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TRANSMISSION ELECTRON MICROSCOPIC STUDY OF PHASE SEPARATION IN GLASSES CONTAINING CERIUM OXIDE

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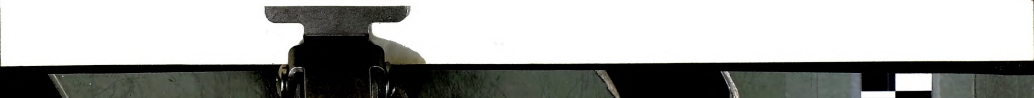

ABSTRACT

TRANSMISSION ELECTRON MICROSCOPIC STUDY
OF PHASE SEPARATION IN GLASSES
CONTAINING CERIUM OXIDE

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The role of cerium oxide as a nucleating agent in lead-silicate, lead-borate, and cerium-phosphate glasses was investigated by transmission electron microscopy. The samples were lead-borate glasses containing 0.0, 2.0, and 8.5 mole percent cerium oxide, and lead-silicate glasses containing 0.0, 0.1 and 0.5 mole percent cerium oxide. A new binary cerium-phosphate glass containing 21 mole percent cerium oxide was also prepared to compare the role of cerium and phosphorus in the nucleation of the crystalline phases.

Thin foils suitable for transmission electron microscopic observation of heat-treated glasses were prepared by a chemical jet-polishing technique. The polishing solutions and polishing conditions were developed during the course of this work. Mechanical polishing was an alternative technique to prepare thin foils of highly crystallized specimens. The heat-treatment schedules of all the glasses were prepared from differential thermal analysis data. Electron and

X-ray diffraction were used to identify the precipitated crystalline compounds.

In both lead-borate and lead-silicate glasses, phase separation preceded crystallization. In binary lead-borate and lead-silicate glasses, cerium-oxide addition enhances phase separation of a lead-oxide-rich glassy phase. Larger additions of cerium oxide addition promote more phase separation in both these systems. In the cerium-phosphate glass, which contains both cerium and phosphorus, cerium is a more effective nucleating agent than phosphorus. In this glass ceric oxide crystallizes first upon heat-treatment and creates nuclei for further crystallization. A fine-grained glass-ceramic that is optically transparent, can be obtained by heat-treating the cerium-phosphate glass in the nucleating-temperature range.

The results are discussed on the basis of the effect of cerium-oxide addition on the host-glass network structure.

TRANSMISSION ELECTRON MICROSCOPIC STUDY OF PHASE SEPARATION IN GLASSES CONTAINING CERIUM OXIDE

by

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CHAPTER I

INTRODUCTION AND HISTORICAL REVIEW

INTRODUCTION

Glass-ceramics are inorganic materials of great technical portance. These are prepared by controlled crystallization of eshaped glass objects to produce a very fine-grained structure. ese materials have superior physical and mechanical properties mpared with crystalline ceramics and inorganic glasses.

The crystalline ceramic objects, which have inorganic non-tallic materials as the essential component, are usually shaped at om temperature but fired at elevated temperatures to promote nding between particles and to minimize porosity. The presence of herent porosity makes crystalline ceramic objects mechanically ak. In addition, keeping close dimensional tolerance becomes fficult.

Some of the disadvantages of crystalline ceramics are avoided inorganic glasses. The articles can be shaped easily at the ftening temperature, where the coefficient of viscosity is less an 10^8 poise, and then cooled to room temperature. This technique oduces an article that is fairly rigid, with coefficient of vis-sity greater than 10^{14} poise.

Numerous definitions of glass are to be found in the literature. The primary difficulty is the proper grouping of the glass within the accepted states of aggregation. Morey [1] pointed out the difficulties involved in arriving at a proper definition of "glass". After a critical discussion of earlier efforts, he suggests the following definition: "A glass is an inorganic substance in a condition which is continuous with, and analogous to, the liquid state of that substance, but which, as a result of reversible change in viscosity during cooling, has attained so high a degree of viscosity as to be for all practical purposes rigid."

Kitaigorodski [2] quoted a definition that was developed by the committee on terminology of the Russian Academy of Sciences: "Glass is a term used for all amorphous solids which are obtained by supercooling a melt regardless of its chemical composition and the temperature region in which the solidification takes place. Because of the increase in viscosity on cooling, glasses assume the properties of solids. The transition from the liquid into the glassy state has to be reversible." Jones [3] defines "glass" as: "a material formed by cooling from the normal liquid state, which has shown no discontinuous change - such as crystallization or separation into more than one phase - at any temperature, but has become more or less rigid through a progressive increase in its viscosity."

The most acceptable definition is that of MacKenzie [4]: "any isotropic material, whether it be inorganic or organic, in which three-dimensional atomic periodicity is absent and the viscosity of which is greater than about 10^{14} poise, may be described as a glass."

In general, glasses are obtained by the supercooling of liquids.

