ABSTRACT

TRANSMISSION ELECTRON MICROSCOPIC STUDIES ON THE ROLE OF VARIOUS NUCLEATING AGENTS ON THE MICROSTRUCTURE OF A BINARY BARIUM BORATE GLASS SYSTEM

by

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The microstructural changes in a binary barium borate glass system of the composition $Ba0.4B_2O_3$ resulting from the addition of various nucleating agents were investigated using transmission electron microscopy. X-ray and selected area electron-diffraction methods were employed to identify the precipitated crystalline phases in the resulting glass-ceramic.

To study the role of variable valence cations; a transition metal $oxide (TiO_2)$, a rare-earth oxide (CeO_2) and a network-forming oxide (P_2O_5) were chosen as nucleating agents. Phase separation into two immiscible glassy phases was found to be a precursor for crystallization in all the barium borate glass systems studied.

Titanium dioxide, when used as a nucleating agent in this glass system, was found to enhance nucleation and produce a coarse grained

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glass-ceramic. The crystalline phase was identified as barium titanate. Whereas additions of cerium oxide produced a fine grained glass-ceramic, both titanium dioxide and cerium oxide, when used as nucleating agents, were found to reduce the undercooling required for nucleation. This indicated that a single heat treatment of the glass system containing either TiO_2 or CeO_2 would be sufficient for the nucleation and crystal growth processes needed for obtaining a glass-ceramic. The dual valence states of both the titanium and cerium ions play an important role in the nucleation and crystallization of this glass system. Although additions of phosphorus pentoxide to the base glass caused phase separation, it did not enhance nucleation or crystallization, unlike titanium dioxide or cerium oxide.

Comparative studies showed that among the three nucleating agents studied in this work cerium oxide is the most effective in producing a very fine-grained glass-ceramic within reasonable heat treatment times and at temperatures high enough to relieve the stresses induced due to the crystallization process.

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CHAPTER I

INTRODUCTION AND HISTORICAL REVIEW

1.1 INTRODUCTION

In recent years there has been a growing interest in glassceramic materials and their applications in modern technology. A glassceramic material essentially is a vitreous material that has been partially or completely crystallized to have desired thermal, mechanical, electronic, magnetic, or optical properties. In glass-ceramics the emphasis is to induce very fine, homogeneously distributed crystals in the glass matrix. These crystals then can grow to a certain desired size or aid in the precipitation of certain phases around them, thus clustering or segregating new phases in the previously homogeneous glass matrix.

One of the main attractive features of glass-ceramics is the relative ease with which any desirable shape can be obtained from molten glasses by molding into the desired shape and then annealing to preserve the geometrical shape desired. The preshaped glass item then can be heat treated at the selected temperature and time combination to induce either partial or complete crystallization.

The achievement of improved and desirable properties in such materials, as compared with the original glassy matrix, has resulted in many studies on controlled property variation with little emphasis on the

basic mechanisms and kinetic considerations leading to such variations. In recent years, however, considerable theoretical and experimental research has been devoted to the processes of nucleation, crystallization, and phase separation in glass systems. The change of glasses to a fairly stable crystalline state, commonly termed devitrification, may proceed either by crystallization of the glass composition as a whole with little of the glassy phase left over, or by precipitation of a crystalline phase of a specific composition as a minor portion of the original glassy matrix. In some cases, glass-in-glass phase separation of one or more component-rich areas occurs in the matrix rather than crystallization.

The process of controlling the crystallization and/or phase separation in glasses is commonly used to produce ceramics with certain properties (1). One widely used technique is to add certain catalysts or nucleating agents that could be hosted in the glass matrix and yet preserve its glassy nature; and then a final heat treatment is used to induce either phase separation and/or crystallization, which could be controlled easily, yielding the final structure with the desired properties.

Until recently, studies on nucleation have been primarily of a theoretical nature because of the very small sizes of the crystalline nuclei (100 Å). These could not be observed readily or detected experimentally until powerful techniques such as electron microscopy, small angle x-ray scattering, and light scattering were applied for the nucleation studies.

In view of the achievements which have resulted from the ability to control crystallization and phase separation in glasses, it cannot

be disputed that an understanding of the processes involved in nucleation, which is believed must necessarily precede crystallization and phase separation, would be extremely valuable and essential. Even in apparently simple glasses, the mechanisms involved are complicated. In catalyzed nucleation leading to phase separation and/or crystallization the role of the nucleating agent used and its concentration are important factors. In this study, some potential nucleating agents have been investigated to determine the role and effectiveness of variable valence cations on the crystallization process of a binary barium-borate glass system.

1.2 THEORIES ON GLASS STRUCTURE

Two of the most recognized theories in explaining glass structures are the Zachariasen (1932) - Warren's (1933) network theory and the crystallite theory by Lebedev (1921) (2). In these theories, the glass structure is explained either by means of a random three-dimensional network lacking long range periodicity, or by the presence of small finite crystallites held together by an amorphous medium.

1.2.1 Zachariasen - Warren network theory:

This theory proposes that an oxide or a compound tends to form a glass when its smallest building unit easily forms polyhedral building groups. The rules set forth by the Zachariasen - Warren's network theory treat the structure of a glass as a random three-dimensional network lacking long-range periodicity.

If a large cation is incorporated by fusion in such a network, for example by fusing Na_20 or CaO, the original network breaks at various

points. The oxygen ions introduced by such a process occupy the free corners of the separated tetrahedra. The large cation fills the larger vacancy produced by the open lattice at this position (i.e. sits in an interstitial site). The splitting and the incorporation of large cations into the interstitials of the network is assumed to take place randomly and uniformly as shown in Figure 1.

According to Zachariasen all cations which participate in glass formation are divided into three main groups (2,3):

1- Network formers: these can form a glass network by themselves, e.g., oxides of Si, B, P, Ge, As, Be, etc. These oxides have predominantly low coordination number of either 3 or 4.

2- Network modifiers: these cannot form glasses alone, but their cations can be accomodated in the glass matrix in interstitial positions and can lead to the modification of the glass matrix properties by donating the anion to the network structure. These are oxides of Na, K, Ca, Ba, etc., and generally have a coordination number of six.

3- Intermediate oxides: these either can take part in the network structure or sit in the interstitial positions. They play a role between the network formers and the network modifiers. Such oxides are Al, Mg, Zn, Pb, Ta, Ti, etc. These have predominantly the coordination numbers 4, 5 and 6. In a multi-linked glass these oxides, according to the composition can reinforce the glass structure as polyhedron-forming units or further loosen up the basic structure as network modifiers.

A further step forward in the understanding of the structure of glasses was achieved in 1942 by Dietzel (4), who introduced the field strength of ions as a basis for the study of glass structure. Dietzel was the first one to study the interaction between the forces exerted by



•Si 00 🔿 Na

Fig. 1

Two dimensional representation of the network structure in sodium silicate glass. The large sodium ions occupy the large cavities resulting from the bridge fractures caused by oxygen.

the ions and the resulting effects during the cooling of the glass melt. The characterization of the grouping of oxides to three main categories by Zachariasen (i.e., network formers, intermediates and modifier oxides) still holds true on the basis of the field strength theory proposed by Dietzel.

Ermolenko (5) argues that the categorization of ions by the different network theories to rigid subdivisions of network-forming and modifier ions is impossible. New concepts of "probable network formers" (Stevels and Stanworth; 1946) (6), or "intermediate elements" (Sunn; 1947) (7) soon had to be introduced. The structure of "invert glass" (5) i.e. glasses containing over 50 mole % of non-bridging oxygen ions, was found to consist of short chains of network former-oxygen polyhedra surrounded by numerous modifier ions. Ermolenko drew the conclusion that many metal oxides, formerly regarded as modifiers, when present in large concentrations in glasses may exist as network-formers. Examples of such elements are, lead (in $Al_2O_3 - CaO - PbO$ system with more than 75 wt.% PbO), magnesium (in $SiO_2 - Al_2O_3 - B_2O_3 - MgO$ system containing up to 80 mole % MgO), calcium (in $B_2O_3 - Al_2O_3 - CaO$ system with up to 80 mole % CaO), zinc, barium (up to 80 mole %), bismuth, tungsten, antimony, molybdenum, thallium and tellurium.

1.2.2 Lebedev's crystallite theory:

The crystallite theory was originally regarded as the direct contradiction to the network theory. In effect, the characteristic feature of the network theory is a statistical distribution of the large cations (modifiers) over a disordered network, whereas the crystallite theory is characterised by the high ordering of the cation positions in

the matrix. According to Lebedev (8), in the case of silicate glasses, the glass structure can be regarded as an accumulation of micro-crystalline clusters of SiO₂ and of different silicates. In compound glasses "the microcrystals" may be either definite chemical compounds or solid solutions which are predicted according to the phase diagram of the system of the corresponding glass composition. The microcrystals, optically undetectable either by visible or ultraviolet light, should be imagined as greatly deformed structural units which possess some degree of ordering towards the crystalline structure of the normal lattice. These structural formations are called "crystallites."

The crystallite theory, as was the case with the network theory, also was developed and adapted by a great number of researchers, particularly of the Soviet school. Valenkov and Porai-Koshits in 1936 (9) concluded from theoretical calculations and x-ray studies that the structure of a crystallite is most regular at the center, where it is practically the same as that of a crystal. The regularity of a crystal lattice decreases toward the periphery. This produces the greatly amorphous intermediate layers which bind the crystallites together. The crystallite diameter is between 8 and 15 Å, which is of the same magnitude of a few unit cells in size.

Later in 1955 Lebedev modified his crystallite theory by the assertion that glass contains disordered as well as ordered zones in the form of well-defined chemical compounds. Lebedev no longer sees any contradictions between the state of the glass defined by this "microheterogeneous" theory and the network theory.

Although these basic concepts of glass structure, Zachariasen and Warren's network theory and Lebedev's crystallite theory, have been

subjected to certain modifications which has brought them nearer to one another, yet they still remain basically different.

1.3 THEORIES ON NUCLEATION AND CRYSTALLIZATION

Tamman (10) carried out classical studies on crystallization in supercooled liquids, which included some inorganic glasses. His work showed the existence of a metastable zone just below the melting point. In this zone, nuclei do not form at a detectable rate. However, crystals can grow if nuclei are provided; i.e. if the melt is "seeded." At temperatures below this region, there are two factors that control the crystallization process:

i- the rate of formation of nuclei, and

ii- the rate of crystal growth.

1.3.1 Homogeneous nucleation:

Homogeneous nucleation is the process where nucleation occurs without the help or presence of any foreign matter in the matrix. Melts which form glasses, and are characterized by rapid increase in viscosity during cooling, show maxima in nucleation and crystal growth rates at definite temperatures. This is due to the fact that at the lower temperatures, the high viscosity acts as a barrier for the atomic rearrangements and diffusion processes which are necessary for nucleation and crystal growth. Typical curves for nucleation and crystal growth rates for a viscous melt are shown in Figure 2.

Making use of the kinetic theory of gases and the concept of thermal fluctuations, the rate of homogeneous nucleation can be expressed as (11);



Rates of nucleation and growth

Fig. 2

Rates of homogeneous nucleation and crystal growth in a viscous liquid

$$J = A e^{-\Delta F^*/kT}$$

where J is the rate of formation of the nuclei, A is a constant, ΔF^* is the maximum activation free energy for formation of these nuclei, k is Boltman's constant and T is the absolute temperature.

Berezhnoi (11) associates the appearance of nuclei for spontaneous crystallization in complex glasses with the diffusion and chemical differentiation of atoms and structural groups. This process leads to the formation of clusters in regions with a composition similar to that of the precipitating crystals. Berezhnoi proposes two mechanisms for the crystallization of multicomponent glasses. The first mechanism requires precrystallization metastable immiscibility. During the segregation process, metastable glass-forming microregions with the composition of the future crystals are formed as a result of the formation of amorphous nuclei of critical size. These regions rapidly become ordered and crystallize. In the second case microregions with the composition of the future crystals emerge in a fluctuating manner due to the increase in the thermodynamic potential. These are not stable and may become resorbed unless their ordering takes place. The formation of these regions proceeds simultaneously with their crystallization.

Homogeneous nucleation, however, is not commonly reported in crystallization studies of glasses due to the fact that it is almost impossible to have an impurity-free matrix. There always will be some impurity in the matrix. Even dust particles on the surface can act as nucleating sites and hence promote surface crystallization.

1.3.2 Heterogeneous nucleation:

Glass can be stimulated toward uniform crystallization by introducing catalyzing particles (nucleating agents). Heat treatment may be necessary for the formation of nuclei if the nucleating agent is completely soluble in the matrix. In catalyzed crystallization, the introduction of submicroscopic particles of the nucleating agent ensures a uniform fine-crystalline product. These particles are highly disperssed at a temperature lower than that required for the rapid growth of crystals of the basic crystallizing phase (11,40). Turnbull (12) modified the equation for homogeneous nucleation rate to

the form:

$$J_c = A^1 \exp \left[-(\Delta F^* f(\theta) + q)/kT\right]$$
, where A^1 is a

constant, q is the activation energy for diffusion of molecules across the phase boundary, $f(\theta)$ is a factor that determines the decrease in the surface energy as a result of the wetting and is given by;

$$f(\theta) = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4} \quad \text{and},$$

 θ is the contact angle between the liquid and the solid surface of the catalyst, and is determined by the equation for the balance of surface tensions;

$$\sigma_{\rm HL} = \sigma_{\rm SH} + \sigma_{\rm SL} \cos \theta$$
 , where

 σ_{HL} is the interfacial energy (tension) between the heterogeneity and the

melt. σ_{SH} is the interfacial energy between the heterogeneity and primary crystal phase, and σ_{SL} is the interfacial energy between the crystal phase and the melt. For any contact angle (θ) less than 180°, the free energy barrier is less for nucleus formation on the surface of the heterogeneity than for homogeneous nucleation. As a result heterogeneous nucleation will occur wherever possible in preference to homogeneous nucleation.

The criteria for the selection of an effective nucleating agent, as suggested by Stookey (13), can be summarized as follows:

1- The crystal structure and lattice parameter for the catalyst crystal and the precipitating crystalline phase should be similar. The allowable deviation in lattice parameter should be within 15%.

2- The catalyst should be readily soluble in the glass at the melting temperature, and should have limited solubility at low temperature.

3- The nucleating agent should have a higher diffusion rate at low temperatures, as compared with the major glass components; i.e., a relatively low activation free energy for the diffusion process.

4- Low free energy of activation for homogeneous nucleation from the melt at low temperatures, which is made possible by the low interfacial energy between the dissolved and the crystalline phases, and by the high degree of supersaturation during cooling.

5- A low interfacial energy at the boundary between the glass and the catalyst crystal.

1.3.3 Phase separation:

In the preceding discussion of catalyzed nucleation it is assumed that the first stage in the process is the separation of submicroscopic crystalline particles. It is highly probable, however, that an alternative mechanism, namely glass-in-glass phase separation, is a precursor for nucleation and crystallization in glass systems.

Stookey (14) pointed out that a number of glass compositions exist which in their molten states form homogeneous liquids but on cooling separate into two liquid or glass phases. In many cases one of the phases takes the form of droplets; this phase will be the one possessing the higher surface tension. In most cases, however, it is likely that two-phase separation occurs very rapidly once the glass is cooled below a critical immiscibility temperature. Two-phase liquid separation is much more likely to occur than homogeneous nucleation of crystallization from a glass. This is because the interfacial energy between two liquids is very small and may be almost zero, whereas that between a glass and a crystalline substance is quite appreciable.

In the nucleation of a liquid phase from a homogeneous liquid solution of two components, it is assumed that the nucleus forms with the equilibrium composition of one liquid phase and grows by the accretion of material from the remaining matrix liquid. The composition of the equilibrium phase is the same as the nucleating phase that forms the discrete particles. In nucleation in a two-component system, the driving force ΔP for nucleation is a function of composition and is given by (15):

$$\Delta P = G_1 - G_m - (C_1 - C_m)(\partial G/\partial C)_{cm} \qquad \text{where,}$$

 G_1 is the Gibbs free energy of the nucleating phase of composition C_1 , and G_m is the free energy of the matrix of composition C_m (normally the bulk composition).

Detailed mathematical treatments of homogeneous, heterogeneous or catalyzed nucleation, phase separation and crystal growth in glass and glass-ceramic systems are reported in the literature. Critical size equations for nucleation as well as rate formulae for nucleation and crystallization are derived in the works of Stookey (1962) (14), Vogel (1971) (2) and Filipovich (1965) (16), to mention only a few.

1.4 LITERATURE REVIEW IN GLASS-CERAMICS

A glass-ceramic is an almost ideal polycrystalline material consisting of very fine (smaller than l_{μ} in ordinary glass-ceramics and about 0. l_{μ} in transparent materials) randomly oriented crystals of almost uniform size, suspended in the matrix without voids or defects. The composition and structure of these crystals may be very diverse and not in accordance with the phase-diagram; i.e., they may be to a certain extent metastable. Their lattice may be distorted, their properties may be new and undergo a number of changes during heat treatment. Prolonged exposure of a glass-ceramic, which nearly always is a metastable crystalline glass system, to high temperatures may transform it into a stable equilibrium state. This may lead to rapid deterioration of its properties as a result of recrystallization with break-down of contacts between the crystals, further crystallization of the residual glass matrix, and grain growth.

Ohlberg et al. (18) used x-ray analysis, electron and optical microscopy techniques, to investigate the crystallization of magnesium aluminosilicate and lithium calcium silicate glasses with titanium dioxide added as a nucleating agent. They concluded that internal nucleation of these glasses is the result of phase separation occurring when the glass is

cooled from the melt. Growth of heterogeneous regions, formed to a critical size (500 Å), leads to crystallization when the glass is reheated. Such crystallization spreads from the "drop" surface either inward or into the matrix.

Goganov and Porai-Koshits (19) utilized small angle x-ray scattering techniques in the investigation of the submicroscopic strucutre of glass. They observed that under certain conditions very small heterogeneous regions (which have a radius of about 50 Ű) are formed in certain optically transparent glasses (sodium borosilicate glasses, low-alkali sodium silicate glasses and lithium silicate glasses). The size of these regions was reported not to alter during heat treatment.

Maurer (20) presented some studies on two of the many physical factors involved in the structure of partially crystallized glasses, namely the diffusion region surrounding the crystallizing centers and amorphous segregation during nucleation. He used light scattering and small angle x-ray diffraction techniques. According to Maurer, the growth of nuclei of a new phase in a viscous medium such as glass might be expected to be diffusion controlled, and thus the scattering centers become complex. In titanium dioxide containing glasses he argues that when ions more polarizable than the average ion in the glass system diffuse to the crystal, the polarization (integrated refractive index difference) of the glass is lowered by about the same amount as that of the crystal is raised. These regions, then, scatter coherently and tend to cancel, so that low light scattering results. It is thus possible to explain why many partially crystalline materials are transparent and are like glass on casual examination. Diffusion regions may also be important for liquid-liquid separations which do not easily crystallize, as in

borosilicate glasses.

