60/40	23.08×10^{12}	10.67×10^{12}	33.75×10^{12}	1/10 u	0.524×10^{-3}	20.37×10^{15}	6.04×10^2
						1/100 u	0.524×10^{-6}	20.37×10^{18}	6.04×10^5
50B	50/50	0/100	--	26.66×10^{12}	26.66×10^{12}	1/10 u	0.524×10^{-3}	50.92×10^{15}	1.91×10^3
						1/100 u	0.524×10^{-6}	50.92×10^{18}	1.91×10^6

Note: u = micron. This calculation is based upon one mole of $Fe_2O_3 \cdot nB_2O_3$.

Table 16

Effect of Scattering on Light Transmission for Various Iron Borate Compositions (50-99.8B)

Composition	d (μ)	x	Q_{ext}	N (Part./μ^3)	Y	I/I_o for ℓ = 1 cm = 10^4 μ
99.8B	1/10	0.598	2.088×10^{-2}	5.32	8.724×10^{-4}	.0002
98B	"	"	"	53.64	8.796×10^{-3}	0
90B	"	"	"	282.1	4.626×10^{-2}	0
80B	"	"	"	603.6	9.898×10^{-2}	0
50B	"	"	"	1,909.8	3.132×10^{-1}	0
99.8B	1/100	0.0598	2.088×10^{-6}	5.32×10^3	8.724×10^{-7}	0.991
98B	"	"	"	5.364×10^4	8.796×10^{-6}	0.916
90B	"	"	"	2.821×10^5	4.626×10^{-5}	0.630
80B	"	"	"	6.036×10^5	9.898×10^{-5}	0.372
50B	"	"	"	1.91×10^6	3.132×10^{-4}	0.044

Table 17

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

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