The difference between a glass and the corresponding liquid or supercooled liquid may be conveniently demonstrated by a specific volume-temperature relationship of the type shown in Fig. 1. On cooling a liquid which normally does not form a glass at the cooling rates employed, from any temperature T through the melting temperature T_m of the material, there will be an abrupt change in the specific volume as shown by curve (a). However, in the absence of crystallization, the liquid can be supercooled through the melting temperature without an abrupt change in the specific volume as shown by curve (b). On further cooling to a temperature region denoted by T_g, when the viscosity of the supercooled liquid has reached about 10^{14} poise, the structure does not relax at the cooling rate employed. This temperature is called "the glass-transition temperature", below which the non-crystalline material is termed a "glass", and path (c) is followed. At such high viscosity, molecular motions are retarded and relaxation times become comparable with or greater than the time generally taken for experimental measurements, thus giving rise to the discontinuity shown in curve (c) of Fig. 1.

Although glassy materials can be easily formed without any pores and with close dimensional tolerances, they develop microcracks that make glass mechanically weak. To minimize the problems with both crystalline and non-crystalline ceramics, one can easily shape the article in the glassy state and then by proper heat-treatment can convert it to become almost completely crystalline. Materials produced by this method are known as "glass-ceramics". These materials exhibit superior physical and mechanical properties compared with crystalline and non-crystalline ceramics produced by conventional means.

Fig. 1. Specific volume - temperature relationship for glass forming system.

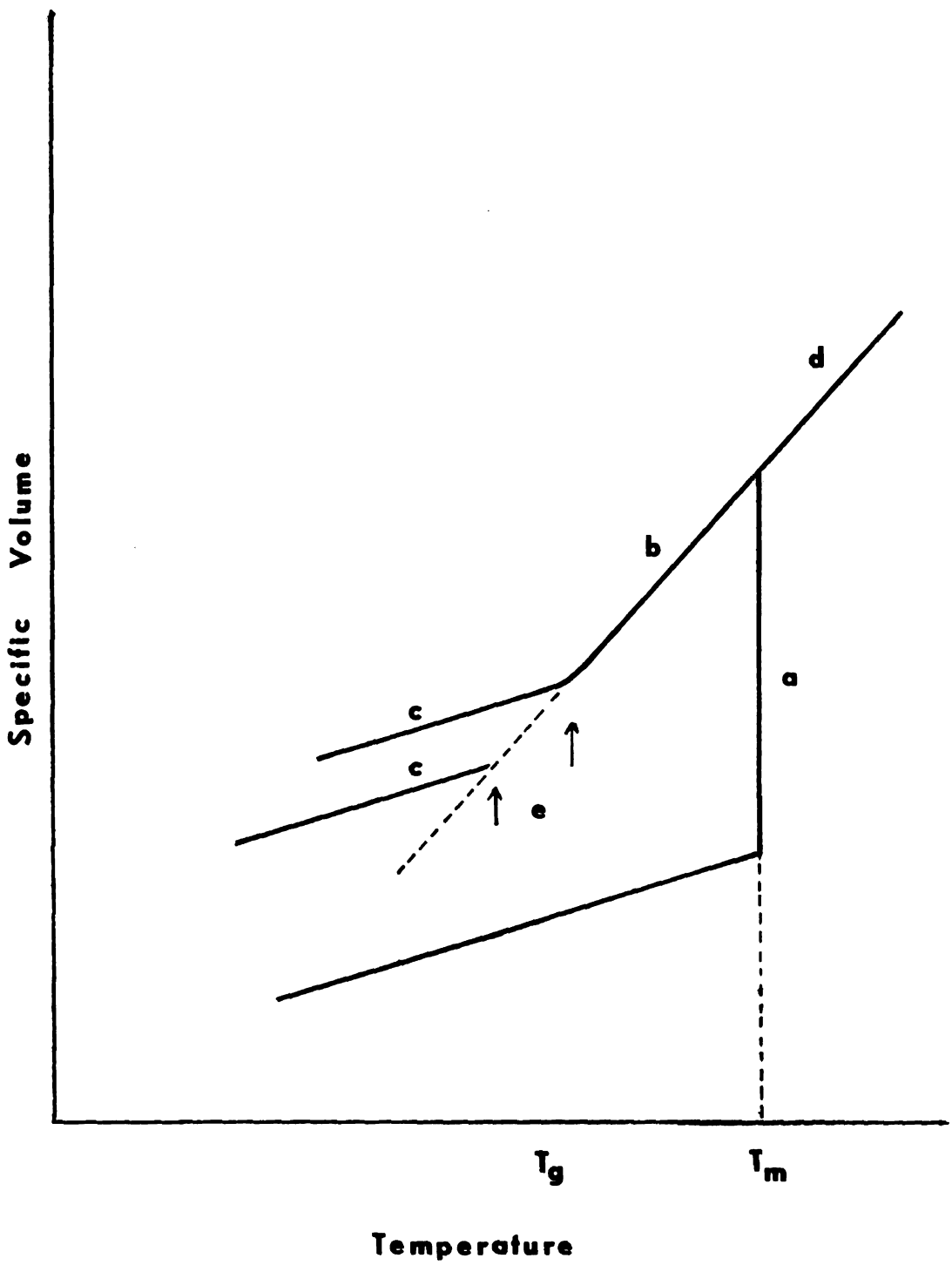
a. Crystal path.