Many crystallizing glasses seem to follow the path of amorphous segregation followed by the formation of crystal nuclei. While detailed knowledge of this amorphous segregation is lacking, it seems to be different from the conventional fluctuations of concentration and density encountered in glasses. Fahmy et al., (21,22), studied the magnetic properties of the glass system of the composition 68 $B_2O_3 - 17$ BaO - 15 Fe_2O_3 mole %. Structural features were analyzed using small angle x-ray scattering coupled with electron microscopy and x-ray diffraction. They reported that on tempering this glass system at a temperature of 590°C, for different times, the magnetic measurements revealed the presence of two different magnetic moments. When investigated by small angle x-ray scattering and electron microscopy, the precipitation of a complex structure of an inner core of a crystalline phase surrounded by a "grape-fruit" skin of a second crystalline phase, one of which is ferrimagnetic was evident.

Hilling (23) theoretically investigated the formation of glassceramic materials with the aid of the Tilton pentagonal-dodecahedral model of silicate glasses and concluded that a glass-ceramic may be formed from a glass of homogeneous structure without preliminary nucleation. Hintz and Kunth (24) consider that only crystallization which begins on the basis of previous phase separation creates uniform distribution of the primary nuclei and results in the subsequent uniform growth of the crystals of the main phase. An appreciable difference between the crystallization rates of the phases formed is a necessary condition. Kitaigorodskii et al., (25) based their analysis of the general relationships in the initial stages of the formation of glass-ceramics and the

description of the possible routes of the process on general thermodynamic considerations.

Roy (26) found that glass with the structure of an ideal supercooled liquid is a rare special case. Every supercooled liquid deviates to a greater or lesser extent from an ideal supercooled liquid with regard to composition, viscosity, rate of cooling, heat treatment, etc. A glass of a given composition can, according to Roy, have a number of structures with different although similar regions of short-range order. If the glass passes through a metastable region of coexistence of two liquids on cooling, it may retain the separated structure. Roy concluded that separation into two glasses is probably the only cause of possible highly dispersed nucleation and subsequent formation of glass-ceramics. Galakhov (27) considers a special type of phase separation in which microseparation (or submicroseparation) may take place when the coexisting liquids or glasses differ only in composition. Within the region of the phase diagram where these microseparation effects take place there is not a single general separation region but a number of separate, "partial" microseparation regions. As a rule they are by the side of the separation dome, which borders the immiscibility gap, and not within it. In this case, heterogeneity regions are not capable of growth during heat treatment of the glass.

Filipovich (16) considers that there is no difference in principle between micro- and macroseparation. The microseparation is a purely fluctuational effect, an initial stage of the macroseparation. In this way, Filipovich classifies the numerous heterogeneity regions from 200 -300 Å to 0.5μ in size reported by Porai-Koshits and Andreev (28), and Aver'yanov (29), in sodium silicate (Na₂0 - Si0₂) and lithium silicate

 $(Li_20 - Si0_2)$ glass systems as fluctuations. Moreover, in one-component glass systems the degree of order may be different in different nucleation regions of fluctuation. For example, Aver'yanov considers it reasonable to assume that the degree of order decreases from the center of the nucleus to its periphery. This region of order fluctuation can be called a crystallite.

Uhlmann (30) cites that crystal nucleation almost invariably takes place at external surfaces, and occasionally, at interior bubble surfaces, in glassy materials. Nucleation at external surfaces of vitreous silica has been shown to be associated with superficial condensed phase impurities, and the nucleation sometimes observed at interior bubble surfaces may well have a similar origin. Internal nucleation has occasionally been noticed after prolonged heat treatment at relatively low temperatures. The resulting crystallization was thought of as being associated with nonuniform concentrations of impurities in the melt.

When many glass-forming materials are cooled into the glassy state and then reheated to a temperature between T_g (the glass transition temperature) and T_E (equilibrium temperature which is the melting point), copious crystallization is frequently observed. Uhlmann (30) believes that homogeneous nucleation in glass-forming materials can be observed only if crystallization on heterogeneities can be avoided or its manifestations identified and eliminated. In the more general case, where crystallization is accompanied by composition changes, the techniques of controlled nucleation and crystal growth have been fruitfully employed in recent years, and form the basis of several important commercial processes (2). In many of these applications the phenomenon of liquidliquid immiscibility occurs as a precursor to the desired crystallization

process. It was reported (31-33), that in the $Li_2O-Al_2O_3-SiO_2$ glass system containing about 5 weight percent TiO_2 ; the crystallization process proceeded as follows: on cooling the glass, liquid-liquid immiscibility takes place, resulting in a phase-separated structure with a characteristic dimension of about 50 Ű. On reheating, a crystalline phase, pyrocholore $Al_2Ti_2O_7$ forms, also on a scale of about 50 Ű. These crystals apparently serve as nucleating agents for β - eucryptite $(Li_2O \cdot Al_2O_3 \cdot 2SiO_2)$ crystals, whose growth results in the formation of a highly crystalline material (31-33). At sufficiently high temperatures the β - eucryptite transforms to β - spodumene $(Li_2O \cdot Al_2O_3 \cdot 4SiO_2)$ and another minor crystalline phase may appear. The final product, a uniform, fine-grained highly crystalline material could not be obtained without heterogeneous catalytic action provided by the pyrocholore. In turn, the formation of this phase in a finely-dispersed form seems to depend upon the phenomenon of liquid-liquid immiscibility.

The process of phase separation and its effects on the properties of glasses are the subject of intense investigations at the present time (1, 15, 17). The pase separation phenomenon is expected to affect the crystallization behavior through its effects on the deriving force for crystallization, on the surface energy barrier to nucleation, and on the material transport process. Numerous articles (1, 34-36), on catalyzed crystallization of glasses have been published recently touching upon the many special problems of glass-ceramics. These problems can be solved only on the basis of more detailed information on nucleated crystallization of glasses. 1.5 <u>SELECTION OF THE BINARY BASE GLASS SYSTEM</u> $(Ba0 \cdot 4B_2 \circ 3)$

Most widely used glass systems are usually multicomponent systems, in which a combination of more than three oxides is used. Most of these systems contain one or more network-forming oxides, such as SiO_2 , B_2O_3 , P_2O_5 ; etc. one or more intermediate oxides, such as MgO, $A1_20_3$, etc. and also some modifier oxides like Na_20 , Ba0, Ca0, etc. It is very difficult to study the microstructure of these systems, and to trace the role of different nucleating agents on the host glass matrix. The presence of many possible interactions among the different species in such multicomponent systems complicate the situation. Binary glass systems have proven to be ideal for such studies due to their relative simplicity. An understanding of such microstructural variations and mechanisms in such simple systems would shed more light on the multicomponent glass systems. Based on that, a binary glass system containing 80 mole percent B_2O_3 and 20 mole percent BaO was chosen. B_2O_3 is a network-former, widely used in commercial and experimental glasses, and ranks second in use and application after SiO₂. BaO is a glass modifier, used in many commercial glass systems. Such a glass system, with the addition of the proper nucleating agent, has the potential of crystallizing various crystalline phases having attractive physical properties (21,22).

One of the obstacles to the extensive use of transmission electron microscopy in the microstructural studies of many glass systems is the instability of most glasses in the electron beam due to their electrically nonconductive nature. This makes the glass specimen vibrate due to charging. Further, low melting glasses will melt under intense beam heating. Preliminary studies on the selected barium-borate system showed

that it is very stable for electron microscopic investigations. Another encouraging feature was the relative success in finding a suitable chemical solution for thinning the glass for transmission electron microscopic observations.

1.6 SELECTION OF THE NUCLEATING AGENTS

Three nucleating agents have been chosen for this work to study their possible role and effect on the microstructure of this base glass. These agents are:

i- a transition metal oxide, titanium dioxide (TiO_2) ,

ii- a rare earth element oxide, cerium dioxide (CeO₂), and

iii- a conventional network-former, phosphorus pentoxide (P_2O_5) .

1.6.1 Titanium dioxide:

Transition metals can exist in different valence states, hence their oxides are potential nucleating agents for crystallizing glasses. Oxides of such metals as Ti, Fe, Cr, Pt, V, Zr and Pd have been studied extensively as nucleating agents. Recent interest in such agents is focused on the precipitation of crystalline phases with very highly desired magnetic and electronic properties (37-39). TiO₂ has been used extensively in precipitating very finely dispersed crystallites in ceramic materials and enamels (11,40). However, the role of TiO₂ in different glass systems can vary. For example; Tomozawa (34,35) reported that TiO₂ did not enhance phase separation in alkali-silicate glasses, but rather may even supress it drastically.

McMillan (40) explains the process involved in titania-catalyzed crystallization of glasses by two different approaches. In the first

explanation, based on homogeneous and heterogeneous nucleation arguments, McMillan suggests that the first stage in the process is the separation of a titania-rich glass phase. The tiny droplets of this phase possibly separated during initial cooling of the glass melt. The separated titaniarich phase is unstable and hence, crystallizes probably by homogeneous nucleation during the reheating of the glass. These crystalline particles which are in a highly dispersed state, then heterogeneously nucleate the crystallization of a major phase from the glass. In the second explanation, in terms of the structural role of the titanium ion, McMillan (40) cites the explanation by Weyl (41). At high temperatures the titanium ion assumes tetrahedral coordination, thus being able to take part in the network of the silicate glass. At lower temperatures, however, the titanium ions tend to assume its equilibrium coordination number of six and in doing so they will no longer be able to occupy network-forming positions. Thus titanium dioxide will separate from the network and forms either a separate phase or combines with another oxide.

The choice of TiO₂ as a nucleating agent in this binary system was made to identify its role as a nucleating agent on the microstructure variations of this glass matrix and in hope of being able to precipitate - by appropriate heat treatment - compounds which exhibit interesting physical properties.

1.6.2 Cerium dioxide:

Rare-earth elements also can exist in different valence states and their oxides are useful nucleating agents. Oxides of rare-earth elements have not yet been explored extensively as crystallization catalysts in glass-ceramics. Cerium dioxide has been used as a catalyst in

photosensitive glasses. It is believed that cerium dioxide promotes both phase separation (in cerium phosphate and lead borate glasses), and crystallization in some other glass systems (e.g. lead silicate system) (42). It has been suggested that the cerous ion may be entering the network structure; whereas the ceric ion may exist in the modifying position in these glasses. The latter is believed to catalyze nucleation in lead borate, lead silicate and cerium phosphate glasses.

The role of cerium dioxide additions to glass systems especially on the phase separation and/or crystallization, is believed to depend mostly on the host glass matrix (42). Comparison of the nucleation characteristics of CeO₂ as a nucleating agent with those of a transition metal oxide, TiO_2 , may shed some light on the basic theories of nucleation. Glasses with small additions of CeO₂ have proved to have attractive optical and photosensitive properties (43-46). It is hoped that the addition of CeO₂ to the selected base glass system may yield similar properties.

1.6.3 Phosphorus pentoxide:

Phosphorus pentoxide is a glass network forming oxide that exhibits the qualities of a nucleating catalyst. Tomozawa (34) reported that P_2O_5 , on being added in low concentrations, has promoted only phase separation in alkali-silicate glasses. Many studies on different glass systems containing P_2O_5 as nucleating agent have been reported in literature. McMillan and Partridge (40) studied the use of metallic phosphate to catalyze the crystallization of a wide range of glass compositions derived from the Li₂O-Al₂O₃-SiO₂, Li₂O-MgO-SiO₂, MgO-Al₂O₃-SiO₂, and Li₂O-SiO₂ glass systems. James and McMillan (84) studied the early stages of crystallization of the Li₂O-SiO₂-P₂O₅ glasses where the electron microscope technique revealed the presence of several small single crystals joined together around a core.

McMillan explains the role of P_2O_5 (40) as a nucleating agent in silicate glass network. The phosphorus ion P^{5+} assumes tetrahedral coordination and therefore provides an example of phase separation due charge difference betwen the principal network-forming ions, Si⁴⁺, and the P⁵⁺ ions. McMillan argues that if the phosphorus - oxygen bonds were all single bonds of the P - 0 type electroneutrality could not be ensured, so that one P - 0 bond per PO₄ tetrahedron would have to be doubly bonded. This process of double-bonding within the silicate network creates conditions favoring separation of phosphate grouping from the silicate network. So, the role of P₂O₅ as an effective nucleating agent has been a matter of controversy (34,40). Phosphorus pentoxide has been selected in this study as a nucleating agent in order to verify the role of an element which has a fixed valency and fixed coordination number against those possessing multi-valent and variable coordination number.

1.7 PURPOSE OF CURRENT RESEARCH

Crystallization of a glass matrix to produce partially or completely crystallized glass-ceramic material can be achieved through nucleation (homogeneous, heterogeneous or catalyzed) and/or phase separation. The mechanism by which this is achieved depends also on the host glass matrix as well as its thermal history. The primary aim of this investigation is to study the effect of different nucleating agents on a binary barium-borate glass system and to investigate their role in the nucleation, phase separation and crystallization. The nucleating
agents chosen for this purpse are:

i- a transition metal oxide, TiO₂,

ii- a rare-earth oxide, CeO₂ and

iii- a network-former oxide, $P_2 0_5$.

The role of P_2O_5 as a nucleating agent that exists in a fixed valency and coordination number will be compared with that of both TiO₂ and CeO₂, which exist in variable valency and coordination states. This will determine whether the existance of the nucleating agent in more than one valence state would enhance crystallization and or phase separation. Furthermore, a comparison between cerium oxide and titanium dioxide should indicate whether there is any significant difference - in their role as nucleating agents - between a rare-earth and transition metal cation, although both can exist in variable valence state having variable coordination numbers.

Another aim is to check whether glass-in-glass phase separation is a precursor to crystallization in this glass. The role of the nucleating agents on the nucleation and growth rates will be studied. The ultimate goal is to check the results against available theoretical models of nucleation and growth with the hope that the results may provide more insight on the fundamental mechanisms of nucleation and crystallization in glass systems.

CHAPTER II

EXPERIMENTAL PROCEDURE

2.1 GLASS PREPARATION

The glass samples used in the course of this study were prepared in two steps from analytical reagent grade chemicals, shown in Table 1. First, the binary base glass batches of composition $Ba0.4B_2O_3$ were prepared. Powders of B_2O_3 and $BaCO_3$ of the appropriate proportions were mixed thoroughly using a ceramic mortar and pestle for sufficient time to ensure homogeneous mixing. The batch was then transfered to a platinum crucible which was placed in a furnace at a temperature of 2280°F (about 1250°C) in an air atmosphere. As sintering of the mixed powders occurred, the batch volume decreased and additional batch material was added every 5 - 10 minutes to produce sufficient volume of the melt. After building the required charge and reaching the molten state, the batch was left at the melting temperature for ninety minutes to ensure homogeneity. After this period, the melt was quenched rapidly in air between two slabs of stainless steel maintained at room temperature. The resulting glass was used as the base glass for preparation of all the glasses studied here. In the second step, glasses having the nucleating agents in their respective proportions shown in Table 2 were obtained. To prepare the glasses containing the nucleating agents, the

Table l

Starting Chemical	<u>Purity %</u>	Lot Number and Supplier
Boron Trioxide B ₂ 0 ₃	100	787842
(Boric Acid Fused)		Fisher Scientific
Barium Carbonate BaCO ₃	99.1	Baker
Titanium Dioxide	99.97	28365
Ti0 ₂		Baker, J. T.
Cerous Oxalate	99.9	21122
Ce ₂ (C ₂ 0 ₄) ₃ •9H ₂ 0		ALFA Inorganic (Ventron)
Ammonium Phosphate (monobasic)	99.97	Mallinckrodt
NH4H2PO4		

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Table 2

Glass Compositions

Glass	Initial Composition				Final Composition					
Code	(mole %)			(mole %)						
	^B 2 ⁰ 3	Ba0	т10 ₂	Ce02	P2 ⁰ 5	^B 2 ⁰ 3	BaO	^{T10} 2	Ce02	^P 2 ⁰ 5
BBa	80 .0	20.0	0.0	0.0	0.0	80.0	20.0	0.0	0.0	0.0
BBaT12	80.0	20.0	2.0	0.0	0.0	78.4	19.6	2.0	0.0	0.0
BB a TilO	80.0	20.0	10.0	0.0	0.0	72.0	18.0	10.0	0.0	0.0
BBaCe2	80.0	20.0	0.0	2.0	0.0	78.4	19.6	0.0	2.0	0.0
BBaCe10	80.0	20.0	0.0	10.0	0.0	72.0	18.0	0.0	10.0	0.0
BBaP0.5	80.0	20.0	0.0	0.0	0.5	79.6	19.9	0.0	0.0	0.5
BBaP2	80.0	20.0	0.0	0.0	2.0	78.4	19.6	0.0	0.0	2.0

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base glass was crushed into a fine powder using a ball mill. The nucleating agents were then added in the powder form in proper proportions. Again the new mixture was mixed thoroughly using the morter and pestle to prepare batches of the new glass. These batches were transferred to a platinum crucible and heated to 2280°F (about 1250°C) to melt the glass. They were held at this temperature for the same length of time as the base glass. This was used as a standard practice in preparation of all the glasses used in this study so as to have these glasses subjected to the same initial treatments. The same technique of air quenching between the two stainless steel slabs was used to obtain sheets of glass of thickness of about 1 - 2 mm. The resulting glass sheets were optically transparent and visually homogeneous. Only in the case of glasses containing the highest concentration of phosphorus pentoxide (2 mole percent P_2O_5) was the resulting glass recrushed and melted for the third time to ensure homogeneity. This glass was noticed to be visually inhomogeneous, having light blue ribbons of phase separated material after melting for the second time. These ribbons disappeared after the third melt, and the resulting glass was then believed to be homogeneous.

During the preparation of these glasses, boron oxide was introduced as fused boric acid (B_2O_3) . Barium oxide was introduced as barium carbonate $(BaCO_3)$, which dissociated into BaO and CO_2 . The effervescence, due to the evolution of CO_2 , greatly helped in stirring the melt during glass preparation and hence contributed to producing a homogeneous glass. Titanium dioxide was introduced as TiO_2 and cerium oxide was introduced as cerous oxalate $[Ce_2(C_2O_4)_3 \cdot 9H_2O]$. Phosphorus pentoxide was introduced as ammonium dihydrogen phosphate $(NH_4 H_2 PO_4)$ to avoid the rather

hygroscopic and reactive phosphorus pentoxide.

2.2 HEAT-TREATMENT SCHEDULES

The heat treatments were carried out by placing small pieces of the glass in graphite crucibles. The graphite crucibles were then placed at the desired temperature in the pretested steady temperature zone of the furnace, for the desired length of time. At the end of the heat-treatment time, the heat treated glasses were quenched in air by placing them quickly on top of a stainless steel slab at room temperature. In order to avoid any variations all the glasses that needed to be heat treated at the same temperature for the same length of time were heat treated simultaneously. Most of the glasses having different nucleating agents exhibited visual color changes, especially after prolonged heat treatment at high temperatures.

2.3 ELECTRON MICROSCOPIC OBSERVATIONS

The electron microscope is a powerful tool for investigating the microstructure in many metallic systems. Sample preparation techniques for the preparation of thin samples of such systems are well developed. Electro-chemical polishing is the most widely used method for preparing metallic foils. A major advantage of transmission electron microscopy in studying the microstructure, is the availability of the powerful selected area diffraction technique to identify the crystalline phases present. In this method the electron diffraction pattern of an area under investigation can be obtained. Thus, whether the phases present are crystalline or amorphous can be verified easily.