b. Supercooled liquid path.

c. Glass formation path

d. Liquid.

e. Transformation temperature range Tg


Specific Volume
d
b
a
c
c
e
T_g
T_m
Temperature

Although, any glassy material can be converted to become crystalline, the tendency for such devitrification will be minimal in most glasses that are relatively stable at room temperature. The crystallization tendency will depend on the difference between the energy of the crystalline and the glassy states. Only when the difference is extremely small one can form a stable glass. In order to promote the crystallization of glass nucleating agents can be added to aid in the crystallization process.

The nucleating agents can be dissolved in the parent glass. After the object is formed, these nuclei are precipitated by reheating the glass to a temperature below its softening point. Such a treatment provides a large number of uniformly-distributed nuclei in the preshaped glass product. The crystals grow on these nuclei from the glassy matrix on prolonged heat treatment. The heat treatment can be continued until the object has become almost 100 percent crystalline.

Although the basis of the glass-ceramic process is to accomplish devitrification of glass, this process must be controlled to ensure that the final material has very fine grain structure. Uncontrolled crystal growth gives rise to a coarse grain structure, consisting of a relatively few large crystals. Such a material would be mechanically weak.

The particular advantages of the glass-ceramic process are that it allows the formation of a material by glass-forming processes which are rapid, economical, automatic, and can be carried out to close tolerances and without any porosity. This process provides new kinds of ceramics having useful combinations of properties not feasible by other processes.

In spite of the scientific and technological progress achieved in the field of glass-ceramics during the past decade there still exist many unresolved problems. One problem is to find new and different

glass systems in which fine-grained crystallization can be produced. Another problem is the search for new additives capable of catalyzing the crystallization of a variety of glasses. The effects of these catalysts in aiding the nucleation and growth processes in glasses is important. Many substances are soluble in molten glass but precipitate out under controlled conditions. Also, one other problem is to find certain techniques to arrange effective heat-treatment schedules to prodcue the desired fine-grained glass-ceramics. The mechanism of phase separation, nucleation and crystallization of glass is far from being understood. Part of the difficulties in solving these problems result from the limitations of the available experimental methods for studying glass-ceramic materials.

The onset of crystallization in glasses is detected commonly by viscosity measurements, differential thermal analysis, and electrical-conductivity measurements. Accurate determination of the microstructure of the glass-ceramics, however, cannot be achieved by these methods. Although replica studies by electron microscopy can reveal the microstructural features, it can not distinguish between crystalline and glassy phases separated out of the glass matrix; further the observations are limited to the surface only. Thin-foil studies by transmission electron microscopy coupled with electron diffraction provides a powerful tool that can be used for investigating the crystallization and phase-separation behavior of different glasses.

The first and major purpose of this work is to study the role of a nucleating agent (cerium oxide) in different simple glass matrices with the intention that the results will contribute to the understanding of nucleation, phase separation, and crystallization of glasses.

A second purpose is to compare the use of the transmission electron microscopy with X-ray diffraction and differential thermal analysis as an effective tool to study the crystallization of glasses. The third purpose is to develop the most efficient and reproducible techniques for thin-foil preparation since the limiting factor for the use of the transmission electron microscope for studying the microstructure of glass-ceramics is the preparation of specimens.

Since transition metals and rare-earth elements can exist in different valence states, their oxides are potential nucleating catatalysts in glasses. Oxides of transition metals such as Ti, Cr, Cu, Zr, Pd, and Pt have been extensively studied as nucleating agents in glasses. The potential of rare-earth oxides as catalysts in glass-ceramics has not been explored in detail. Among the oxides of rare-earth elements, cerium oxide has been used as a nucleating agent in photosensitive glasses, and such glasses have special properties and applications. To name a few - these glasses can be used for stabilization against radiation-induced coloration, for suppression of optical absorption induced in the visible spectrum by ionizing radiation, and as a gamma-radiation dosimeter. For these reasons cerium oxide was chosen as the nucleating agent in this study. The role of cerium oxide on the microstructure of glass is part of the basis for further studies of physical properties.

Phase diagrams of PbO - B_2O_3 and PbO - SiO_2 systems show that commercially useful lead borate and lead silicate glasses can phase-separate into two immiscible liquids when heat treated. The existence of different coordination for boron in borate glass and silicon in silicate glass facilitates the study of the role of the nucleating

agent in different network structures. The large differences in the atomic number for lead (Z = 82), boron (Z = 5), and silicon (Z = 14), will cause high contrast of phase-separated regions in the electron micrograph as a result of the difference in electron absorption of the different ions present in these glasses. For these reasons lead-borate and lead-silicate glasses were chosen as the binary glass matrices.

To prepare a single-component glass system in which the nucleating agent CeO_2 can be incorporated, the three major network formers, namely SiO_2, B_2O_3, and P_2O_5, were considered. Preliminary trials showed that P_2O_5 can form a glass easily with CeO_2 under normal melting conditions. As a result phase separation, nucleation, and growth of crystals were studied by transmission electron microscopy in lead-borate and lead-silicate glasses containing cerium oxide, as well as in cerium-phosphate glass.

In summary, cerium oxide was chosen as the nucleating agent because of the future potential of such glasses, and the glass matrices were chosen for commercial importance and experiental convenience in study by transmission electron microscopy.

B. HISTORICAL REVIEW

Glass-crystalline materials, such as glass-ceramics, including the photosensitive type are a class of materials that have gained importance in the last few decades. They are of unusually great interest because of their extremely favorable combination of mechanical, thermal, chemical, electrical and physical properties. By heat

treatment of preshaped special glasses, scientists succeeded in preparing materials with a fine crystalline structure and with significantly higher mechanical strength, thermal stability, and electrical-insulating properties than existed in the original glasses. The technical development of these new products in the United States of America was started at Corning Glass Works in 1947. A great number of patents and reports, especially those of S. D. Stooky at Corning demonstrate the varied applications of such materials. The production and application of glass-ceramics were very successful, despite lack of explanation of the mechanisms involved.

In the determination of equilibria in the system lithia-alumina-silica, Roy et al [5] observed an enormous increase in crushing strength of these glasses after crystallization heat-treatment. The general experience with a large number of similar systems, shows that quite frequently glass objects become much stronger on crystallization.

The formation of nuclei of the new phase of the material within a different phase of the same material in the absence, or without the help of foreign particles, is termed "homogeneous crystallization" by Stookey [6]. "Heterogeneous crystallization," also called a "Catalyzed crystallization," occurs with the help of a foreign agent acting as a catalyst. In glass-ceramics technology "crystallization catalyst" is a substance capable of influencing not only the rate of the phase transformation but also its course.

Catalyzed crystallization in glass can be classified into (1) crystallization of the dissolved substance, where crystallization of small amounts of the catalyst does not produce a significant change in the glass structure, and (2) crystallization of the solution of catalyst

in the glass during which the very structure of glass changes, with catalyst ions entering into the structural network.

a. Homogeneous or Spontaneous Crystallization

Ostwald [7] showed that spontaneous crystallization may occur only in highly supersaturated solutions. Tammann [8] in his investigation of the crystallization of inorganic glasses, determined the existence of two metastable regions shown in Fig. (2). In the first metastable region (zone a) just below the melting point, the nuclei are not formed at any measurable rate; however, the crystals, if they have been formed at all, are capable of growing. The second region (zone b), in the lower temperature range, is characterized by a low rate of formation of nuclei, since the high viscosity of glass here inhibits spontaneous crystallization and the growth of crystals.

Kuznetsov [9] explained the spontaneous formation of nuclei in the supercooled liquid on the basis of the molecular-kinetic theory of matter. The molecules, which are in continuous thermal motion, possess completely determined kinetic and potential energies, which diminish with decreasing temperature. In liquids the molecules have larger kinetic energy than that in solids. It follows that the energetic molecules in the liquid are incapable of forming stable nuclei, since, owing to thermal motion, may accidental clustering of them will rapidly break up the nuclei. With decreasing temperature and, consequent decreasing kinetic energy of the molecules, however, the clusters formed by them become more stable. Therefore the formation of the nuclei is possible below a certain given temperature. If the nucleus has very small dimensions, it may again disappear,

Fig. 2. Schematic for the crystallization of a viscous liquid (Tammann [8].

T: Heating Temperature

v: Rate of Formation of the Nuclei.

V: Rate of Crystal Growth.

ıce the stored potential energy is greater for the surface-layer lecules than for the inner molecules. When the nucleus attains certain given size at which the number of surface molecules is ıall enough in comparison with the number of internal molecules, t is not annihilated, but grows at the expense of the molecules f the supercooled liquid.

Weyl [10] pointed out that for spontaneous crystallization to take place in the solution, not only is the formation of local clusters of molecules of the dissolved substance or the fluctuation in density necessary, but also the presence of an arrangement of the molecules corresponding to their arrangments in the crystals.

Berezhnoi [11] associated the emergence of nuclei of spontaneous crystallization in complex glasses with the diffusion and chemical differentiation of atoms and structural groups which form clusters in regions whose composition is similar to that of the precipitating crystals. Two mechanisms are possible for the crystallization of multicomponent glasses: a mechanism requiring precrystallization metastable immiscibility, and a mechanism not requiring it. In the first case, metastable glass-forming microregions are formed during the segregation process owing to the formation of amorphous nuclei of critical size. These regions then rapidly become ordered and crystallized. In the second case, the microregions which emerge in a fluctuating manner, owing to the increase in the thermodynamic potential, are not stable and may become resorbed unless their ordering takes place. The formation of these regions proceeds simultaneously with their crystallization.