The major handicap in the use of the electron microscope in

investigating glass and glass-ceramic microstructures is the difficulty in thin sample preparation of such materials. Some of the techniques that are used currently in preparing samples thin enough to transmit the electron beam from glass and glass-ceramic materials are:

i- The powder method (40): in this method fine glass powder held on support films is used. The major criticism of this method is that, in some glass-ceramic systems, the crystalline phases may separate out on crushing, thus providing misleading information about the microstructure.

ii- Blown glass films (40): in this method, blown glass films are given the required heat treatments and then transferred to the electron microscope. The disadvantage of such a technique is that the changes that may take place in such thin films may not be a true representative of the bulk.

iii- Mechanical polishing (88,89): extensive mechanical polishing by various time consuming methods can be used to provide thin films for electron beam transmission.

iv- Ultramicrotomy (90,91): thin foils can be prepared by cutting the glasses with diamond blades and this is a suitable method for soft glasses. It becomes more difficult for hard glass systems as the one used in the present study.

v- Ion thinning (91): the specimen can be thinned by continuous bombardment with accelerated ions. The major disadvantage in the use of this technique is that it takes a long time to produce the desired thin samples and there may be radiation damage to the prepared samples.

vi- Chemical thinning (92,93): different chemical thinning techniques to obtain thin samples of nonmetallic materials and glasses

were developed by many researchers. Some of the successful methods were those developed by Washburn et al., (93), and by James and McMillan (92). The major difficulty in these procedures is to find the right chemical solution for the systems under investigation. Since glass systems exhibit different and wide range of compositions, each system by itself needs a different chemical solution for thinning. One of the main requirements of the solvent is that it must not preferentially attack the glass system under investigation. Preferential attack may lead to dissolving completely or to a great extent one or more of the components in the system and hence lead to a false representation of the microstructure. The standard way of obtaining the proper chemical solution is by trial and error to suit the glass system under investigation. Once the proper chemical solution is found, the thinning process itself requires only a short time, in most cases. Further, it gives the true microstructure that represents the bulk.

vii- Replication techniques (91): the replica of the surface to be studied can be prepared by well developed techniques. Etched surfaces can be replicated to reveal their microstructural features. One or two-stage replicas could be utilized in practice. In the first method, a carbon film is deposited directly on the surface to make an impression of it. The film is then floated with hydrofluoric acid (for glass specimens), picked up on a microscope grid, washed, and then used for observation. This method provides a negative impression of the true surface. In the second method a positive impression of the surface is produced. First, the features of the surface are transferred onto a cellulose acetate tape. Thin carbon film is then deposited on the tape using an evaporator. Finally, the cellulose tape is dissolved in

acetone, and the positive replica of the surface as present in the carbon film can be used for observation. In both methods of replication, a heavy metal (Pt, Cr, or Pt-Pd) is used to preshadow either the surface or the cellulose acetate tape to improve the contrast of the features on the carbon film. The major criticism of the replication techniques is that the replicas represent surface features only, and that they may or may not be representative of the bulk.

James and McMillan's (92) thinning procedure was slightly modified and used during the course of this study. Glass sections of about one to two millimeters thick were suspended in the chemical solution by tweezers. The chemical solution was placed in a beaker placed in a water bath to keep the temperature of the solution uniform. The temperature of the bath was maintained at about 40°C. The solution was stirred with a magnetic stirrer to produce an agitation effect and to remove the chemical reaction products away from the reaction area. The thinning was usually continued until perforation occurred in the glass sample. Perforation, usually occurred simultaneously at more than one point in the sample. Great care should be devoted to watching the specimen at the final stage of thinning. The sample should be removed and washed with distilled water as soon as the first perforation takes place; otherwise, continued thinning may result in rounding off the thin edges of the perforated area. Regions around these perforations have wedge-shaped areas, thin enough for electron transmission. This method yielded relatively large areas thin enough for transmission electron microscope observations. The most suitable chemical solution for the glass systems used in this study was found to be a solution of 4% nitric acid in water. Fortunately, there was no need to search for a new chemical solution for glasses

having different nucleating agents studied in this work. The time needed for preparation of the thin samples by this method ranged between 15 minutes to two hours, depending on the glass used. The major difficulty surmounted, mainly by experience in this work, was the means by which the thin areas were transferred to the electron microscope grid. These thin areas were identified by using a light microscope by observing the extinction fringes around the perforations. A microscope grid was then placed under the thin area and its position was rechecked with the optical microscope. The thin area was then chipped onto the grid using the sharp edge of the tweezers. With great care, another microscope grid was placed on top of the chipped glass sample. The two copper electron microscope grids sandwiched the sample in between, preventing it from falling during the final transfer to the specimen holder. Another important reason for sandwiching the thin glass specimen between the two copper grids was to minimize the charge build up on the glass surface during electron bombardment in the electron microscope. Otherwise, due to the poor electrical conductivity of the glass, electrostatic charge builds up in the sample, making it to vibrate.

Two stage preshadowed carbon replicas were also used during the course of this study. Platinum preshadowing was used to enhance the contrast. The freshly fractured glass surface was etched with 5% HF in distilled water for 10 - 15 seconds to reveal the surface microfeatures.

In preparing the samples for electron microscope observations, great care must be exercised to eliminate the artifacts due to preparation, which can give misleading information.

2.4 OPTICAL MICROSCOPIC OBSERVATIONS

Some of the glass samples used in this study exhibited extensive grain growth on prolonged heat treatment at high temperatures. Due to the size of these crystals, optical microscopy had to be used to study the microstructures. For this purpose, samples were mounted on metal substrates by means of bees wax. The surface of the samples was then polished through the standard metallurgical polishing procedure. Grinding was done with abrasive papers having grits 240 (about 45μ), 320 (about 37μ), 400 (about 25μ) and 600 (about 15μ). The specimens were finally polished in the polishing wheel with 0.3μ and 0.05μ alumina powder. The polished surfaces were then etched with 10% HF solution in water for 30 seconds so as to reveal the microstructures. The surface was then studied with an optical microscope at various magnifications.

2.5 X-RAY POWDER DIFFRACTION ANALYSIS

X-ray diffraction of powders has always been a powerful tool in the positive identification of crystalline materials. Since each material has a distinct powder pattern, x-ray diffraction can be used to check for crystallinity (the glass by itself yields diffuse x-ray patterns). On the other hand, crystalline materials have distinct sharp peaks at specific Bragg angles. The position of these peaks and their relative intensities can be used to identify the crystalline phases present. X-ray diffraction, however, can only identify the crystalline phases that exist in sufficiently large volume fraction of the material, since the intensity of the diffracted peak depends, among other factors, on the amount of the crystalline phase present.

In this study, the glass samples were crushed to fine powders (100

mesh size), and x-ray diffraction patterns were obtained using the G.E. XRD-6 diffractometer with Cu K α radiation.

Thin films for transmission electron microscopy were obtained by chemical thinning. Two stage plastic-carbon replica, optical microscopy, electron and x-ray diffraction were used to study the phase separation, nucleation and crystal growth in the various barium borate glasses used in this work. All these techniques combined gave a cross-check on each other, especially in the case of having any superficial features or artifacts in any stage of either preparation or observation.

2.6 QUANTITATIVE ANALYSIS

The average size of the precipitated phases was directly measured off electron micrographs of the heat treated glass samples. Random selection of a large number of particles was made, and their sizes were averaged out and taken as the average particle size (this is represented by symbol D throughout this work). A point count method was used to calculate the volume fraction, V_{f} , of the precipitated phase particles. A square 16 point grid was used; the number of particles that coincided with the intersections of the grid lines were counted, and the ratio was obtained. This process was repeated 10 - 15 times for each sample by moving the grid across the electron micrograph in equi-spaced intervals. Finally averaging the calculated ratios yielded a measure of the volume fraction (represented by the symbol V_f throughout this work).

In calculating the number of the precipitated phase particles per unit area a different size square mesh representing an area of one square micron was used. The number of particles falling in the square area was counted. Again the squares were moved in equi-distance steps, and the

particles counted again. The average was obtained after ten similar moves. The number of particles per unit area will be referred to as N. The number of particles per unit volume, referred to as N_v , was then obtained - following a similar analysis used by Tomozawa (35) - from N using the relation:

$$N_{\rm M} = N/(D + \Delta)$$

where D is the average diameter of the spherical particle and Δ is the thickness of the thin glass sample, which was assumed to be, for all practical purposes, almost the same for all glass samples used (about 1000 Ű). Actually, the chemical thinning method used in this study produces wedge-shaped thin foils. Considering a uniform sample thickness, however, is an approximation.

During heat treatment, the phase-separated regions present in the glasses under investigation will not only experience variations in size, volume fraction etc. but also will experience variations in their composition. The change in composition during heat treatment will continue until crystallization takes place in the phase-separated regions. Such compositional variations, however, cannot be identified with the techniques employed in this work.

CHAPTER III

EXPERIMENTAL RESULTS

3.1 BARIUM BORATE BASE GLASS (Ba0.4B₂0₃)

3.1.1 Microstructural studies:

Electron micrographs displaying the microstructure of the as-quenched base glass are shown in Figure 3. The average size of the inhomogeneities present in this glass, as shown in the transmission electron micrograph of Figure 3(A), was about 411 A. In Figure 3(B) a two-stage, platinum preshadowed replica electron micrograph is shown. This micrograph displays the same microstructural features of the asquenched base glass. The average size of the inhomogeneities was found to be about 442 A° , which agrees very well with the size calculated from the transmission electron micrograph of Figure 3(A). These inhomogeneities are of glass-in-glass phase separated areas. The microstructures observed after five, twenty-four and seventy-two hours of heat-treatment at 450° C are illustrated in Figure 4(A), (B), and (C) respectively. Dark, almost spherical, regions of the size of about 388 Å are shown in Figure 4(A). The absence of a sharp electron diffraction pattern of this structure indicates that these regions are glass-in-glass phase separated areas. These dark areas became distinct on further heat treatment, as shown in Figure 4(B). The average size of these areas was found to be





Fig. 4

Transmission electron micrographs of the base glass heat treated at 450 C (A). for 8 hours (B). for 24 hours (C). for 72 hours The electron diffraction pattern belongs to the selected area shown in Fig. 4(C).

about 218 Å. It appears that the glass-in-glass phase separated areas of Figure 4(A) have started to experience some sort of nucleation process enroute to crystallization. Figure 4(C) illustrates the development of crystalline particles of the size of about 137 Å, after 72 hours of heat treatment. The sharp electron diffraction pattern of this specimen shows the crystalline nature of various areas. Analysis of the electron diffraction pattern, coupled with that of the x-ray diffraction pattern, identifies the crystalline phases present as being boron oxide (B_2O_3) and barium boron oxide (BaB_2O_4) .

The microstructural changes experienced by the base glass during heat treatment at 500°C are shown in Figure 5. As shown in Figure 5(A), after one hour of heat treatment at 500°C, the base glass phase separates. Small dark inhomogeneities of the size of about 123 Å separate out. These regions become more distinct after heat treatment of the glass for eighty hours and segregate into larger clusters as shown in Figure 5(B). The size of the small particles at this stage is about 210 Å, while that of the segregated areas is about 772 Å. Even after 120 hours of heat treatment at 500°C, this glass did not crystallize. However, the phase separated regions appear to have a smaller size as shown in Figure 5(C). The size of these regions is found to be 177 Å, and are more uniformly distributed. Longer heat treatment for 152 hours at this temperature leads to a more distinct separation of these phase separated regions which are about 160 Å in size, as shown in Figure 5(D). No apparant crystallization, however, has taken place.

Figure 6(A), (B), (C) and (D), displays the sequence of microstructural changes of the base glass when heat treated at 590° C for thirty minutes, one, five and eighty hours respectively. Again, phase separated



regions of the sizes 338, 408, 293 and 267 A[°] are shown in the micrographs of Figure 6. The absence of sharp electron diffraction pattern indicated that these are glass-in-glass phase separated regions.

In the samples heat treated for ten minutes at 650°C, it was noticed that the size of the precipitated regions, was much smaller (135 \mathring{A}), than that of the regions present in the as-quenched base glass (411 \mathring{A}). Even at the early heat treatment times of one and five hours, there is not much change in the size of these regions (129 and 185 \mathring{A} respectively). A drastic change in the microstructural features shows after ten hours of heat treatment at 650°C. The predominent feature is, the precipitation of light areas (462 A° in size) with smaller dark interconnected regions in the background. This sequence of the microstructure changes is illustrated in Figure 7(A), (B), (C) and (D). The complete crystallization of the base glass into large grained crystals was finally achieved by heat treatment at 650°C for 24 hours. The crystalline phases were identified as boron oxide (B_2O_3) , and barium boron oxide $(Ba B_2 O_4)$ by x-ray diffraction. This microstructure is shown in the optical micrograph of Figure 7(E).

3.1.2 Quantitative analysis of the microstructure of the base glass:

Table 3 displays the average particle size (D), the volume fraction (V_f), number of particles per one square micron (N) and per unit volume (N_v), for the base glass after different heat treatment schedules. The plot of the average size (D) against heat treatment time (for each heat treatment temperature) is shown in Figure 8. The sizes observed at the maximum peaks are believed to be the size of the glass-in-glass phase separated regions. The minima may be associated with the



Transmission electron micrographs of the base glass heat treated at 590°C (A). for 30 minutes (B). for one hour (C). for 5 hours (D). for 80 hours Electron diffraction pattern belongs to the selected area shown in Fig. 6(D).



Fig. 7

Transmission electron micrographs of the base glass heat treated at 650°C (A). for 10 minutes (B). for one hour (C). for 5 hours (D). for 10 hours Electron diffraction patterns polarities selected areas shown in Fig. 7(C) and (D).



Fig. 7 (continued)
(E).Optical micrograph of the base glass heat treated at
(E).Optical micrograph of the base glass heat treated at
650°C for 24 hours.

Table 3

Heat Treatment	Time	N	N _v x10 ⁻⁸	D.	۷ _f	
Temperature	Hour	#/µ ²	#/Å ³	Å		
As-quenched		313 362	0.22 0.25	411 442	0.81 0.88	*
450°C	8 24 72	1213 1081 1309	0.87 0.89 1.15	388 218 137	0.76 0.72 0.59	
500°C	1 80 80 120 152	2720 374 1242 1242 1309 1091	2.42 0.29 1.03 0.70 1.11 0.94	123 300 210 772 177 158	0.63 0.76 0.78 0.78 0.89 0.82	* S Sa
590°C	1/2 1 5 80	277 742 326 509	0.21 0.53 0.23 0.40	338 408 393 267	0.32 0.30 0.34 0.58	
650°C	1/6 1/2 1 5 10	1437 128 2112 1328 373 579	1.27 0.10 1.87 1.12 0.26 0.46	135 335 129 185 462 362	0.58 0.20 0.94 0.73 0.55 0.40	1 d
N : number per N _v : number per	one s unit	quare mi volume.	cron area.			

Quantitative analysis of the microstructure of the barium borate glass system.

,	•	Sindiri	pur creres.	Lu	•	large areas
	•	light	aroac	А	•	dark aroas

D^V: average particle size. V_f: volume fraction. S^f: small particles. La : large areas. l : light areas. d : dark areas. * : data taken from replica electron micrographs.



of the barium-borate base glass.

onset of crystallization by the nucleation process. Activation energy calculations derived from plots of Log N_v vs. 1/T, for this glass system, will be shown and discussed in a later chapter.

3.2 BARIUM BORATE GLASSES CONTAINING TITANIUM DIOXIDE

3.2.1 Glass containing two mole percent titanium dioxide3.2.1.1 Microstructural studies:

Phase separated particles of about 160 Ű in size are the predominent feature in the transmission electron micrograph of the asquenched glass containing 2 mole percent TiO₂ shown in Figure 9(A). However, a few large segregated regions (about 670 Ű size), marked by "X" on the micrograph, were also observed. Figure 9(B) illustrates the microstructure of the same glass as revealed by the replica electron micrograph. Small particles in the background are of about 198 Ű in size and a few larger particles of an average size of about 670 Ű are also present. Seventy-two hours of heat treatment at 450°C produced distinct microcrystals of the size of about 170 Ű, as shown in Figure 9(C). The crystallinity of the precipitated phase was verified from electron diffraction. Analysis of the electron and x-ray diffraction patterns of the crystalline phases indicates that the crystalline phases present are barium titanate (Ba_2TiO_4 and $BaTiO_3$) and barium boron oxide (BaB_2O_4).

Heat treating this glass at 500°C for ten hours resulted in the microstructure shown in Figure 10(A). The transmission electron micrograph reveals dark, almost sperical regions with an average size of 213 Ű as well as light regions with an average size of 273 Ű. It is believed that the dark regions are barium-rich regions, whereas the light ones are boron-rich (or barium depleted) regions. The absence of a sharp electron



Fig. 9

- (A). Transmission electron micrograph of the as quenched barium-borate glass containing 2 mole% titanium dioxide.
- (B). Two stage preshadowed replica electron micrograph of the same glass shown in (A).
- (C). Transmission electron micrograph of the barium-borate glass containing 2 mole % titanium dioxide heat treated at 450 $^{\circ}\mathrm{C}$ for 72 hours.

Regions marked X in (A) and (B) indicate large segregated phase separated areas.



Transmission electron micrographs of the barium-borate glass containing 2 mole% titanium dioxide heat treated at $500^{\circ}C$ (A). for 10 hours (B). for 24 hours (C). for 80 hours. Electron diffraction pattern belongs to the selected area shown in Fig. 10(C). diffraction pattern indicated that these regions are glass-in-glass phase separated regions. On further heating of the glass at the same temperature for 24, and 80 hours, the phase separated regions became larger and more distinct. After eighty hours of heat treatment the average size of the dark regions was found to be about 368 Ű, while the size of the light regions became 518 Ű. This is shown in Figure 10(C). The electron diffraction pattern given in this figure indicates crystallization. The crystalline phases were identified as barium titanate (Ba Ti 0_3) and barium boron oxide (Ba B₂ 0_4).

Heat treatment of the glass containing two mole percent TiO₂ at 590°C for different periods of time resulted in the microstructural features shown in Figure 11. The replica electron micrograph of the sample heat treated for ten minutes and shown in Figure 11(A) reveals the presence of dark regions of average size of 256 Å. The microstructure remained almost unchanged after 30 minutes of heat treatment at 590°C as illustrated by the transmission electron micrograph shown in Figure 11(B). The average size of the dark areas present in this micrograph is about 224 A. Further heat treatment at 590°C for one hour resulted in well defined, almost spherical dark regions with an average size of 620 Å, as shown in the replica electron micrograph of Figure 11(C). Those dark regions shown in Figure 11(A), (B), and (C) are glass-in-glass phase separated areas. These phase separated areas lead to crystallization of this glass on further heat treatment at 590°C for longer times. The microstructure of the glass after five hours of heat treatment at 590°C is shown in Figure 11(D). The average particle size was found to be 290 A. The spotty electron diffraction pattern shown in Figure 11 is for the selected area shown in Figure 11(D). Again, the crystalline phases present were



Fig. 11

Electron micrographs of the barium-borate glass containing 2 mole% titanium dioxide heat treated at 590 C (A). for 10 minutes (replica)

- (B). for 30 minutes (TEM)
- (C). for one hour (recli a



identified as barium titanate and barium boron oxide. Figure 11(E) is the microstructure of the glass heat-treated for ten hours at 590°C. The average particle size in this figure is about 270 Ű. Finally, treatment of the glass at 590°C for eighty hours gave rise to opaque spots in the matrix. The microstructure of this specimen is shown in Figure 11(F). The structure of the left over glassy areas in the matrix has inhomogeneities of the size of 168 Ű. The large crystals grown in this glass matrix, however, are best seen in the optical micrograph of Figure 11(G), which illustrates that the structure is mainly composed of large crystals (indicated by an arrow) with average size of 2.5 microns embedded in a glassy matrix. These crystals correspond to the crystalline regions (marked areas) in the transmission electron micrograph shown in Figure 11(E).

The transmission electron micrographs, shown in Figure 12(A), (B), (C), and (D), represent the microstructural features of this glass when heat treated at 650°C for ten minutes, thirty minutes, one hour, and five hours, respectively. Dark particles of 283 Å[°] in size are seen dispersed in the microstructure shown in Figure 12(A) after ten minutes of heat treatment. These regions crystallize ultimately, on further heat treatment for longer times, and acquire sizes of 237 Å[°], 142 Å[°], and 103 Å[°] when heat treated for thirty minutes, one hour, and five hours respectively, as shown in Figure 12(B), (C) and (D). Electron diffraction patterns indicate that crystallization has started in the specimen heat-treated for five hours. Further heat treatment of this glass for eight hours leads to the precipitation of large crystals with little of the glassy matrix left over. These crystals are shown in the optical micrograph of Figure 13(A) and are about 2.3 microns in size. Figure 13(B) displays



Transmission electron micrographs of the barium-borate glass containig 2 mole% titanium dioxide heat treated at 650 $^{\circ}\mathrm{C}$

(A).	for 10 minutes	(B).	for	30 minutes
(C).	for one hour	(D).	for	5 hours



Fig. 13

Optical micrographs of the barium-borate glass containing 2 mole% titanium dioxide heat treated at $650^{\circ}C$ (A). for 8 hours (B). for 10 hours

the presence of 659 micron size crystals with very little of the glassy matrix after ten hours of heat treatment. The crystalline phase was identified as barium titanate and barium boron oxide.

3.2.1.2 Quantitative analysis of the microstructure of the glasses containing two mole percent TiO₂:

The average size (D) as well as the volume fraction (V_f) number per one square micron area (N) and per volume (N_v) of particles present in the barium borate glass containing two mole percent titanium dioxide are listed in Table 4. Figure 14 displays the plots of D in A° vs. heat treatment temperatures. The curve for 590°C heat treatment exhibits a maximum at about one hour, which is believed to signify the phase separation process leading to crystallization on prolonged heat treatment. The plot for the 650°C heat treatment exhibits a minimum at about five hours and then rises sharply. The minimum is believed to correspond to the nucleation process, and the sharp rise is more likely to indicate that this temperature is the growth temperature for the crystalline phases precipitated. Plots of log N_v vs. 1/T as well as activation energy calculations will be discussed later in Chapter IV.

3.2.2 Glasses containing ten mole percent titanium dioxide:

3.2.2.1 Microstructural studies:

The microstructure of the as-quenched glass containing ten mole percent TiO₂ is shown in Figure 15(A). The average size of the dark regions present in the glass was found to be about 157 A°. The microstructure of this glass after heat treatment at 450°C for 72 hours is presented in Figure 15(B). The predominent feature of the

Table 4

Quantitative analysis of the microstructure of the barium borate glass containing two mole percent titanium dioxide.

Heat Tr	reatment	Time	N	N _v x10 ⁻¹	8 D	۷ _f	
Tempera	iture	hour	#/µ ²	#/A ^{°3}	Å		
As-quen	iched		1165 387 34	1.01 0.32 0.02	154 198 672	0.45 0.59 0.13	* S * La
450°C		72	1850	1.58	168	0.46	
500°C		10 24 80	454 1187 174 461	0.36 0.98 0.12 0.34	273 213 518 367	0.18 0.81 0.31 0.62	1 d 1
590°C		1/6 1/2 1 5 10 80 80	864 1264 44 778 471 845	0.69 1.03 0.03 0.60 0.37 0.72	256 224 620 290 270 168 2.5m	0.56 0.68 0.20 0.49 0.58 0.47 0.44	* * 0
650°C		1/6 1/2 1 5 8 10	479 1587 2982 4608	0.37 1.28 2.61 4.18	283 237 142 103 2.3m 659m	0.55 0.61 0.53 0.60 0.68 0.53	0 0
N : NV : Vf : Sf :	number pe number pe average p volume fi small pan	er one ser unit particle raction. rticles.	quare n volume size.	nicron ar • La :	ea. size in m large par	nicron. ticles	

- l : light areas.
 d : dark areas.
 data taken from optical micrographs.
 * : data taken from replica electron micrographs.






Transmission electron micrographs of the barium-borate glass containing 10 mole% titanium dioxide

- (A). as quenched
- (B). heat treated at 450°C for 72 hours

microstructure as displayed by Figure 15(B) is the presence of small crystalline phase of about 158 A° in size.

The sequence of microstructural changes as exhibited by this glass when heat treated at 500°C for different times is shown in Figure 16. In Figure 16(A) the transmission electron micrograph reveals the microstructure of the glass heat treated for five hours. The average size of the dispersed phase is about 337 Å. There exist, however, some large globules of approximately 0.15 micron in size. On further heat treatment at the same temperature for ten and twenty-four hours, the average sizes became 163 Å and 178 Å respectively as shown in Figure 16(B) and (C). The electron diffraction pattern of the selected area of Figure 16 (A) indicates the onset of crystallization in this system at this temperature and time of heat treatment. The optical micrograph of this glass shown in Figure 16(E), when heat treated at 500°C for eighty hours, reveals a structure with average size of about 1.6 microns.

Figure 17 illustrates the microstructural changes as experienced by the glass containing ten mole percent TiO_2 when heat treated at 590°C for different periods of time. After ten minutes of heat treatment at 590°C, fine particles were found dispersed in the glass matrix. The average size of these particles is about 72 Ű and the microstructure having these aprticles is shown in Figure 17(A). The dark dispersed regions, shown in the transmission and replica electron micrographs given in Figure 17(B) and (C), are glass-in-glass phase-separated areas. After heat treatments for thirty minutes and one hour the average sizes are 79 Ű and 255 Ű, respectively. The precipitated phases apparently started to crystallize at longer heat treatment times of two, five, and ten hours at 590°C as shown in Figure 17(D), (E) and (F); the respective



Transmission electron micrographs of the barium-borate glass containing 10 mole% titanium dioxide heat treated at 500 $^\circ\text{C}$

- (A). for 5 hours
- (B). for 10 hours
- (C). for 24 hours



- Fig. 16 (continued)
 - (D). transmission electron micrograph of the barium-borate glass containing 10 mole% titanium dioxide heat treated at 500° C for 80 hours.
 - (E). optical micrograph of the same glass heat treated at 500 $^\circ\mathrm{C}$ for 80 hours.



- (A). for 10 minutes
- (B). for 30 minutes
- (C). for one hour



particle sizes were 130 Ű, 183 Ű, and 320 Ű after these treatments. The crystallinity of these precipitated phases was identified by the electron diffraction patterns showed in Figure 17. The crystalline phases present were identified as barium titanate ($BaTiO_3$) and barium boron oxide (BaB_2O_4). After the longest heat treatment time of eighty hours at 590°C, the microstructure of this glass had large crystals embedded in the matrix. This is shown in the optical micrograph in Figure 17(G). In this figure, the average size of the small crystals is about three microns, and that of the larger ones is seven microns.

The heat treatment of this glass at 650°C for different periods of times resulted in the microstructures shown in Figure 18. After ten minutes of heat treatment at 650°C, the microstructures appeared to have two distinct features: dark regions of an average size of about 130 \mathring{A} , and light regions of an average size of about 190 A. The light regions are believed to be barium-depleted (or boron-rich) regions. After thirty minutes of heat treatment at 650°C, the dark regions became more distinct and their average size became about 265 \AA° . The microstructural change that took place during ten and thirty minutes of heat treatment is believed to be of the glass-in-glass type phase separation. The particle size was found to be about 135 Å after one hour of heat treatment at 650° C. These particles are crystalline in nature; and were identified as bariumtitanate and barium boron oxide crystals. The sequence of microstructural change for the ten minutes, thirty minutes and one hour periods are shown in Figure 18(A), (B), and (C), respectively. The heat treatment of this glass at 650°C for three hours leads to the precipitation of large crystals of about 2.6 microns in size, as shown in Figure 18(D). Further heat treatment for five and ten hours leads to predominant crystal growth.



Transmission electron micrographs of the barium-borate glass containing 10 mole% titanium dioxide heat treated at $650^{\circ}C$

- (A). for 10 minutes
- (B). for 30 minutes
- (C). for one hour



Optical micrographs shown in Figure 18(E) and (F), display the microstructures having large grains after such heat treatments.

3.2.2.2 Quantitative analysis of the microstructure of the glasses containing ten mole percent TiO_2 :

Average sizes D, as well as volume fractions V_f , N and N_v values of the barium borate glass containing ten mole percent TiO₂ after various heat treatment temperatures and times are shown in Table 5. Plots of D vs. heat treatment time for the different heat treatment temperatures are shown in Figure 19. The plots of Log N_v vs. 1/T and the activation energy calculations will be discussed in Chapter IV.

3.3 BARIUM BORATE GLASSES CONTAINING CERIUM OXIDE

3.3.1 Glass containing two mole percent cerium oxide

3.3.1.1 Microstructural studies:

The microstructure of the as-quenched glass containing two mole percent cerium oxide is shown in Figure 20(A). On rapid cooling of the molten glass batch, dark spherical regions separate. The average size of these inhomogeneities is about 205 A°. As a result of heat treating this glass at a temperature of 450°C for seventy-two hours the precipitation of fine particles of average size 156 A° dispersed in the glassy matrix occurred as shown in Figure 20(B).

Heat treating the glass containing two mole percent cerium oxide at 500°C for different periods of time results in the microstructural changes shown in Figure 21. After five hours of heat treatment the glass matrix structure is still very similar to that of the as-quenched glass. The average size of the dispersed phase grew to become 229 Å as shown in

Table 5

Quantitative analysis of the microstructure of the barium borate glass containing ten mole percent titanium dioxide.

Heat Treatment	Time	N	N _v x10 ⁻⁸	D	۷ _f		
Temperature	hour	#/µ ²	#/A ^{°3}	Å			
as-quenched		3008	2.6	157	0.63		
450°C	72	1320	1.13	158	0.68		
500°C	5 10 24 80	409 2004 1812 832 624	0.31 1.72 1.54 0.68 0.50	337 163 178 217 248 1.6m	0.79 0.74 0.75 0.71 0.73 0.80	* 0	
590°C	1/6 1/2 1 2 5 10 80	5984 200 3520 888 552	5.55 0.16 3.12 0.75 0.42	72 79 255 130 183 320 2.9m 7.2m	0.60 0.46 0.79 0.78 0.75 0.59 0.14	* 0 0	S La
650°C	1/6 1/2 1 3	328 1660 1124 3680	0.28 1.47 0.89 3.24	190 130 265 135 2.6m	0.29 0.70 0.63 0.79	1 d 0	
N : number ne	r one so	ouare mi	cron area.				

ł

	•	number per one square m	icivii are	a.
N,	:	number per unit volume.		
D	:	average particle size.	•••	
_ع۷	:	volume fraction.	m	: size in micron.
s'	:	small particles.	La	: large particles.
1	:	light areas.	d	: dark areas.
0	:	data taken from optical	microgra	phs.
*	:	data taken from replica	electron	micrographs.







Transmission electron micrographs of the barium-borate glass containing 2 mole% cerium oxide

- (A). as quenched
- (B). heat treated at 450°C for 72 hours

Figure 21(A). The electron diffraction pattern of this selected area exhibits sharp rings that may indicate the onset of a crystallization process. Further heat treatment at 500°C for ten hours resulted in the microstructure shown in Figure 21(B). Although phase separated regions are apparent, a few small crystals are also present in the matrix. The presence of these crystals is substantiated by the sharp spotty electron diffraction rings as shown in this figure. The precipitated phase becomes more distinct and grows to an average size of 517 Å[°] after twenty-four hours of heat treatment at 500°C, as shown in Figure 21(C). This is believed to be a process of glass-in-glass phase separation of an amorphous phase surrounding the crystals (identified as cerium oxide crystals, CeO₂) already present. A secondary crystallization process follows leading to the microstructure of Figure 21(D). The final average size of the precipitated crystalline phase reaches a value of 157 Å[°].

After thirty minutes of heat treatment at a higher temperature of 590°C the phase-separated regions are distinct and their average size is about 190 Ű. These regions are shown in the transmission electron micrograph of Figure 22(A). After one hour of heat treatment at the same temperature, no apparent change was observed except that the separated regions were more distinct as shown in Figure 22(B). These regions became interconnected after two hours of heat treatment, with an average size of about 590 Ű. The electron diffraction pattern of this selected area indicates that the phase separation process is still in progress. Distinct, dispersed spherical regions of size 120 Ű are present in the microstructure after five hours of heat treatment, as shown in Figure 22(D). On further heat treatment for eighty hours, the small areas became interconnected again, and the electron diffraction pattern does not



0.5 µ

Transmission electron micrographs of the barium borate glass containing two mole percent cerium oxide, heat treated at $590^{\circ}{\rm C}$

- (A). for thirty minutes
- (B). for one hour



Fig. 22 (continued)

Transmission electron micrographs of the barium borate glass containing two mole percent cerium oxide, heat treated at $590\,^{\rm O}{\rm C}$

(C). for two hours, with electron diffraction pattern shown

,

- (D). for five hours
- (E). for 80 hours



Transmission electron micrographs of the barium borate glass containing two mole percent cerium oxide, heat treated at 650^{0}C

- (A). for ten minutes
- (B). for thirty minutes



Fig. 23 (continued)

Transmission electron micrographs of the barium borate glass containing two mole percent cerium oxide, heat treated at 650⁰C

(C). for one hour (D). for five hours (E). for ten hours Electron diffraction patterns belong to the respective areas

indicate a distinct crystallinity of the matrix.

After heat treatment at 650°C for ten minutes, phase separated regions of size 167 Å are formed as shown in Figure 23(A). These regions grew to sizes of 250 Å and 450 Å on further heat treatment to thirty minutes and one hour as shown in Figure 23(B) and (C), respectively. The electron diffraction patterns obtained for the selected area of Figure 22(C) indicate clearly the presence of crystalline phase (identified as cerium oxide CeO_2) in the heat treated glass matrix. Sharp electron diffraction rings persist for the structures of the glasses heat treated for five and ten hours as shown by Figure 23(D) and (E). Cerium oxide (CeO_2) was again identified as the crystalline phase present; however, another crystalline phase, believed to be barium cerate $(BaCeO_3)$, was also present. The average size of the crystalline phases present in the glass heat treated for ten hours at 650°C is 277 Å . Optical microscopic observations of the glass heat treated at 650°C for ten hours, shown in Figure 24(A) does not reveal any features. It should be mentioned that after the ten hour treatment at 650°C the originally transparent glass became translucent. Further heat treatment at 650°C for twenty-four hours, resulted in the complete opacity of the glass. The optical microscope revealed the presence of large grains as shown in Figure 24(B).

3.3.1.2 Quantitative analysis of the microstructure of the glasses containing two mole percent CeO₂:

Table 6 displays values of the average particle size (D), volume fraction (V_f) , number of particles per square micron (N) and number of particles per unit volume (N_v) for the glasses containing two



Table 6

Quantitative analysis of the microstructure of the barium borate glass containing two mole percent cerium oxide.

Heat Treatment	Time	N	N _v x 10 ⁻⁸	D	۷ _f
Temperature	hour	#/µ ²	#/A ^{°3}	A	
as-quenched		619	0.51	205	0.25
450°C	72	1284	1.1	159	0.87
500°C	5 10 24 80	1072 168 1468	0.87 0.11 1.27	229 517 157	0.54 0.68 0.78
590°C	1/2 1 2 5 80	640 1936 4400 5040	0.54 1.63 3.93 4.6	190 185 500 119 83	0.63 0.48 0.81 0.81
650°C	1/6 1/2 1 5 10 10 24	956 256 816	0.82 0.18 0.64	167 250 453 277 	0.80

* +

N : number per one square micron area. N : number per unit volume. D : average particle size. V : volume fraction. *f : data taken from replica electron micrographs.

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mole percent cerium oxide heat treated at different temperatures for different periods of time. The plot of D vs. heat treatment time is shown in Figure 25. The curves exhibited maxima at about 25, 2 and 1 hour for heat treatment temperatures of 500° C, 590° C, and 650° C respectively. Plots of Log N_v vs. 1/T as well as activation energy calculations will be shown and discussed later in Chapter IV.

3.3.2 Glasses containing ten mole percent cerium oxide

3.3.2.1 Microstructural studies:

The as-quenched glass containing ten mole percent CeO_2 exhibited a structure consisting of phase separated regions in the glassy matrix. The average size of these regions is about 258 Å[°], and they are uniformly distributed over the matrix of the as-quenched glass. This structure is shown in the transmission electron micrograph of Figure 26(A). Figure 26(B) illustrates the microstructure of the same glass when heat treated at a temperature of 450°C for seventy-two hours. The glass-in-glass phase-separated regions, which are about 150 Å[°] in size, are interconnected over wide areas.

Heat treatment of this glass at 500°C for periods of time ranging between one and one hundred fifty-two hours resulted in the microstructures shown in Figure 27. The average particle size of the separated regions shown in Figure 27(A) of the glass heat treated for one hour is about 185 Ű. These regions become larger in size (about 283 Ű) and fewer in number after three hours of heat treatment. This microstructure is shown in Figure 27(B). A fine dispersed crystalline phase is formed after five hours of heat treatment at 500°C, as shown in Figure 27(C). The crystallinity of this phase was verified from the electron diffraction



Transmission electron micrographs of the barium borate glass containing ten mole percent cerium oxide

- (A). as quenched
- (B). heat treated $at\,450^{0}\text{C}$ for 72 hours



Transmission electron micrographs of the barium borate glass containing ten mole percent cerium oxide, heat treated at 500^{0} C

- (A). for one hour
- (B). for three hours
- (C). for five hours



Fig. 27 (continued)

Transmission electron micrographs of the barium borate glass containing ten mole percent cerium oxide, heat treated at $500^{\rm O}{\rm C}$

- (D). for 10 hours
- (E). for 80 hours
- (F). for 152 hours

pattern. This crystalline phase, of average size of 185 A° , was identified as CeO₂. After ten hours of heat treatment, the average size of these crystals was found to be about 100 A° as shown in Figure 27(D). On further heat treatment at 500°C for eighty and one hundred fifty-two hours the crystalline precipitated phase grows to 185 A° and 247 A° respectively. The progress of such growth is shown in Figure 27(E) and (F) respectively.