Heterogeneous, or Catalyzed Crystallization

Stooky [6] shows that the maximum free energy change of nuclei mation is small at the melting temperature of the crystalline phase. decreases with increasing degree of supercooling or supersaturation. is free energy change depends also on the degree of matching of the ystalline structures of the catalyst and the crystallizing phase. the presence of an effective catalyst, the free energy change is ıch lower in comparison with the free energy change of nuclei forma- ion in homogeneous crystallization, and this is why the rate of nu- :leation is many times larger in the presence of a catalyst than in its absence. This is based on the fact that the nucleation rate is proportional to the probability of forming a stable nucleus. The rate of nucleation I, is given by the equation

$$I = A \exp\left(- \frac{\Delta G^*}{kT} \right)$$

where A is the proportionality constant

ΔG^* is the maximum free energy change of nuclei formation

k is Boltzman constant

T is the absolute temperature

It turned out that glass may be stimulated toward crystallization by introducing catalyzing particles and by subsequent heat treatment, which is necessary for the formation of nuclei to start as well as for the growth of crystals.

Stooky [6 and 12] has suggested the following criteria for the selection of effective catalysts:

1. Ready solubility of the catalyst in the glass at the melting nd heat-treatment temperatures, and its limited solubility at low temeratures.

2. Low energy activation for homogeneous nucleation from the nelt at low temperatures, achieved by low interfacial energy between the dissolved phase and the crystalline phases, and by the high degree of supersaturation during cooling.

3. A higher diffusion rate at low temperatures as compared with the major glass components, i.e. a relatively low activation energy for the diffusion process.

4. A low interfacial energy at the boundary between the glass and the catalyst crystal for effective wetting.

5. Similarity in the crystal structure and closeness of the lattice parameters for the catalyst crystal and the precipitating crystalline phase.

In contrast with Stooky's views, Weyl [13] believes that the rate of nucleus formation depends on the distribution of the chemical bonds inside the system. Similar crystal structures between the catalyst and crystallizing phase and other structural factors are inadequate to produce this process by themselves. For instance, despite the similar structures of cristobalite and silica glass, the transition of glass into cristobalite proceeds very slowly without a catalyst. According to Weyl [13], the nucleation of the crystalline phase and the oriented growth of crystals with similar lattice parameters (epitaxial growth) are entirely different phenomena. By recognizing the large effect of external and internal interphase surfaces on the formation of nuclei in glass, Berezhnoi [11] infers that this process, in contrast

) epitaxial growth, does not need any preferred lattice parameter, and
iat the function of the colloidal particles of gold and platinum as
atalysts of this process is certainly not based on epitaxy.

Meyer [14], in examining the tendency of glasses to hetero-
geneous crystallization ascribes a greater significance to the tempera-
ture dependence of the rate of crystal growth, K_g than to the rate of
nucleus formation. This conclusion is based on the fact that glass with
a high K_v rate is still capable of being worked well in the glassy state
if its K_g rate is sufficiently small. Attempts are being made to find
compositions for which both K_v and K_g have low value.

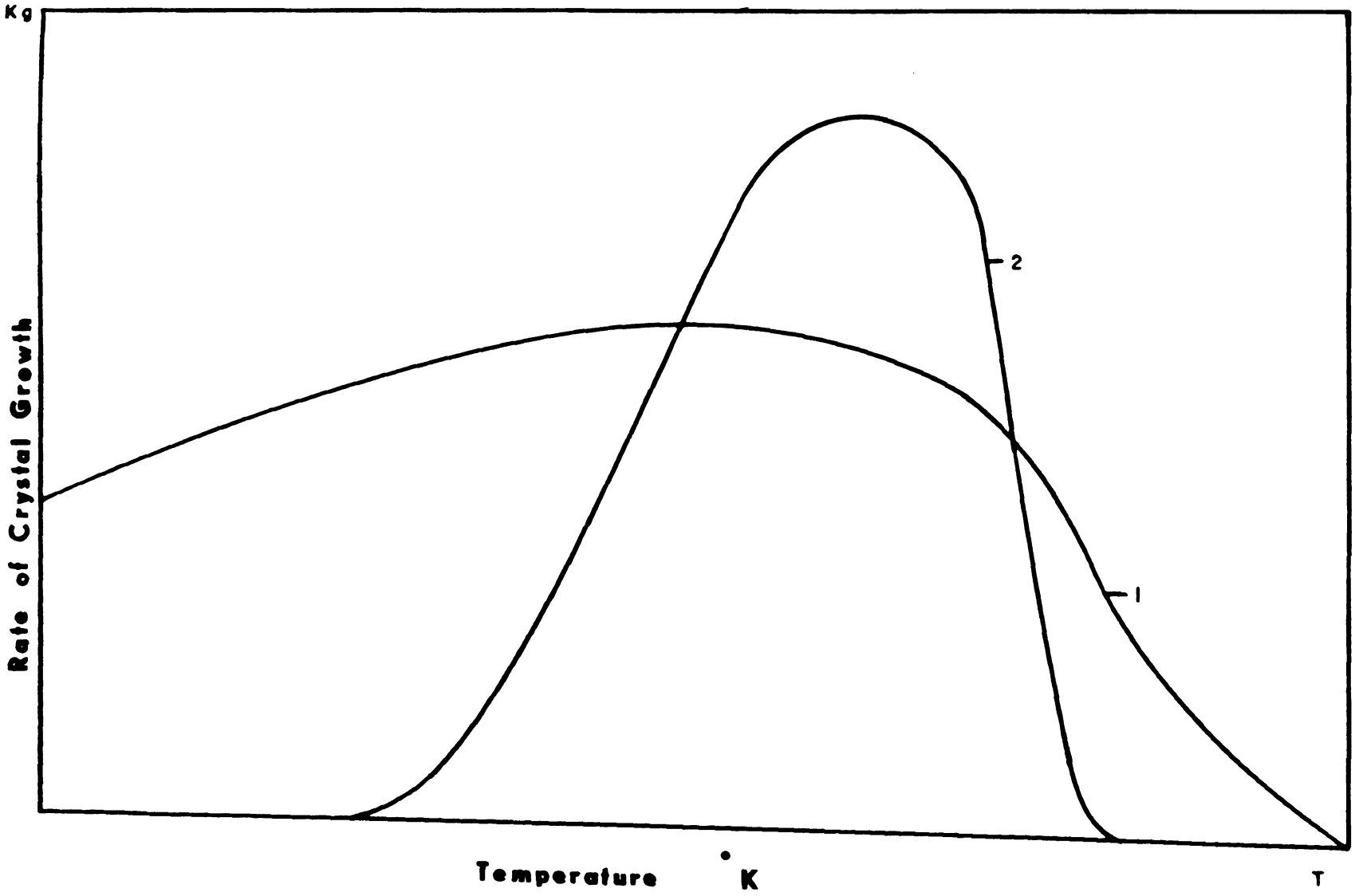
On the one hand, K_g must be sufficiently small within the tem-
perature region to allow time for the processing of glass articles by
blowing, pressing, drawing, and casting. On the other hand, K_g must
be sufficiently large within the temperature region of crystallization
so as to effect a relatively rapid completion of crystallization. During
the processing of glass, K_v must, for all practical purposes, be equal to
zero, while within the region of the transformation temperature, it
should attain a high value.

Both the absolute height of the maximum of the K_g versus T
curve and the shape of the curve have significance. Meyer [14] con-
siders glasses with sloping K_g curves, the maximum of which ranges from
10 to 25 microns per minute (Fig. 3, Curve 1), to be the most favorable
for the preparation of glass-ceramics. Glasses with such curves will
readily crystallize at a marked rate of devitrification below the soft-
ening temperature. In glasses with a sharp maximum of K_g (Fig. 3
Curve 2), the crystallization proceeds in a heavily softened state,
which makes these glasses unsuitable for the crystallization of preshaped
glass products.

Fig. 3 Typical temperature dependence of the growth rate of crystals (Meyer [14]).

T: Heating temperature.

K_g: Growth rate of the crystals.


Kg
Rate of Crystal Growth
2
1
Temperature °K
T

c. Phase Separation and Catalyzed Crystallization

Two-phase separation in oxide glasses or melts is a possible means of catalyzing crystallization. The two-phase separation to be effective should take the form of colloidal particles of one phase dispersed in the other phase. A number of oxides induce this type of phase separation in glasses either during cooling the glass from the molten state, or during reheating of the glass.

The silicate network, built up of tetrahedral SiO_4 groups, can accommodate other tetrahedral or triangular groups by linking them in the network. In some cases, the composite network may be stable, so that during cooling of the melt or reheating of the glass, a single-phase system is maintained. In other cases, however, separation into two phases may occur rather easily, and one phase will be rich in silica and the other is rich in the added network-forming oxide. This tendency was observed by McMillan [15] for certain types of borosilicate glass, indicating that the network-forming groups containing boron ions tend to be incompatible with those containing silicon ions.