Precipitated regions of about 193 Å in size are seen in the microstructure of the glass samples heat treated at 590°C for one hour shown in Figure 28(A). After five hours of heat treatment, the average size of these regions (195 Å) was almost unchanged, as shown in Figure 28(B). Longer heat treatment at 590°C for twenty-four hours and eighty hours resulted in the precipitation of crystals of sizes of 183 Å and 152 Å as shown in Figure 28(C) and (D), respectively. X-ray and electron diffraction analysis indicated the presence of two crystalline phases, viz., cerium oxide (CeO₂) and barium cerate (BaCeO₃).

Heat treatment of this glass at 650°C for ten minutes yielded the microstructure displayed in Figure 29(A). The average size of the phaseseparated regions was found to be about 280 Ű. Further heat treatment at 650°C for thirty minutes resulted in finer, more uniformly distributed phase-separated regions of 143 Ű in size, as shown in Figure 29(B). Inspection of the electron diffraction pattern shows a few sharp rings signifying the start of crystallization of the matrix. After one hour of heat treatment at 650°C, the average size of the separated regions was about 87 Ű. Again, the sharp electron diffraction rings shown along with this microstructure in Figure 29(C) indicate the presence of some crystalline phase. The crystals grew, after five hours of heat treatment at 650°C, to a size of 151 Ű as shown in Figure 29(D). The continued





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Transmission electron micrographs of the barium borate glass containing ten mole percent cerium oxide,heat treated at 590^{9} C

Α).	for one hour	(B).	for	five hours
C).	for 24 hours	(D).	for	80 hours





Fig. 29 (continued)

Transmission electron micrographs of the barium borate glass containing ten mole percent cerium oxide,heat treated at $650^{\circ}C$

- (D). for five hours (E). for ten hours
- (F). optical micrograph of the same glass heat treated at 650^{0}C for ten hours

Electron diffraction patterns belong to respective areas

Table 7

Quantitative analysis of the microstructure of the barium borate glass containing ten mole percent cerium oxide.

Heat Treatment	Time	N	N _v x10 ⁻⁸	D	۷ _f		
Temperature	hour	#/µ ²	#/A ^{°3}	Å	·		
as-quenched		584	0.46	258	0.53		
450°C	72	1872	1.63	150	0.75		
500°C	1 3 5 10 80 152	1232 408 1492 2640 1300 916	1.04 0.32 1.26 2.40 1.10 0.84	184 283 185 100 185 247	0.63 0.70 0.78 0.69 0.71 0.71		
590°C	1 5 24 80	872 1308 1628	0.73 1.10 1.41	193 195 183 152	0.49 0.75 0.81		
650°C	1/6 1/2 1 5 10	342 880 3936 3160 	0.27 0.77 3.62 1.88	280 143 87 152 1.3m 4.1m	0.72 0.76 0.81 0.80	0	S La

: number per one square micron area. N

number per unit volume.average particle size.

N D V S f O m : size in micron. : volume fraction.

: small particles. La : la : data taken from optical micrographs. La : large particles.



heat treatment at 650°C for ten hours resulted in the rapid growth of large crystals, and the resultant microstructure could not be revealed by the electron microscopic observations. The electron diffraction pattern obtained, however, indicates clearly their crystallinity (Figure 29(E)). Two different size crystals, of the sizes 1.3 and 4.1 microns were present in the microstructure of the glass heat treated at 650°C for ten hours, as shown in Figure 29(E). The crystalline phases were identified as cerium oxide (CeO₂) and barium cerate (BaCeO₃).

3.3.2.2 Quantitative analysis of the microstructure of the glasses containing ten mole percent CeO₂:

The average particle size (D), volume fraction (V_f), number of particles per square micron (N) and per unit volume (N_v) for the glasses containing ten mole percent cerium oxide are shown in Table 7. The plots of D vs. heat treatment time, shown in Fig. 30, exhibit minima at about ten and five hours for the heat treatment temperatures of 500°C and 650°C respectively. The curve for the 500°C heat treatment has a maximum at about three hours, while that for 650°C rises steadily. Activation energy calculations, derived from the slope of the plot of log N_v vs. 1/T, will be presented in Chapter IV.

3.4 BARIUM BORATE GLASSES CONTAINING PHOSPHORUS PENTOXIDE

3.4.1 Glass containing 0.5 mole percent phosphorus pentoxide 3.4.1.1 Microstructural studies:

The microstructure of the as-quenched barium borate glass containing 0.5 mole percent $P_2^{0}_{5}$ is shown in Figure 31(A). The average size of the precipitated particles is about 163 Å[°]. When this glass was



Transmission electron micrographs of the barium borate glass containing 0.5 mole percent phosphorus pentoxide

(A). as quenched

(B). heat treated at 450°C for 72 hours
heat treated at 450°C for seventy-two hours the average size of the precipitated phase (170 Å[°]) remained almost the same (Figure 31(B)). No sharp electron diffraction pattern could be obtained, and hence it was concluded that these particles represent glass-in-glass phase separated regions.

Heat treatment of this glass at 500°C for different periods of time resulted in the microstructures illustrated by the transmission electron micrographs in Figure 32. Distinct dark regions of about 190 Ű in size were found dispersed in the structure after one hour of heat treatment at 500°C. These separated regions tended to become interconnected after twenty-four hours of heat treatment and their average size was found to be about 168 Ű. The heat treatment at 500°C for seventy-two hours also produces highly interconnected phase separated regions. After 120 hours of heat treatment, discrete phase separated regions of about 215 Ű in size appear again. This sequence of microstructural changes is displayed in Figure 32(A), (B), (C), and (D), respectively. No crystallization occurred during the course of heat treatment at this temperature.

Heat treatment of this glass at 590°C for thirty minutes resulted in the microstructure shown in Figure 33(A). The light regions (about 245 Ű in size) seen in this micrograph are believed to be a boron-rich phase. Darker areas, which are interconnected, were found to be of about 163 Ű in size. Further heat treatment at 590°C for one hour resulted in the dark regions (about 373 Ű in size) becoming more distinct, leaving behind an interconnected microstructure of the light regions. Longer heat treatment at 590°C for five hours marked the presence of a dispersed phase of less spherical particles of about 238 Ű in size, as shown in Figure 33(C). These particles became finer (193 Ű) and more





Transmission electron micrographs of the barium borate glass containing 0.5 mole percent phosphorus pentoxide heat treated at 590°C

(A). for thirty minutes

(B). for one hour



Fig. 33 (continued)

Transmission electron micrographs of the barium borate glass containing 0.5 mole percent phosphorus pentoxide heat treated at $590^{9}C$

- (C). for 5 hours
- (D). for 24 hours
- (E). for 104 hours

homogeneously distributed in the matrix as a result of heat treatment for twenty-four hours. The average size of such regions appears to stay almost the same after heat treatment for one hundred and four hours (about 200 A°) at 590°C. This sequence is shown in Figure 33(D) and (E), respectively. Absence of crystallization even after 104 hours of heat treatment at 590°C can be verified from the electron diffraction pattern presented for the selected area shown in Figure 33(E).

A ten minute heat treatment of the glass at 650°C resulted in the microstructure consisting of glass-in-glass phase-separated regions of 393 A° in size, as shown in the electron micrograph of Figure 34(A). After thirty minutes of heat treatment at this temperature the particles became smaller, 169 A° in size [Figure 34(B)]. These dark regions became highly interconnected, leaving separated light regions (297 Å $\stackrel{\circ}{\text{ n}}$ in size), after one hour of heat treatment as shown in Figure 34(C). Further heat treatment for five hours resulted in larger white regions (308 A). Figure 34(D) illustrates the microstructure of the glass after five hours as revealed by the transmission electron microscopy. The optical micrographs of Figure 35(A) and (B) display the microstructure of this glass after ten and twenty-four hours, respectively, of heat treatment at 650°C. The average size of the dispersed phase after ten hours of heat treatment was found to be about 16.5 microns. The predominant microstructure in the glasses heat treated for twenty-four hours are small phase separated regions (about two microns in size) uniformly distributed in the matrix. There are also some regions about twenty microns in size.





Optical micrographs of the barium borate glass containing 0.5 mole percent phosphorus pentoxide,heat treated at $650^{\circ}C$ (A). for 10 hours (B). for 24 hours

3.4.1.2 Quantitative analysis of the microstructure of the glasses containing 0.5 mole percent P_2O_5 :

Table 8 summarizes the results of the average size (D), volume fraction (V_f), and number per square micron area and per unit volume (N and N_v , respectively) measurements for the glasses containing 0.5 mole percent P_2O_5 . The plots of D vs. heat treatment time for different heat treatment temperatures of this glass system are shown in Figure 36. The curve for the 500°C heat treatment exhibits a very broad maximum at about 25 hours. For the 590°C heat treatment the maximum is at about two hours heat treatment time. In the case of 650°C, the curve experiences a minimum at about five hours and rises sharply where it becomes almost horizontal at about twenty-four hours. It is to be noted that the curves for the 500°C and 590°C did not show any increase after the initial maxima.

3.4.2 Glasses containing two mole percent phosphorus pentoxide3.4.2.1 Microstructural studies:

The microstructure of the as-quenched glass containing two mole percent P_2O_5 as revealed by transmission electron microscopy is shown in Figure 37(A). Dispersed particles of about 350 Ű in size are clearly seen in this microstructure. Heat treatment at 450°C for seventy-two hours leads to the precipitation of fine particles (135 Ű), as shown in Figure 37(B). These regions are still glassy in nature.

The heat treatment at 500°C, when carried out for different periods of time, resulted in the microstructures shown in Figure 38. After five hours of heat treatment at this temperature, phase-separated regions of about 143 A° in size were present in the microstructure as shown in

Table 8

Heat Treatment	Time	N	N _v ×10 ⁻⁸	D	۷ _f	
Temperature	hour	#/µ ²	#/A ^{°3}	Å		
as-quenched		1100	0.95	163	0.75	
450°C	72	1588	1.36	170	0.78	
500°C	1 24 80 120	840 2528 588 844	0.71 2.16 0.45 0.70	190 168 320 215	0.38 0.65 0.74 0.69	
590°C	1/2 1 5 24 104 152	464 936 480 837 760 1008 1248	0.37 0.83 0.35 0.68 0.64 0.84 1.07	245 163 373 238 193 200 170	0.33 0.68 0.44 0.46 0.74 0.74 0.38	1 d
650°C	1/6 1/2 1 5 10 24	1232 564 	1.05 0.43 	393 169 137 325 297 237 16.5m 1.95m 20 3m	0.60	d 1 d 1
				20.311	0.13	La

Quantitative analysis of the microstructure of the barium borate glass containing 0.5 mole percent phosphorus pentoxide.

N	:	number per one square micron	area.		
N,	:	number per unit volume.			
DV	:	average particle size.			
٧ _ع	:	volume fractions.	m	:	size in micron.
S'	:	small particles.	La	:	large particles.
1	:	light areas.	d	:	dark areas.



of the barium borate glass containing 0.5 mole percent phosphorus pentoxide.



Fig. 37

Transmission electron micrographs of the barium borate glass containing two mole percent phosphorus pentoxide (A). as quenched (B). heat treated at 450° C for 72 hours





Figure 38(A). Some of these regions appear as clusters. Longer heat treatment at the same temperature for ten hours resulted in more uniformly distributed phase-separated regions (about 178 Ű in size) as shown in Figure 38(B). These regions ultimately grew to about 438 Ű in size after the heat treatment was continued for twenty-four hours. Heat treatment for seventy-two hours resulted in the separated regions becoming highly interconnected and light (boron-rich) regions separate out distinctly. Similar features were also observed after 120 hours of heat treatment. This sequence of micrographs is presented in Figure 38(C), (D) and (E) respectively.

The microstructures resulting from the heat treatment of this glass at 590°C for different intervals of time are shown in Figure 39. After thirty minutes of heat treatment at this temperature well-defined phase separated regions (238 \mathring{A}) appeared as shown in Figure 39(A). Further heat treatment for one and five hours resulted in a microstructure of phase separated areas of almost the same size (172 Å and 167 Å, respectively). These regions grew to a size of about 262 Å on further heat treatment for ten hours. This sequence of microstructural changes is shown in Figure 39(B), (C), and (D), respectively. Boron-rich regions separated out while the dark regions became interconnected when the glass was heat treated at this temperature for twenty-four hours (Figure 39(E)). Prolonged heat treatment for 104 hours of this glass at 590°C, resulted in the boron-rich regions (light contrast) becoming more distinct (1107 Å in size) and the dark regions (2253 Å in size) coalesced, as shown in Figure 39(F). Barium-depleted areas (boron-rich) surrounding these dark regions also can be seen in this microstructure. The absence of sharp electron diffraction pattern points out the fact



(C). for five hours





(C). for ten hours

that these regions are still glassy.

After ten minutes of heat treatment at 650°C, the structure of this glass showed dark, separated regions (468 Å in size) interconnected and surrounded by light regions. On further heat treatment at this temperature for one hour, the dark regions grew (1050 Å $^{\circ}$ in size) and coalesced. These micrographs for the ten minute and one hour heat treatments are given in Figure 40(A) and (B), respectively. The dark areas grew larger (about 1127 A° in size) with further heat treatment for ten hours (Figure 40(C)). The absence of sharp electron diffraction patterns during these heat treatment times again indicated that the precipitated phases were not crystalline. The optical micrographs shown in Figure 41 illustrate the microstructure for this glass heat treated at 650°C for ten and twenty-four hours. The transmission electron microscopy could not be used to reveal the microstructure, because of the relatively large size of the phase-separated regions. The separated regions in the ten hour heat treated samples were found to have sizes of 13 and 39 microns for the small and larger regions, respectively. Figure 41(B) is an optical micrograph of the specimen heat treated at 650°C for twenty-four hours.

3.4.2.2 Quantitative analysis of the microstructure of the glasses containing two mole percent P_2O_5 :

Results of the measurements of the average size (D), volume fraction (V_f), number per square micron (N), and per unit volume (N_v) of this glass are presented in Table 9. Curves for D vs. heat treatment time plotted in Figure 42 for the different heat treatment temperatures show features that are similar to the curves presented for the glass having 0.5 mole percent P₂0₅. The 500°C curve exhibits a minimum at





Table 9

Quantitati	ve analys [.]	is of the	e microstruc	ture of	the	barium	borate	glass
containing	two mole	percent	phosphorus	pentoxic	le.			

Heat Treatment	Time	N	N _v x10 ⁻⁸	D	۷ _f		
Temperature	hour	#/µ ²	#/A ^{°3}	Å			
as-quenched		584 388	0.44 0.29	332 350	0.41 0.46	*	
450°C	72	1820	1.60	135	0.51		
500°C	5 10 24 80 120	1216 2000 296 1080	1.06 1.70 0.20 0.92	143 178 438 342 173	0.46 0.60 0.45 0.75		
590°C	1/2 1 5 10 24 104	744 1680 960 852 8 131	0.60 1.43 0.82 0.68 0.01 0.01	238 172 167 262 2253 1107	0.50 0.75 0.69 0.73 0.46 0.43	d 1	
650°C	1/6 1 10	432 	0.29	468 1050 1127 13m 39m	0.53 0.85 0.48	0 0	S La

Ν	:	number per one square micron	area.		
N.	:	number per unit volume.			
DV	:	average particle size.			
٦٧	:	volume fraction.	m	:	size in micron.
S'	:	small particles.	La	:	large particles.
1	:	light areas.	d	:	dark areas.
*	:	data taken from replica elec	tron m	icr	ographs.





The curve for 650°C is extrapolated beyond 10 hours of heat treatment. *

about five hours and a maximum at about sixty hours. The curve for the 590°C heat treatment has a minimum at three hours, then rises steadily, indicating continuous growth of the precipitated phase. For the 650°C heat treatment the cruve changes its slope at about five hours.

3.5 <u>RELATIVE EFFECTIVENESS OF TITANIUM DIOXIDE, CERIUM OXIDE AND</u> PHOSPHORUS PENTOXIDE AS NUCLEATING AGENTS

3.5.1 Glasses in the as-quenched state:

The microstructure of the different glass systems in the asquenched state used in this study are shown in Figure 43. It can be seen from this figure that all the glasses in the as-quenched state have phaseseparated. The base glass seems to have phase-separated regions of the largest average size (about 425 Å[°]). This fact indicated that the different additions of various nucleating agents inhibited, to a varying degree, the initial phase separation of the as-quenched base glass.

Table 10 summarizes the D, V_f , N, and N_v values for these glasses. The number of particles per square micron is found to have increased in different orders on the addition of nucleating agents to the base glass. The maximum value of N was observed in the glasses containing ten mole percent titanium dioxide.

3.5.2 Glasses heat treated at 450°C:

The chosen heat treatment time for comparison of the microstructures of each of these glasses at 450°C was seventy-two hours. The base glass and glasses containing two and ten mole percent titanium dioxide have shown crystalline regions (of about 160 Ű in size). The predominant features of their microstructures are presented in Figure 44. The volume fraction of these crystalline regions became larger on addition



Fig. 43

Transmission electron micrographs of the as quenched glasses contai

- A. No nucleating agent
 - B. 2 mole % titanium dioxide
 - C. 10 mole % titanium dioxide



Fig. 43 (continued)

Transmission electron micrographs of the as quenched glasses containing

- D. 2 mole % cerium oxide
- E. 10 mole % cerium oxide
- F. 0.5 mole % phosphorous pentoxide
- G. 2 mole % phsophorous pentoxide

Table 10

Comparison of the quantitative data for all the glass systems used in the as-quenched state.

Glass	N	N _v ×10 ⁻⁸	D	۷ _f		
Code	#/µ ²	#/A ^{°3}	A°			
BBa	313 362	0.22 0.25	411 442	0.81 0.88	*	
BBaTi2	1165 387 34	1.01 0.32 0.02	154 198 672	0.45 0.59 0.13	* *	S La
BBaTil0	3008	2.60	157	0.63		
BBaCe2	619	0.51	205	0.25		
BBaCe10	584	0.46	258	0.53		
BBaP0.5	1100	0.95	163	0.75		
BBaP2	584 388	0.44 0.29	332 350	0.41 0.46	*	

- N : number per one square micron area. N : number per unit volume. D : average particle circulation

- V Sf * volume fraction. :
- La : large particles. : small particles.
- data taken from replica electron micrographs. :



Transmission electron micrographs of barium-borate glasses heat treated at 450°C for 72 hours.

- A. No nucleating agent.
- B. 2 mole % titanium dioxide
- C. 10 mole % titanium dioxide



G. 2 mole % phosphorous pentoxide

Average size	and volume	fraction of	the	precipitated	regions	in glasses
heat treated	at 450°C fo	or 72 hours.			-	-

	BBa	BBaTi2	BBaTil0	BBaCe2	BBaCe10	BBaP0.5	BBaP2
D	137	168	158	159	150	170	135
۷ _f	0.59	0.46	0.68	0.87	0.75	0.78	0.51

Table 11

of titanium dioxide, as seen in Table 11. Additions of cerium oxide in two and ten mole percent to the base glass resulted in inhibiting the crystallization of the glass heat treated at this temperature for seventytwo hours. However, this addition resulted in the precipitation of fine phase-separated areas as seen in Table 11. The same effect of inhibiting the crystallization process occurred on adding phosphorus pentoxide to the base glass. Instead, glass-in-glass phase separated regions precipitated. In both cases of cerium oxide and phosphorus pentoxide additions, the volume fraction of the precipitated regions increased to about 0.8. The two mole percent phosphorus pentoxide was almost the same (about 0.51) as the base glass.