McMillan [15] suggested two basic reasons for this incompatibility between different types of network structure. The first of these is based upon geometrical considerations. If triangular or tetrahedral groups are introduced into the network, considerable distortion of the Si-O-Si bonds in the region of the foreign structural groups will occur. Though a small number of foreign structural groups may be accommodated, there will be increasing disturbance of the arrangement of the SiO_4 groups as the proportion of foreign groups increases. As a result, separation into two phases may occur to permit the silicate network to exist in an undisturbed form in one phase and the network of the foreign

groups in the other phase. There is another possible type of phase separation which is also dependent upon geometrical effects within the glass network. For many ions a tendency exists for the coordination number to decrease with increasing temperature [15]. Thus an ion could, for example, exist in tetrahedral coordination at high temperatures, and octahedral coordination at low temperatures. Under these circumstances the ion could take part in tetradehral network-forming groups at high temperatures, but on cooling it would tend to assume octahedral coordination. This type of grouping would be incompatible with the silicate network of tetrahedral groups. As a result, there would be a tendency for two-phase separation to occur.

The second basic reason, McMillan [15] suggested, is based on the incompatibility between different types of network-forming structural groups. The differences between the charge of the principal network-forming ions (silicon) and that of the other ions which assume a network-forming position could lead to instability. For example a tetrahedral unit in which the central cation has a higher charge than the silicon ion may be difficult to accommodate in the silicate network. A possible two-dimensional representation of such a network is given in Fig. 4-a. If this arrangement actually occurred, it would be highly unstable because electroneutrality cannot be ensured for the regions of the network around the X^{5+} ion. In such a structure each of the XO_4 will bear an excess unit positive charge. It is unlikely that this charge could be neutralized by interstitial ions since they would have to be negatively charged. Electroneutrality could be ensured if one of the oxygen ions around the pentavalent ion were doubly bonded to the central cation as shown in Fig. 4-b. Such an arrangement

Fig. 4. Possible arrangements of silicate networks containing pentavalent network-forming cations (McMillan [15]).

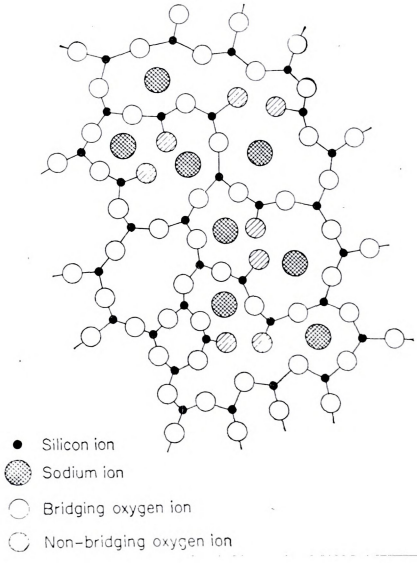
Si Silicon ion

O Oxygen ion

might not be particularly stable, however, since the tetrahedral units containing the pentavalent ion would be asymmetrical, and in the regions surrounding these units there would exist marked disturbance of the bonding in the silicate network. Under these circumstances, separation into two phases would be likely to occur.

The effect of interstitial cations is also important in determining whether two-phase separation will occur. McMillan [15] pointed out that the structure of a silicate glass is a rather open one, containing holes or interstices between the linked SiO_4 tetrahedra which can accommodate various cations such as alkali or alkaline-earth ions as shown in Fig. 5. In silicate glasses, the arragement of the oxygen ions will be largely determined by the forces exerted by the silicon ions but, depending on their electrostatic field strengths, the interstitial cations will influence the arrangement in attempting to achieve their equilibrium states of coordination. Such ions will then impose constraints on the neigboring silicon-oxygen bonds, and lead to distortion of the Si-O-Si bond angles. For ions of low field strength, the effect will be small and can be accommodated by minor distortion of the silicon-oxygen bonds. For interstitial cations of high field strength, on the other hand, the disturbances will be so great that separation into two phases may occur in order to lower the free energy of the system. One phase will be rich in silica, and will contain only a small number of the interstitial cations which can be incorporated without resulting in serious disturbances of the bonds in the network; in this phase, the silicon ions exert the controlling influence in determining the arrangement of the oxygen ions. The other phase, will contain a high proportion of interstitial cations,

Fig. 5. Two-dimensional representation of the structure of soda-silica glass (McMillan [15]).


Silicon ion
Sodium ion
Bridging oxygen ion
Non-bridging oxygen ion

and their coordination requirements will have a predominating influence on the structure of the melt or glass. The number of oxygen ions which are bonded to only one silicon ion will be high in this phase, so that the network will be weakened, and in some cases a coherent silicate network may no longer exist. As a result, the phase rich in the network modifying cation may tend to crystallize rather more easily than that rich in silica.