3.5.3 Glasses heat treated at 500°C:

The microstructure of the base did not show any evidence of crystallization at short heat treatment times at this temperature. However, glasses containing two and ten mole percent of titanium dioxide or cerium oxide have exhibited a crystalline microstructure of fine crystals $(100 - 300 \text{ Å}^\circ \text{ in size})$ after ten hours of heat treatment. On the other hand, glasses containing 0.5 or two mole percent of phosphorus pentoxide had common featured microstructures with glass-in-glass phase separated regions (168 and 178 Å respectively). These microstructures are shown in Figure 45. Comparison of the microstructures of all these glasses as a result of prolonged heat treatment for eight hours can be made by observing the electron micrographs of Figure 46. While growth of the precipitated regions was a common factor of all these glasses heat treated at this temperature for eight hours, only glasses with additions of ti-tanium dioxide or cerium oxide crystallized. Base glass and glasses with



Fig. 45

Transmission electron micorgraphs of barium-borate glasses heat treated at 500°C:

- A. No nucleating agent heat treated for one hour
 - B. 2 mole % titanium dioxide heat treated for ten hours
 - C. 10 mole % heat treated for ten hours







different phosphorus pentoxide additions experienced glass-in-glass phaseseparated regions in their microstructures. D, V_f , N, and N_v values are given for these different glasses heat treated at 500°C for eighty hours in Table 12.

3.5.4 Glasses heat treated at 590°C:

Short heat treatment at this temperature for one hour of all these glasses resulted in the microstructural features shown in Figure 47. The base glass as well as glasses containing two mole percent titanium dioxide, 0.5 and two mole percent phosphorus pentoxide exhibited microstructures with glass-in-glass phase separated regions (408 Å, 620 Å, 373 A°, and 172 A°, respectively). The start of a crystallization process in the glasses containing ten mole percent titanium dioxide and two mole percent cerium oxide, can be observed from their respective microstructures shown in Figure 47. Only glasses containing ten mole percent cerium oxide are shown to have crystalline preceipitated regions (about 200 A° in size) in their microstructure. Prolonged heat treatment at 590°C for 80 and 104 hours resulted in the microstructural features shown in Figure 48. The microstructure of the base glass as well as those containing 0.5 and two mole percent phosphorus pentoxide is shown to consist of glass-in-glass phase-separated regions. Crystalline regions, however, are found in the microstructure of the glass containing different concentrations of titanium dioxide and cerium oxide $(D_{Ti2} = 2.5 \text{ microns},$ $D_{T110} = 2.9$, and 7.2 microns, $D_{Ce2} = 82 \text{ Å}^{\circ}$, and $D_{Ce10} = 152 \text{ Å}^{\circ}$).

3.5.5 Glasses heat treated at 650°C:

At the early stages of heat treatment of these glasses at

Table 12

Glass Code	N	N _v ×10 ⁻⁸	D	۷ _f	
	#/µ ²	#/A ^{°3}	Å		
BBa	374 1242 1242	0.29 1.03 0.70	300 210 772	0.76 0.78 0.78	* S La
BB aTi2	174 461	0.12 0.34	518 367	0.31 0.62	1 d
BB aTilO	832 624	0.68 0.50	217 248 1.6m	0.71 0.73 0.80	* 0
BBaCe2	1468	1.27	157	0.78	
BBaCe10	1 300	1.10	185	0.71	
BBaP0.5	588	0.45	320	0.74	
BBaP2			342		

Comparison of the quantitative data for all the glass systems heat treated at 500°C for eighty hours.

N N DV	::	number per one square micron are number per unit volume. average particle size.	a.		
٧٢	:	volume fraction.	m	:	size in mic ron.
S'	:	small particles.	La	:	large particles.
1	:	light areas.	d	:	dark areas.
*	:	data taken from replica electron	mic	rog	raphs.
0	:	data taken from optical microgra	phs.	•	

. .



Fig. 47

 $\mbox{Electron micrographs of barium-borate glasses heat treated at 590°C for one hour$

- A. No nucleating agent (TEM)
- B. 2 mole % titanium dioxide (replica)
- C. 10 mole " titanium dioxide (replica)


Electron micrographs of barium-borate glasses heat treated at 590°C for one hour (continued)

- D. 2 mole % cerium oxide (TEM)
- E. 10 mole % cerium oxide (TEM)
- F. 0.5 mole % phosphorous pentoxide (TEM)
- G. 2 mole % phosphorous pentoxide (TEM)



Fig. 48

Transmission electron and optical micrographs of barium-borate glasses heat treated at 590°C

- A. No nucleating agent heat treated for 80 hours (TEM)
- B. 2 mole % titanium dioxide heat treated for 80 hours (optical)
- C. 10 mole % titanium dioxide heat treated for 80 hours (optical)



Fig. 48 (continued)



- D. 2 mole " cerium oxide heat treated for 80 hours (TEM)
- E. 10 mole % cerium oxide heat treated for 80 hours (TE")
- F. 0.5 mole " phosphorous pentoxide heat treated for 104 hours (TEM)
- G. 2 mole ' phosphorous pentoxide heat treated for 104 hours (TEM)



- A. No nucleating agent
- B. 2 mole 5 titanium dioxide
- C. 10 mole " titanium dioxide





Fig. 50

Transmission electron and optical micorgraphs of barium-borate glasses

heat treated at 650°C for ten hours

- A. No nucleating agent (TEM)
- B. 2 mole % titanium dioxide (optical)
- C. 10 mole % titanium dioxide (optical)



650°C for one hour the same trend was seen for heat treatment at 590°C for prolonged times. The base glass and glasses containing phosphorus pentoxide experienced glass-in-glass phase-separated microstructure. The glasses containing titanium dioxide and cerium oxide were crystalline. The crystalline regions in such glasses constituted about 0.5 of the total volume in the glasses containing two mole percent, and about 0.8 for the ones containing ten mole percent additions of both titanium dioxide or cerium oxide. The microstructures for all these glasses are shown in Figure 49. Longer heat treatment at 650°C for ten hours resulted in crystalline precipitates in all glasses except those containing additions of phosphorus pentoxide, as shown in Figure 50. However, these glasses with phosphorus pentoxide as the nucleating agent did exhibit crystalline precipitates after twenty-four hours of heat treatment at 650°C. All the crystalline phases precipitated in the microstructures of all these glasses after prolonged heat treatment times were observed to be relatively larger than those precipitated at lower heat treatment temperatures.

CHAPTER IV

DISCUSSION

4.1 <u>STRUCTURE AND CRYSTALLIZATION BEHAVIOR OF THE BARIUM BORATE</u> BASE GLASS

The two basic models describing the structure of boron oxide glasses are : (47)

i- the random network model, and

ii- the molecular model.

Figure 52 illustrates the different possible arrangements of both boron and oxygen ions as described by these two models.

The random network of planar BO_3 - triangles was first introduced by Zachariasen (48). The main objection to this model was that it failed to explain many physical properties of vitreous and liquid boron oxide (47). According to this model, the boron atom may be regarded as centered in the plane of an equilateral triangle, while the oxygen atoms are present in the corners of this triangle. These triangles are then linked together by their corners forming a random network. This structure is shown in Figure 51(A). The idea of boroxol rings as the main constituent of boron oxide glass structure was proposed by Goubeau and Keller (49) and was substantiated by Krogh-Moe (50). The structure of boron oxide glass based on the six-membered boroxol ring is shown in Figure 51(B). The more or



- (A). schemetic representation of a random b ron-exponent network in boron oxide glass.
 - (B). schematic representation of a rubber become on network with a high proportion of boroxol rings
 - (C). quasicrystalline model for boron oxide class, b = b = B angles are 180 .
 - (D). molecular models for her notified to $i = B_2 O_6 = molecule model.$ $ii = B_3 O_1 = molecule model.$
 - (E). the structure of the former a structure
 - term O

less random network models do not require two-dimensional layer structures, as implied by the schematics of Figure 51. In fact, the BO_3 triangles assume all orientations in space and form an interconnected three dimensional network. Quasicrystalline models based on the planar BO_3 triangles have also been proposed by Borelli and others (51). This model describes two-dimensional ordered regions in the glass composed of twelve membered rings with a B - O - B bond angle of 120° or 180° as shown in Figure 51(C).

The molecular model, proposed by Fajan and Barber (52), describes the boron oxide glass structure as built up of B_40_6 molecules as shown in Figure 51(D). According to this model the molecules are mutually interlinked by weak intermolecular bonds. Many other models could also be found in the literature describing the structure of boron oxide glasses (53 to 58). Among these models describing boron oxide glass structure a random three-dimensional network of B0₃ triangles with a comparatively high fraction of six-membered rings (boroxol rings) seems to give the best explanation for observed behavior of boron oxide glasses.

It is also conceivable that a random network of four-fold irregular coordinated boron atoms exists in the glassy phase. For example, in zinc borate glasses the number of four-coordinated boron atoms is much lower than in crystalline compounds of the same composition. The structure of linked rings is very different from both the random network of siliconoxygen tetrahedra in vitreous silica and the crystalline form of $B_2O_3(58)$. Many multicomponent borates show wide compositional ranges of glass formation as reviewed by Rawson (59).

The base glass system used in the course of this study is a barium borate glass system containing twenty and eighty mole percent of BaO and B_2O_3 respectively. This composition is indicated on the phase diagram shown in Figure 52. Barium oxide is a modifying oxide and is incapable of taking part in the continuous network. The effect of such oxide on glass systems is to break the structure by introducing higher concentration of non-bridging oxygen ions. An interesting structure is based on the phenomenon of twin networks, described by Krog-Moe (47), as being quite common in borate structures. Such a structure should also be considered for boron oxide glass. The network consists of two kinds of basic units: a triborate group and a boroxol group in the ratio one to two. The boroxol group is the six-membered ring shown in Figure 51(B). The triborate group differs from the boroxol group in having one of its three borons in four-fold coordination (Figure 51(E)).

Cahn (63) approaches the phase separation process in boric oxidesilica glass systems by suggesting that the additions of Na₂O to this system cause three-fold to four-fold coordination changes of oxygen atoms around boron atoms, which lead to the phase separation in this system. In light of this suggestion, additions of barium oxide to boric oxide glasses most likely results in the change from three-fold to four-fold coordination of oxygen around boron. After giving up their oxygen ions to the network, barium ions sit in the modifying (interstitial) positions of the glass network. Upon quenching the glass from the melt barium cations segregate and barium-rich regions separate out in the glass matrix.

In summary, when barium oxide is added to the boron oxide glass network barium donates its oxygen ions and sits in the modifier positions of the network. This donated oxygen can participate in the glass matrix in either of the following possibilities:



- i- it may enter the network, causing local breakdown in some bonds, increasing the concentration of the non-bridging oxygen in the network. This behavior will result in local charge unbalance; or
- ii- it may help in tetrahedrally coordinating some of the triangularly coordinated boron ions of the network. This will give rise to some B - 0 bonds with bond strength of 4/3. In such case the valence of oxygen is not satisfied and so a situation of charge unbalance is created.

Regardless of which of the above mechanisms operates; the local charge unbalance caused is inevitable and can lead to phase separation of the glass matrix.

This explains the separated regions observed in the microstructure of the as-quenched barium-borate glass, shown previously in Figure 3.

Heat treatment at low temperatures, resulted in the nucleation and crystallization of these separated regions. This was clearly observed in this study when the as-quenched barium borate glass, with barium-rich separated regions present in its microstructure, was heat treated at 450°C. The electron micrographs, presented earlier in Figures 5 and 6 of the resulting microstructure of this base glass when heat treated at intermediate temperatures (500°C and 590°C), indicate clearly that there is no tendency for crystallization at these temperatures. They did, however, show indications of the growth of the precipitated amorphous regions. At higher heat treatment temperatures (650°C), greater growth rate of the crystalline phases was evident, particularly at long heat treatment times as shown in Figure 7. This behavior of the microstructural changes observed in this heat treatment schedule indicate that the nucleation rate maximum (around 450°C) and the growth rate maximum (around 650°C) are very well separated.

From the above discussion, and the phase diagram of $Ba0-B_2O_3$ system shown in Figure 53, one can expect that the crystalline phases precipitated during the course of heat treatment of this glass system are barium boron oxide (BaB_2O_4) and boron oxide (B_2O_3). This was evidenced by electron and x-ray diffraction results obtained for this system.

4.2 <u>STRUCTURE AND CRYSTALLIZATION BEHAVIOR OF THE GLASSES CONTAINING</u> TITANIUM DIOXIDE

In the production of many types of glass-ceramics, titanium dioxide is used as the crystallization catalyst. It is introduced into the glass batch in amounts of 2-20 weight percent. Titanium dioxide, which supplies nuclei with diameters of approximately 50 Ű, may cause many components of glasses to crystallize (11). The presence of more than twenty percent titanium dioxide in alumino-silicate glasses results in the precipitation of crystalline TiO_2 , and decreases the content of desirable crystalline compounds; or, it would produce spontaneous crystallization during the cooling of the glass from the melt. Increasing the TiO_2 content within the range of 2-20 weight percent increased the number of nuclei present and thereby facilitated crystallization.

Titanium dioxide, when added to glass systems, is believed to act as an intermediate oxide which enters the glass network. However, the extent to which it does so has not been elucidated. Ermolenko (5) suggests that, when titanium dioxide is added to glass systems in large amounts (more than 75%), it assumes network forming positions and hence must be regarded as a network-forming oxide.

In the study of the microstructure of lithium alumino silicate $(Li_20 - Al_20_3 - Si0_2)$ glass systems by infrared absorption methods

Alekseev et al. (32) observed that small amounts of TiO₂ have a significant influence on the structure of the crystalline phase deposited in the glass of eucryptite composition. Alekseev (33), Maurer (66), Janakiramarao (68 and ¢9), Stookey (67), Kondrat'ev (31) and Buzhniskii (70) studied the role of titanium dioxide as a nucleating agent on the crystallization of many glass systems. Their data indicates that the presence of titanium dioxide enhances glass-in-glass phase separation in various glass systems. The ultimate crystallization of the glassy matrix results in the nucleation of such regions on heat treatment. The two basic mechanisms described in their work leading to the glass-in-glass phase separation as a result of additions of titanium dioxide to the various glass systems used can be summarized as

1- incompatibility of the (TiO_6) groups and other groups in different glass systems (e.g. SiO_4 in silicate glasses, GeO_4 in germinate glasses, $(Al O_4)$ or AlO_6 in aluminate glasses), which leads to the separation of one or more phases.

2- coordination number change of titanium ions from four at high temperatures to six at lower temperatures resulting in local disturbance and hence to the formation of metastable regions that phase separate upon cooling the melt. As an example, consider the description provided by Kondrat'ev (31) in explaining the role of titanium dioxide in the glass system $\text{Li}_20\text{-Al}_20\text{-Si0}_2\text{-Ti0}_2$. Aluminum oxide may be present in a glass as (Al 0_4) and (Al 0_6) groups. On the addition of titanium dioxide to glasses containing (Al 0_6) units, titanium tends to complete its coordination sphere with six oxygen atoms taken from (Al 0_6) octahedrons. The compound $\text{Al}_20\text{-}^3\text{-Ti0}_2$ is then formed, containing (Al 0_2), (Al 0_4) and (Ti 0_6) units. Kondrat'ev (31) could not confirm the presence of $\text{Al}_20\text{-}^3$. either the presence of such a crystalline phase in very small volume fractions or its existence in the glassy form. When the amount of titanium dioxide introduced into the glass exceeds the amount of aluminum oxide in octahedral coordination, titanium begins to enter the aluminosilicate network in the form of (TiO_4) units, which are converted into deformed (TiO_6) units. This leads to subdivision of the aluminosilicate component with ultimate formation of a microcrystalline structure. Kondrat'ev (31) summarizes the formation of crystallization centers in lithium aluminosilicate glasses containing titanium dioxide in the following two possible schemes:

1- formation of the compound $Al_2O_3 \cdot TiO_2$ at a high temperature which then separates out in the form of microdroplets (which may not crystallize) when the glass is cooled. Crystallization of the principal phase begins at the resultant phase boundaries; or,

2- separation of the amorphous compound $Al_2O_3 \cdot TiO_2$ as a first step. The next phase that should separate out is titanium dioxide, but by this time the glass has already cooled and the process is frozen. On heat treating in the precrystallization period, however, titanium dioxide begins to crystallize and the principal crystalline phase of the metastable solid solution grows on it. Kondrat'ev (31) finally pointed out that conditions for crystallization of titanium dioxide in the precrystallization period are very unfavorable, and that formation of (TiO₆) units must proceed with great distortion of their symmetry.

The role of titanium dioxide additions in some glass system, however, is believed to result in the immediate crystallization of such glasses or by a crystallization process that is mainly initiated by the precipitation of rutile (TiO_2) crystals which assist in the final crystallization of the whole glass matrix into fine, uniformly distributed crystals. This view is substantiated by the work of Petrovskii (71), Shelyubskii (65), and Galant (72). In describing such a mechanism Petrovskii and coworkers concluded that an induction period exists during which aluminum groupings (in lithium aluminosilicate glasses) surround one titanium center. Petrovskii based his argument on the role of titanium dioxide on coordination number changes. He showed that during crystallization of alkali silicate glasses containing titanium dioxide the coordination number of titanium ions changes from four to six. The change of coordination number in the solid phase is due to a change of bond character. Petrovskii describes this as the latent driving force for the microcrystallization process. He further assumes that the crystallization of the glass actually begins at the instant when titanium passes into six-fold coordination, just as in titanium enamels.

Galant (72), using available data on the linear variations of refractive index and density of titania-containing silicate glasses over a wide range of titanium dioxide concentrations, suggested that the coordination number of titanium does not alter in alkali silicate glasses. Moreover, in glasses containing K_2^0 , glassy potassium meta- and dititanates have been obtained, implying that under certain conditions titanium acts as a network former. So with the one coordination number of six titanium can act both as a network former and as a modifier in such glass systems. It may be further assumed, as a first approximation, that (Ti0₆) octahedra with broken edge bonds, joined mainly by their corners, are network formers. The same (Ti0₆) octahedra without sufficient breakdown of the edge bonds, are modifiers and favor crystallization.

In the present study, as was mentioned in Chapter III, it was seen

that the addition of two and ten mole percent titanium dioxide to the barium borate $(Ba0 \cdot 4B_2O_3)$ base glass system resulted in precipitation of amorphous regions in the early heat treatment stages at low temperatures (500°C and 590°C). For prolonged heat treatments at low temperatures and at reasonably short heat treatment times at higher temperatures (650°C), the crystallization process proceeded to the ultimate crystallization of the glass matrix. The size of the precipitated crystals and their volume fraction were seen to depend on the amount of titanium dioxide added to the system.

Upon addition of titanium dioxide to the barium borate glass system, one of the following situations could be considered to explain the phase separation and crystallization of the resulting glass system;

i- assume that boron ions retain their three-fold coordination in the glass network, and that titanium ions assume three-fold coordination in the network as intermediate ions. Furthermore, assuming that titanium ions enter the network as Ti⁴⁺ ions at lower temperatures (i.e. on cooling the glass melt), one then expects that the titanium ions have to be doubly bonded to oxygen ions in the network to preserve their electrical neutrality, as shown in Figure 53(A). McMillan (40) pointed out that pentavalent ions in tetrahedrally coordinated glass system might not be particularly stable. This is due to the fact that the triangular units containing the tetrahedral ion would be assymetric, and in the regions surrounding these units there would exist marked disturbance of the bonding in the borate network, separation into two phases would ultimately occur. These phase-separated regions, most likely amorphous in nature, are bariumtitanium compound-rich regions, boron-rich regions or a combination of the These regions nucleate on further heat treatment resulting in the two.



Fig. 53 (A).

Schematic representation for the arrangement of the different ions in the network of the barium borate glass containing titanium dioxide. crystallization of the final crystalline phases.

ii- assuming that the titanium ions (with four-fold coordination at high temperatures) will associate themselves with the already existing four-fold coordinated boron ions created by the gain of the oxygen donated by barium ions, the titanium then enters the network positions alongside the boron ions as shown in Figure 53(B). On cooling the melt, titanium tends to assume its low temperature six-fold coordination and so separates out of the network. In doing so titanium ions are more likely to associate with the relatively free barium ions in forming barium-titanium rich compounds leaving behind boron-rich regions in the glassy matrix phase. These precipitated regions are most likely of the glass-in-glass type since there was no evidence of their crystallinity during early heat treatment stages. Next, these amorphous regions nucleate and result in the crystallization of the crytalline phase.

iii- a combined possibility of the above mentioned mechanisms is also highly probable since it is possible that the base glass could very well contain regions where boron is triangularly coordinated and regions where boron is tetrahedrally coordinated. In that case, a mixed effect of the two mechanisms enhances the phase separation process.

iv- another possible mechanism is one in which titanium donates its oxygen to the network. Titanium, then, can exist either in the modifier position or enters the glass network. If titanium enters the network as a four-fold coordinated ion, it will not create any local charge unbalance since it satisfies both the bonding arrangements and the electroneutrality of the surrounding ions as shown in Figure 53(C). However, if titanium changes its coordination from four (at high temperatures) to six (at lower temperatures on cooling), it can not be accommodated



Fig. 53 (continued)

Schematic representation for the arrangement of the different ions in the network of the barium borate glass containing titanium dioxide. any more in the glass network. This will create charge unbalance leading to phase separation.

To summarize, in all the arguments based on boron ions existing in three-fold coordination, irrespective of what titanium does when added to the glass matrix (i.e., whether it enters the network as three- or four-fold coordinated or sits in the modifier position), it will cause local charge unbalance even at high temperatures, except as described in the last case of Figure 53(C). The charge unbalance will be only created when titanium ions change their coordination on cooling. This will be also the case when titanium assumes four-fold coordination in a network where boron may be assumed to be present in tetrahedrally coordinated groups. So, the addition of titanium dioxide to the bariumborate glass system will result in either

a- increasing the number of tetrahedrally coordinated boron ions, or
b- break the network at more points, thereby increasing the concentration of non-bridging oxygens.

Regardless of what the case is, the titanium ion will be forced out of the network. In this case, the titanium ion will associate itself with the relatively free barium ions, forming a barium-titanium rich compound that separates out. Since it is known that titanium ions can exist in more than one valence state (namely Ti^{3+} or Ti^{4+}), it is proper to attempt to define the role of ions exhibiting such dual existence. A comparison can be made with the reported role of the dual valency of iron ions in glass systems, as reported by Banerjee (73). He reported that all the observations of magnetic susceptibility and color changes in iron-containing glass systems can be attributed to the presence of multicomponent paramagnetic carriers, such as Fe^{++} ions, Fe^{+++} ions,

covalently bonded iron and iron oxides with particles smaller than the magnetic domains. The relative content of each form depends on the composition of the original glass, iron concentration, thermal history, method of preparation, etc. The most important conclusion arrived at by Banerjee was that two or more forms of iron, including electrovalent forms, were present simultaneously in certain glasses. Weyl (74) and others attributed the color changes of glasses containing iron to constant interaction between Fe^{++} and Fe^{+++} ions present in the glassy matrix. In the present work, there were no observable coloration changes in the barium borate glass containing titanium dioxide after various heat treatments. The only change in color resulting in the glasses containing ten mole percent titanium dioxide (as-quenched and heat treated) can be attributed to the increased concentration of the titanium content. Consequently, any strong interaction between Ti^{3+} and Ti^{4+} ions can be ruled out. In other words the Ti^{3+} and Ti^{4+} ions (if present simultaneously), most likely are far apart and are not interacting strongly. However, the resulting precipitate will depend on the relative amounts of Ti^{3+} and Ti^{4+} ions present.

In conclusion, the presence of titanium as variable valence ions in the barium borate glass system, does play a very important role in the phase separation and crystallization of this glass system. Glassceramic materials having high dielectric constants and low dielectric losses are prepared from glasses of the $Ba0-Al_20_3-Si0_2-Ti0_2$ system (41, 73 and 74). When such a system is subjected to heat treatments, crystalline compounds such as barium titanate which have ferroelectric properties can be precipitated. In order to prevent the formation of barium titanosilicate or any other titanium compounds in general, Ba0

should be present in excess. Since the stoichiometric ratio of BaO : TiO_2 is 1 : 1 in BaTiO_3, the ratio of BaO : TiO_2 in the glass should exceed this ratio in order to insure the formation of BaTiO_3. Indeed, this proved to be true from the results obtained during the course of this study. Barium oxide was present in excess (20 mole percent) relative to titanium dioxide (2 and 10 mole percent) in all the glasses containing titanium dioxide. The x-ray diffraction analysis coupled with electron diffraction analysis indicated clearly that the crystalline phases present in this glass system were barium titanate (BaTiO_3) and barium boron oxide (BaB_2O_4).

4.3 <u>STRUCTURE AND CRYSTALLIZATION BEHAVIOR OF THE GLASSES CONTAINING</u> CERIUM OXIDE

Cerium is one of fifteen elements which follow barium in the periodic table. These elements are known as the lanthanide (or rare earth) elements. Throughout the series of lanthanide elements, the number of valence electrons is roughly constant of three in most of their ionic compounds (77). The two elements of the lanthanide group that readily show a higher valence state of four are cerium and terbium. Ce(IV) and Tb(IV) are very powerful oxidizing agents (77); with Ce(IV) being the most stable of the four-valent states. The ionic radius of Ce³⁺ in oxides is 1.1 Å and in borides is about 1.85 Å. On the other hand, the ionic radius of Ce⁴⁺ is 1.01 Å while that of Ce²⁺ is assumed equal to the ionic radius of Ba²⁺ at 1.35 Å (77). The Ce³⁺ ion is known to be colorless while the Ce⁴⁺ ion exhibits yellow coloration which is attributed to a charge transfer of an electron from a ligand to the f-orbitals of Ce (77). When cerium is present in the cerous oxide

 (Ce_2O_3) it assumes a coordination number of six which is most stable at low temperatures or a coordination number of seven which is most stable at high temperatures (77).

The lanthanides have two common features with the transition metal series, namely (77)

- 1- a systematic gradation of property from one element to the next, which may be broken at the half-filled and at the completelyfilled sub-shell;
- 2- a variable valence, which in the lanthanides has a very minor effect, but becomes a major effect in the transition elements where the core becomes more exposed and therefore sensitive to the environment.

Cerium oxide has been used extensively in the field of glass-ceramics in the preparation of photosensitive glass-ceramic systems. Stookey (78) showed that the incorporation of minor additions (up to 0.05 percent) of cerium dioxide to glasses containing copper have resulted in improving their photosensitivity. This was attributed to the ease with which electrons are released from cerium by the reaction:

$$Ce^{3+} + h_v \rightarrow Ce^{4+} + e^{-}$$

In the improved glasses this reaction then takes the form;

$$Ce^{3+} + Cu^{+} + h_{\nu} \rightarrow Ce^{4+} + Cu^{+}$$

This type of reaction in which the cerium ions donate electrons to copper results in the precipitation of copper atoms and hence to the formation of the latent image in the irradiated photosensitive glasses. The irradiated portions of the glass therefore contain higher concentrations of copper atoms than the unexposed portions and, as a result, nucleation and crystallization of copper will take place more easily in the irradiated regions. Cerium may be introduced in the photosensitive glasses in the form of CeO_2 or as a preparation containing 75% CeO_2 . It should be added in a reasonable amount since less than 0.005% CeO_2 in the glass is not effective. However, additions of more than 0.05% CeO_2 are undesirable and harmful since it absorbs the short-wave length electromagnetic rays (11). Many photosensitive glass-ceramic systems based on cerium oxide additions are reported in the literature (11 and 2).

In a recent study by Levy et al., (79) on the growth and decay of color centers in barium aluminoborate glasses containing cerium, it was concluded that the suppression of the radiation-induced coloring can be attributed to the simultaneous presence of both charge states of cerium ions, namely Ce^{3+} and Ce^{4+} . Additions of cerium oxide to glass systems to study its role as a nucleating agent on the phase separation, nucleation, and crystallization of such glass-ceramic systems is not reported in the literature. In a recent study (42), however, it was reported that a binary cerium phosphate glass system of the composition of 21 mole percent CeO₂ and 79 mole percent P_2O_5 contains both cerous and ceric ions. For this system, arguments were made that the cerium ions are present in the glass network partially as network-modifying ions (ceric ions) and partially as network-forming ions (cerous ions). During the crystallization process of this glass system, ceric oxide crystals separated out in the early stages of heat treatment and acted as nuclei. Glass-in-glass phase separation of cerium-rich phase occurs around these ceric-oxide crystals. Therefore the ceric oxide crystals grow, leading

to the final crystallization of the whole glass matrix on prolonged heat treatments. It was also concluded that in this cerium phosphate glass system, cerium was more effective than phosphorous as a nucleating agent. Additions of cerium oxide to a lead borate glass system (42) introduced more oxygen ions, hence increasing the concentration of the nonbridging oxygen ions in the system. This increase in the nonbridging oxygen promoted the instability of the lead borate glass system and resulted in the separation of two amorphous phases upon heat treatment of the glass. The net effect of cerium oxide additions to the lead borate glass system was reported as enhancing phase separation and consequently the crystallization in this system of the composition 66-72.5 B_2O_3 , 25.5-27.5 PbO, O-2 and 8.5 CeO₂ in mole percent. In a lead silicate glass system of the composition 29.2-30 SiO₂, 70-70.7 PbO (in mole percent), additions of 0.1 and 0.5 mole percent CeO2 did not enhance phase separation in the annealed condition (42). However, it did enhance phase separation during heat treatment in the nucleation-temperature range. This study of the role of cerium oxide as a nucleating agent on the three glass systems mentioned above concluded that the crystallization mechanisms depended on the host glass matrix.

In the study by Levy et al. (79) of color centers in barium aluminoborate glasses containing cerium, it was reported that the presence of Ce ions as Ce^{3+} or Ce^{4+} depends mainly on the way in which the glass is prepared. When the glass was prepared under partial reducing conditions, the glass was assumed to contain a mixture of Ce^{3+} and Ce^{4+} . On the other hand, the glasses prepared under totally reducing conditions were assumed to contain almost all the cerium as Ce^{3+} . Accordingly, if the glass is prepared in an oxidizing atmosphere (air), one expects to find

Ce as a mixture of Ce^{3+} and Ce^{4+} with a ratio of Ce^{3+}/Ce^{4+} less than one; i.e., the Ce^{4+} are in excess as compared to Ce^{3+} .

In the present study, additions of two and ten mole percent cerium oxide to the barium borate glass system $Ba0.4B_2O_3$ were used. Cerium oxide was introduced to the base glass as cerous oxalate $(Ce_2(C_2O_4)_3 \cdot 9H_2O)$. The glasses were prepared in air; it is reasonable to expect that cerium is present as a mixture of Ce^{3+} and Ce^{4+} with Ce^{3+}/Ce^{4+} ratio less than one. As stated before in sections 4.1 and 4.2, barium oxide will most likely donate its oxygen ions to tetrahedrally coordinate the triangular boron oxide units. Of course, this process will create some nonbridging oxygen ions. However, since the barium content is small (20 mole percent) the concentration of the nonbridging oxygen ions will probably be small. As in the case of titanium dioxide containing glasses, the role of cerium can be discussed on the basis of boron being in three or four-fold coordination states. The charge on the cerium ions being three or four plus will play a major role in the phase separation and crystallization due to local charge disturbances. The schematic models will be similar to the ones presented earlier for titanium containing glasses (Figure 53). One also can account for the phase separation on cooling the melt on the basis of a coordination number change, similar to the process mentioned in section 4.2 in the case of titanium dioxide containing glasses. Subsequently, upon heat treatment, the separated phases nucleate and finally crystallize after long periods of heat treatments at low temperatures or after short periods at higher temperatures. It is worth noting here that in this glass system containing cerium oxide, the crystallization process resulted in the precipitation of fine crystals. Even at the higher temperature of 650°C the microstructure of these glasses consisted of fine

crystals, unlike the case of titanium containing glasses or even the base glass where large grains of crystalline material precipitated at 650°C.

Again, the presence of the cerium ion in a variable valence state $(Ce^{3+} \text{ and } Ce^{4+})$ in the barium borate glass system plays a major role in the phase separation and crystallization processes in this system. Two crystalline phases present in the crystallized barium borate glasses containing cerium oxide were confirmed by both x-ray and electron diffraction analysis. These two crystalline phases were identified as cerium oxide (cerianite CeO_2) and barium cerate (BaCeO_3). A third crystalline phase, rich in boron (e.g. boron oxide B_2O_3), was also expected to be present in these glasses. Neither x-ray nor electron-diffraction analysis, however, confirmed its presence.

4.4 <u>STRUCTURE AND CRYSTALLIZATION BEHAVIOR OF THE GLASSES CONTAINING</u> PHOSPHORUS PENTOXIDE

Phosphorus pentoxide is one of the oxides categorized as glass forming oxides. Phosphate glasses, in general, are not widely used in commercial applications. However, phosphorus pentoxide has been used in many commercial glass systems as a nucleating agent. Many glass systems are reported to show a tendency to induced crystallization because of the presence of small amounts of phosphorus pentoxide. Phosphate glasses are normally composed of long chains or cyclic rings in their network (80). They are usually weak and chemically indurable, since their structure dissociates easily in many aqueous solutions.

Berezhnoi (11) cited the work of Stookey (81 and 82) in which Stookey studied the transformation of glass systems of CaO - P_2O_5 - Al_2O_3 - SiO_2 into glass-ceramics. Stookey showed that in such glasses containing P_2O_5

hardened droplets of phosphate-containing glassy regions were precipitated and dispersed through the bulk of the glass structure. These regions, which segregated during cooling of the melt, served as nucleating sites on which crystals grew during heat treatment.

Tomozawa (34) studied the effect of minor additions of oxide nucleating agents such as P_2O_5 , TiO_2 and ZrO_2 on the glass-in-glass phase separation of binary alkali-silicate glasses, in particular $Na_2O - SiO_2$ glass system by measuring the immiscibility temperatures and the kinetics of phase separation. He reported that P_2O_5 enhances the immiscibility boundary as well as the kinetics of phase separation. Tomozawa has also cited the works of Phillips et al. (83), James et al. (84), Harper and others (85), who investigated the effect of P_2O_5 on phase separation and crystallization of the $Li_2O - SiO_2$ glass system. He reported various authors who found that additions of one mole percent phosphorus pentoxide enhanced the separation of these glasses into two immiscible glass phases.

In studies of a phosphate optical glass consisting of P_2O_5 , BaO, Al₂O₃, B₂O₃ and As₂O₃ Vogel (2) reported that this glass crystallized very easily. The crystalline phase was identified as aluminum metaphosphate, Al(PO₃)₃. Doremus (15) describes the structure of phosphate glasses and crystals as made up of phosphorus-oxygen tetrahedra. However, the pentavalent phosphorus ion has a double bond to one of its surrounding oxygen atoms. It is likely then, that the structure of glassy P₂O₅ is a three-dimensional network of these phosphorus-oxygen tetrahedra, each tetrahedron being bonded to three rather than four other tetrahedra as in vitreous silica. It is also possible, according to Doremus, that sheets of PO₄ tetrahedra exist in some phosphate glasses, although there is no direct evidence for their presence.

McMillan (40), describes the effect of incorporation of a pentavalent ion (such as P_2O_5 ions) in a tetrahedrally coordinated glass network (silicate glass systems). In such a case, each of the PO_4 tetrahedra will bear an excess unit positive charge and it is unlikely that this could be neutralized by interstitial ions since these would have to be negatively charged. The only way that electroneutrality could be insured is if one of the oxygen ions around the pentavalent ion were to become doubly bonded to the central cation. Since this arrangement is not stable due to the asymmetry of the tetrahedral units containing the pentavalent ion, such a situation leads to separation into two phases. Moreover, McMillan (40) reported evidence of two-phase separated regions in glasses containing 0.5 - 6 weight percent phosphorus pentoxide. The two-phase separation process was necessary for nucleation catalysis leading to crystallization of a wide range of glass compositions derived from the Li_20 - Al_20_3 - Si0_2 , Li_20 - Mg0 - Si0_2 and Mg0 - Al_20_3 - Si0_2 systems. He did not elaborate, however, on the mechanism by which metallic phosphates catalyzed the crystallization of these glass systems.

In the present study, additions of 0.5 and 2.0 mole percent phosphorus pentoxide (which is a network-forming oxide) to the base barium borate ($Ba0.4B_20_3$) glass system were made to investigate its role as a nucleating agent on the phase separation, nucleation and crystallization of this binary system. As was shown from the data presented earlier in Chapter III, all the glasses containing P_20_5 have experienced different degrees of phase separation during almost all heat treatments. Only at the high temperature of 650°C, when the glasses were heat treated for at least twenty-four hours, did the glass systems experience crystallization. The phase-separated regions were amorphous. This amorphous phase

separation phenomenon can be described in terms of the above mentioned theories and models cited from the literature. As a network-forming ion, phosphorus enters the glassy network in network-forming positions, taking part in its structure. The barium borate glass network, as described before, may have regions where the boron ions became tetrahedrally coordinated and regions where the boron ions still preserve their three-fold coordination states. When the pentavalent phosphorus ions enter the network, it becomes doubly bonded in one or two places to the oxygen ions to preserve their electroneutrality. This is shown in Figure (54). Due to this double bonding process, the concentration of nonbridging oxygen increases. The network then becomes more loose. The presence of loose network structure in this case was evidenced by the fact that all glasses containing phosphorus pentoxide dissolved very easily in the solution used for chemical thinning during the preparation of transmission electron microscope samples. While it took about 30 - 90 minutes on the average to prepare thin areas of all the other glasses studied in this work (with original thickness of about 1 - 1.5 mm.), it took about 10 - 20 minutes to achieve the same result with glasses containing P_2O_5 . This loose structure which was the result of the incompatibility between the two network-forming ions (namely boron and phosphorus ions) is strongly believed to promote phase separation of the glass system into two relatively more stable amorphous regions. One such region will be undoubtedly phosphorus-rich, the other will be boron-rich. Heat treatment of this glass results in a rearrangement of the two amorphous regions in which more stable glassy regions finally appear. Once these amorphous boron-rich regions are created, they tend to be more stable and hence the glassy matrix becomes less susceptible to the crystallization process. Moreover,



Fig. 54 (A)

Schematic representation for the arrangement of the different ions in the network of the barium borate glass containing phosphorus pentoxide.



Fig. 54 (B) (continued)

Schematic representation for the arrangement of the different ions in the network of the barium borate glass containing phosphorus pentoxide.

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it is believed that the phosphorus ions will associate with the barium ions present in the modifying position actually forming phosphorusbarium rich regions. This was arrived at by the observations of the transmission electron micrographs, shown earlier, of the microstructure of these glass systems. The light contrast regions must be those that are rich in boron, while the darker ones represent the barium-phosphorus rich regions. From x-ray and electron diffraction analysis, the boronrich regions were identified as boron oxide (B_2O_3) . The barium-phosphorus rich regions may be either Barium orthophosphate $[Ba_3(PO_4)_2]$ or barium pyrophosphate $(Ba_2P_2O_7)$. Exact identification of which of the barium phosphate compositions was present was extremely difficult due to the relatively diffuse electron diffraction pattern and the broad peaks of the x-ray diffraction pattern.

It should be mentioned here that additions of two mole percent phosphorus pentoxide to the base glass resulted in visually observable phase separated ribbons in the as-quenched glass. This of course, necessitated crushing the resulting glass and remelting it to produce a more homogeneous glass. One can explain this phase separation of the as-quenched glass containing two mole percent phosphorus pentoxide on the basis that the phosphorus pentoxide was not well distributed throughout the matrix. Thus, upon cooling, segregation of phosphorus ions in the loose network resulted in macroscopic local phase separated regions. Crushing the glass and remelting resulted in redistribution of the phosphorus ions more uniformly in the matrix and hence confining the phase separation process, due to the incompatibility between boron and phosphorus ions to a micro-scale.

4.5 RELATIVE EFFECTIVENESS OF THE NUCLEATING AGENTS

In accounting for data on phase separation in sodium silicate glass system containing ZrO_2 , TiO_2 , and P_2O_5 (in minor concentrations) as nucleating agents, Tomozawa (34) used the ionic field strength theory of Dietzel as a basis for his arguments. He compared the cationic field strength of those nucleating agents $(Z/a^2, where Z is the valence of the$ ion and "a" is its atomic separation in A°) with that of Si⁴⁺. It appeared that cations with larger Z/a^2 values than that of Si⁴⁺ increase the immiscibility region and enhance phase separation (e.g. P_2O_5); and cations with smaller Z/a^2 values than that of Si⁴⁺ decrease the immiscibility regions and supress phase separation (Ti and Zr ions). Values of Z/a^2 along with ionic radii, atomic separation and Z/r values are given in Table 13. On the same basis of Tomozawa's arguments, one would expect that minor additions of TiO_2 or CeO_2 would reduce the phase separation in the present system, since the Z/a^2 value for Ti⁴⁺ and Ce⁴⁺ (1.04 and 1.17 respectively) are smaller than that of both B^{3+} and B^{4+} (1.33 and 1.65, respectively). This is most certainly is the case, since minor additions of two mole percent of TiO_2 or CeO_2 to the barium borate glass system used in this study in the as-quenched state resulted in suppressing the phase separation, as evidenced by the data shown in Table 10. On the other hand, this argument for glasses containing P^{5+} ions does not hold true, since Z/a^2 for P_2O_5 (1.91) is certainly higher than that of B^{3+} and B^{4+} yet additions of $P_2 O_5$ resulted in suppressing the phase separation process in the as-quenched state as seen from Table 10.

Moreover, increased concentrations of either TiO_2 or CeO_2 (which are intermediates depending on their coordination number) did indeed promote further phase separation, increasing the immiscibility as was speculated

Table 13

Field strength of cations in oxides

	^	•		^					
Ion	r A	a A	Z/r	Z/a ²					
Ba ²⁺	1.34	2.75	1.49	0.26					
Zr ⁴⁺	0.79	2.20	5.06	0.83					
Ti ⁴⁺	0.68	1.96	5.88	1.04					
*Ce ⁴⁺	1.01	1.85	3.96	1.17					
в ³⁺	0.23	1.5' 1.35"	13.04	1.33 1.65	8 11	:	C.N. C.N.	-	4 3
Si ⁴⁺	0.42	1.59	11.43	1.58					
Р ⁵⁺	0.35	1.62	14.29	1.91					

coordination number or valency.
ionic radius. Ζ

r

a

atomic separation.
data extrapolated from plots given by Phillips and Williams (77). *

C.N. : coordination number.

by Tomozawa (34). This also is seen from the data shown in Table 10 for these glasses in the as-quenched state. The role of P_2O_5 as a nucleating agent, however, does not follow the same trend. This may be due to the fact that P_2O_5 by itself is a glass former not an intermediate. Table 10 indicates taht phase separation decreased due to increased additions of P_2O_5 , contradicting arguments presented by Tomozawa (34). It is further noted that the increased additions of P_2O_5 (up to two mole percent), further suppressed phase separation in the as-quenched state. It appears that the role of the intermediate nucleating agents is different from that of glass forming nucleating agents. These nucleating agents, although suppressing phase separation of the base glass in the as-quenched state, have peculiar behavior toward crystallization. Of these agents, the network former, P_2O_5 , did not promote extensive crystallization. On the other hand, TiO_2 additions promoted coarse-grained crystallization, while CeO₂ additions promoted fine-grained crystallization at high heat treatment temperatures. Thus, it appears that Tomozawa's arguments hold true for such glasses containing TiO_2 or CeO_2 when they receive nucleation and crystallization treatments. However, the temperature at which this phenomenon was observed was higher than that of the base glass, as to be expected, since the nucleating additive suppress the undercooling required for the nucleation process.

On the basis of this work, however, one cannot argue that glasses that have higher phase separation crystallize more extensively since the results contradict - to some extent - such a hypothesis. The descrepancies observed during the course of this work could be attributed to the fact that the glasses used in this work were quenched from the molten state, whereas the glasses studied by Tomozawa (34) were annealed from

the molten state.

Another point that should be noted and accounted for is that TiO_2 seemed to be less effective than CeO_2 as a nucleating agent in this barium borate glass system. Additions of CeO_2 resulted in the precipitation of fine crystals at relatively shorter heat treatment times at the same heat treatment temperature as compared to additions of TiO_2 to the same base glass system. This probably can be accounted for on the basis of the compatibility of the Ba²⁺ ions and the Ce⁴⁺ ions. This is arrived at by checking the relative compatibility in the ionic radii of the Ti⁴⁺ (0.68 Å[°]), Ce⁴⁺ (1.01 Å[°]), and Ba²⁺ (1.34 Å[°]) ions, shown in Table 13. This indicates that cerium ions associate more readily with barium ions and precipitate finer crystals than those precipitated in glasses containing titanium ions.

In all the glasses studied, phase separation preceeded crystallization, although, glasses containing phosphorus pentoxide showed more extensive phase separation than the other glasses. The fact that glasses containing phosphorus pentoxide did not crystallize easily, indicates that phase separation alone is not sufficient for the crystallization of the glassy systems used. In glasses containing titanium dioxide and cerium oxide the phase separated regions are much smaller in size, indicating that these agents did play important roles in the phase separation process. Consideration of the relative effectiveness of these nucleating agents suggests that variable coordination numbers of the cation present in the nucleating agent is the most effective criterion for nucleation and crystallization of these glass systems.

4.6 NUCLEATION RATE AND ACTIVATION ENERGY STUDIES

Nucleation rate vs. temperature curves were found to exhibit the classical bell-shaped plots as shown in Figure 55. The nucleation rate maximum (near a temperature of about 475° C) has its lowest value for the barium borate glasses containing no nucleating agents as shown in Figure 55(A). Minor additions of two mole percent titanium dioxide did not result only in a higher value of the nucleating rate peak (by a factor of 10), but also shifted this peak towards a higher heat treatment temperature of about 650°C as shown in Figure 55(B). Additions of ten mole percent titanium dioxide resulted in the highest value for the nucleating rate among all the glasses used in this study (by a factor of 10 compared with the 2 mole percent TiO_2), as well as a shift towards higher temperature ($675^{\circ}C$), as displayed in the plot of Figure 55(C). The same features were exhibited in the nucleation rate peaks of glasses containing two and ten mole percent cerium oxide as far as the relative magnitude and position in the temperature scales. However, the magnitude of the nucleation rate peak for the glasses containing ten mole percent cerium oxide was not as drastically changed (compared with glasses containing two mole percent) as in the case for glasses containing titanium dioxide; [Figure 55(B)-(D)]. The relative positions of these peaks are at about 570°C for glasses containing two mole percent cerium oxide and at about 650°C for these glasses containing ten mole percent cerium oxide. Hence, the addition of nucleating agents to the barium borate glass system not only results in shifting the position of the nucleation rate peak, but also results in a change of its relative magnitude. Both these variations in the nucleation rate peak, magnitude and position are dependant on the amount of the nucleating agent used.





(A). for barium-borate base glass.

(B). for barium-borate glass containing 2 mole% titanium dioxide.

(C). for barium-borate glass containing 10 mole% titanium dioxide.



Fig. 55 (continued)

Nucleation rate vs. heat treatment temperature

- (D). for barium borate glass containing 2 mole % cerium oxide.
- (E). for barium borate glass containing 10 mole % cerium oxide.

Addition of the nucleating agents decreases the required supercooling for forming stable size nuclei. In this respect, titanium dioxide is the most effective and cerium oxide is the next best. The heat treatment temperature for forming good glass-ceramics, however, should be so chosen to have viscous flow in the glass to dissipate the stresses due to the volume changes involved during crystallization. Further, the crystalline product produced should be very fine grained to achieve maximum mechanical strength and impact strength. Considering these aspects, cerium oxide is a more effective nucleating agent than titanium dioxide. Phosphorus pentoxide did not promote any considerable crystallization; as a matter of fact it suppressed crystallization.

In a recent study of the nucleation and crystallization of glassy CdGeAs₂, Rishbud (86) calculated the activation energy associated with the kinetic barrier to nucleation. He obtained a value of 12.5 Kcal/mole for this activation energy. In his calculations, Rishbud explains that the exponential term containing ΔF^* in the Turnbull-Fisher equation (12) represents the thermodynamic barrier to nucleation, and the term containing "q" represents the kinetic barrier to nucleation. He further argues that on the low-temperature side of the nucleation maximum of the nucleation rate curve, only the term containing "q" is of significance. Following Rishbud's arguments, plots of $\log_{10} N_v$ versus 1/T for the data of Figure 55 obtained on the low temperature side (<650°C) yielded a straight line for each glass system. The activation energy determined from the slope of each straight line for each glass system is shown in Table 14. These values represent the energies associated with the kinetic barrier to nucleation in each system. As can be seen from this table, the barium borate base glass containing no nucleating agent has the lowest activation



Table 14

Calculated activation energy values

Glass	Activation Energy KCal mol ⁻¹				
BBa	3.66				
BBaTi2	9.85				
BB a Til0	13.25				
BBaCe2	14.17				
BBaCe10	5.48				

• .

energy value (about 3.7 Kcal/mole). In other words, the base glass can nucleate and crystallize at lower heat treatment temperatures than the glasses containing titanium dioxide or cerium oxide. This is in agreement with the data shown previously in Chapter III. The values of the corresponding energies obtained for glasses containing two and ten mole percent titanium dioxide are fairly close (9.9 and 13.3 Kcal/mole respectively), indicating that the increased concentration of titanium dioxide in the glass matrix did not have a marked influence on the nucleation mechanism. On the other hand, in glasses containing two and ten mole percent cerium oxide the corresponding values for the activation energies are 14.2 and 5.5 Kcal/mole, respectively. These values indicate that increasing the concentration of cerium oxide in the glass system lowers the nucleation barrier, resulting into more available nucleating sites. This situation resulted in the crystallization of fine grained crystals distributed uniformly in the glass matrix. This may be attributed to the suggestions proposed in an earlier study (41). Some of the cerium ions may be entering the network and the rest may be entering the modifying positions. It is probably that more cerium ions exist in the modifying positions in glasses containing higher percentages of CeO₂ additives, increasing the available nucleating sites, hence decreasing the kinetic barrier for nucleation. The results also suggest that, such a situation might exist at higher concentrations of TiO_2 (higher than 10 mole percent), since the kinetic barrier appears to be increasing up to ten mole percent, additions of TiO₂ studied in the course of this work.

The well separated nucleation and growth rate peaks in the case of the base glass system resulted in the crystallization of a fine grained, weak glass-ceramic on prolonged heat treatments. The weakness of the

resulting glass-ceramic in this case can be attributed to the fact that at this low temperature the glass matrix did not attain enough viscous flow to dissipate the stresses created in it because of crystallization. The production of a more mechanically strong glass-ceramic in such a case where the nucleation and growth rate peaks are well separated may require two heat treatment schedules. A heat treatment schedule at a low temperature corresponding to the nucleation temperature will result in precipitation of enough nucleating sites. Another heat treatment at a higher temperature (the growth temperature), where the matrix is viscous enough to relieve the stresses associated with the crystallization process, will ultimately result in the desired glass-ceramic. On the other hand, glasses containing titanium dioxide or cerium oxide may require a single heat treatment schedule to attain the desired glassceramic. Since additions of titanium dioxide or cerium oxide were found to shift the nucleation peak to higher temperatures (closer to that of the growth rate peak), it is more likely that both nucleation and growth rate curves will overlap over a range of temperatures. A single heat treatment in this range will create enough nucleating sites and result in the growth of the precipitated crystals. Furthermore, since these temperatures are relatively high, the glass matrix will be viscous enough to relieve the stresses associated with the crystallization process and will result in stronger glass-ceramic. Indeed, this was shown to be the case for such glasses containing titanium dioxide or cerium oxide as nucleating agents, with those glasses containing cerium oxide crystallizing in finer grained crystals as shown earlier.

4.7 GENERAL REMARKS

The crystallization of the glass systems used in this study (particularly those containing titanium dioxide or cerium oxide) can be viewed in the light of three characteristic stages. Stage I is a glassin-glass phase separation process followed by stage II and stage III, which can be associated with the nucleation and crystallization processes, respectively. In stage I, at the early heat treatment times, a marked increase in the size of the precipitated phases was clearly noted. This is believed to correspond to the growth of the amorphous phase precipitated because of the addition of the nucleating agent. During stage II. at relatively longer heat treatment times, a sharp decrease in the size of the precipitated phases was observed. This decrease in the dropletlike microphase can be explained in terms of the appearance of the nuclei (e.g. cerium dioxide in cerium oxide containing glasses) and the break up of this segregated phase into smaller droplets, rich in titanium dioxide or cerium oxide. Vogel (2) has described a similar phenomenon in titanium dioxide containing glasses. In his studies, he has reported that the phase separated regions in stage I can break up into smaller sizes. The final stage, stage III, is a growth stage of the crystalline phase, during which a much slower increase in size took place after quite long heat treatments with a noticeable incubation time. The incubation time involved in each glass system was found to be dependent on the relative concentration of the nucleating agent as well as on the heat treatment temperature. Figures illustrating characteristic plots of size versus heat treatment temperatures were shown earlier in Chapter III. At high heat treatment temperatures, stage I and stage II may not be noticed easily because of the very short incubation time that may be associated

with them. On plotting the number per unit volume versus heat treatment time, one expects to see a curve with three stages corresponding to the ones mentioned earlier, but behaving in an opposite fashion. Figure 57 shows a comparative plot of size and N_v vs.heat treatment time to illustrate this effect.

As can be noticed, cerium oxide is the most effective nucleating agent in producing a fine-grained crystalline structure at a relatively high enough temperature. Although titanium dioxide promotes crystallization in this binary barium borate glass, it tends to produce coarsegrained crystalline precipitates. Phosphorus pentoxide, in spite of enhancing phase separation in the heat treated glasses does not promote extensive crystallization.



CHAPTER V

CONCLUSIONS

- 1- Variable coordination number of the cation in the nucleating agent is a very important criterion in defining the role of the nucleating agent. The presence of variable valence cations, like TiO_2 or CeO_2 , tend to promote crystallization in the barium borate glass of composition $BaO.4B_2O_3$.
- 2- Phase separation is a precursor for crystallization in the barium borate glass system. It is not a sufficient condition, however, for promoting crystallization in this system.
- 3- Titanium dioxide promotes nucleation as well as growth of crystals in this system. As a result, it produces coarse-grained glassceramics.
- 4- Of the three nucleating agents studied in this work, cerium oxide is the most effective nucleating agent. Cerium oxide produces a very fine-grained glass-ceramic within reasonable heat treatment times at temperatures high enough to relieve the stresses induced because of the crystallization process.
- 5- Additions of cerium oxide or titanium dioxide reduce the undercooling required for nucleation.
- 6- Glasses containing titanium dioxide can produce crystals having

attractive physical properties, namely barium titanate (BaTiO₃).

- 7- Phosphorus pentoxide, although it promotes phase separation, does not enhance nucleation or crystallization of the barium borate glass system.
- 8- Cationic field strength arguments do not necessarily hold true in the case of the as-quenched barium borate glass system of the composition $Ba0.4B_2O_3$ containing TiO_2 or CeO_2 . The descrepancy experienced in the interpretation may, however, be attributed to the difference in specimen preparation procedure (quenched versus annealed).
- 9- Four percent nitric acid aqueous solution is the best solution for chemical thinning of all the glasses used in this study in the process of preparing sections thin enough for transmission electron microscopic studies.

CHAPTER VI

SUGGESTIONS FOR FURTHER RESEARCH

1- Since glasses containing cerium oxide or phosphorus pentoxide have exhibited some interesting visible changes in color, it would be worthwhile to carry out optical studies on these glasses. It is believed that studies of property variations such as refractive index and absorption spectrum and correlation to the microstructural changes discussed in the present study would shed more light on the role of such nucleating agents in this barium borate glass.

2- As was stated earlier in Chapter V, during the preparation of thin samples of the different glasses used, different degrees of resistance to the chemical thinning process were observed. Moreover, some glasses were observed to break more easily than others. This points out the fact that the nucleating agents used also played a significant role on the mechanical properties of such glass systems. Hence, studies of the mechanical properties as affected by the microstructural changes induced by the additions of the different nucleating agents definitely will prove to be of great value.

3- Further studies of the magnetic and ferroelectric property variations of barium borate glasses containing titanium dioxide or cerium oxide are believed very important, since the crystalline phases

precipitated in such systems are believed to have interesting magnetic and ferroelectric properties.

4- Hot-stage electron microscopy is not utilized extensively to study the microstructural changes during heat treatment. Prolonged interaction of the electron beam with the glass system makes it very difficult to obtain representative electron micrographs (40). Since the barium borate glass system used in this study was very stable under the influence of the electron beam, it is believed that it would be a good candidate for the application of the hot-stage electron microscopic techniques in studying directly the microstructural variations due to heat treatment. This way, a full detailed picture of the microstructural changes taking place in this system, particularly at the very early stages of heat treatment, would be obtained.

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