One of the best known examples of an oxide nucleation catalyst is titanium dioxide. Stooky [16] showed that it was effective in amounts of 2 to 20 weight percent in a wide variety of glass compositions. Titanium dioxide is soluble in the molten glass, but during cooling or subsequent reheating it precipitates in the form of large numbers of submicroscopic particles that can be utilized to assist the development of major crystalline phases. The processes involved in titania-catalyzed crystallization of glasses are complex, and so far they have not been fully explained. The simple idea that crystals of rutile are first precipitated and then act as heterogeneous nuclei for the crystallization of other phases is not correct. Although this explanation could be valid for some glasses, it cannot be true in all cases because rutile does not always appear as a crystalline phase. It seems much more likely that the first stage in the process is the separation of a titania-rich liquid (or glass) phase. This phase, which appears as tiny droplets (an emulsion), possibly separates during the initial cooling of the glass-melt; it does not usually crystallize during cooling of the glass although it may be more highly ordered than the surrounding glass matrix. The emulsion phase is unstable and crystallizes during reheating, probably by homogeneous

nucleation. The crystalline particles so formed, which are of colloidal dimensions and are in a highly dispersed state, heterogeneously nucleate the crystallization of major phases from the glass.

Evidence that two-phase liquid separation plays an important part in the crystallization of certain types of glass containing titania was obtained by Maurer [17], who investigated the behavior of a magnesia-alumina-silica glass containing titania. By studying the light-scattering characteristics of the glass after heat-treatment to various temperatures, he obtained valuable information concerning the initial stages of the crystallization process. The experimental results suggested that the glass contained an emulsion phase even before heat-treatment. Annealing of the glass had little effect on the extent of emulsion formation, and this finding indicated that two-phase liquid separation had occurred during the early stages of cooling of the molten glass. Prolonged heat-treatment at the same temperature resulted in a fairly clear X-ray diffraction pattern, the crystalline phase being identified as magnesium titanate. Maurer also showed that the smallest particles present were about 25 Å in diameter and that the average particle diameter increased to about 175 Å after heat-treatment at 770°C.

McMillan [15] suggested that the tendency of titanium dioxide to induce two-phase separation might be explained in terms of the structural role of the titanium ion. Titanium dioxide is considered to have an intermediate effect with regard to glass structure. At least some of the titanium ions present in a glass can then occupy the centers of network-forming groups. The size of the titanium

ion (0.68 Å) is such that it would normally be expected to assume a coordination number not greater than four. It has been suggested by Weyl [18] that at high temperatures the Ti^{4+} ion may assume a coordination of four, following the general rule that coordination number tends to decrease with increasing temperature. At high temperatures, therefore, the groupings of the oxygen ions around titanium dioxide will be compatible with the silicate network, and titanium dioxide will be miscible with the melt. During cooling of the melt the tendency will be for the titanium ions to assume the equilibrium coordination number (six) for lower temperature, and in doing this they will no longer be able to occupy network-forming positions. Thus titanium dioxide will be displaced from the silicate network, and will appear as a separate phase, possibly in combination with another oxide. For certain compositions, of course, rapid cooling of the glass melt may permit the high temperature state of coordination of the titanium ion to be frozen in, with the result that some titanium ions may remain in network-forming position. This state would be unstable however and during reheating of the glass it is likely that two-phase separation would occur.

A network-forming oxide which exhibits the characteristics of a nucleation catalyst is phosphorus pentoxide. The phosphorus ion, p^{5+} assumes tetrahedral coordination, and therefore provides an example of phase-separation as a result of charge difference between the principal network-forming ions, Si^{4+}, and the foreign network-forming ions p^{5+}. As has been shown in Fig. 4, if all the phosphorus-oxygen bonds were all single bonds of the P-O type, electroneutrality

could not be ensured so that one phosphorus-oxygen bond per PO_4 tetrahedron would have to be a double bond. The presence of this type of double-bonded oxygen ion within the silicate network creates conditions favoring separation of phosphate grouping from the silicate network. It is likely that these groups would not separate as phosphorus pentoxide, but rather that this oxide would separate out in combination with an alkali or alkaline earth oxide. The phase which separates out may be crystalline but it is quite likely to be glassy. Electron-microscopy and X-ray diffraction studies of glasses containing phosphate induced two-phase separation do not reveal any evidence of cyrstalline regularity within the phase which has separated. In certain phosphate opacified glasses, definite crystals of calcium phosphate have been identified, but these were soda-lime-silica glasses, quite different in composition from the glasses in which phosphate nucleation has been utilized. Quite small concentration of P_2O_5 are effective in inducing the desired two-phase separation necessary for nucleation catalysis. Amounts ranging from 0.5 to 6 weight percent appear to represent the optimum proportion. McMillan and Partridge [19] have described the use of metallic phosphates to catalyze the crystallization of a wide range of glass compositions derived from the Li_2O-Al_2O_3-SiO_2, Li_2O-MgO-SiO_2 and MgO-Al_2O_3-SiO_2 systems. The same nucleation method has also been successfully applied to Li_2O-ZnO-SiO_2 glasses.

James and McMillan [20] studied the early stages of crystallization in a Li_2O-SiO_2-P_2O_5 glass by transmission electron microscopy.

Several small single crystals joined together around a central core were observed in these specimens. These crystalline regions were identified as lithium disilicate. Possible explanations of the core are discussed in terms of a region of different chemical composition or a central region of disorder. The observations are also compared with the growth of crystal spherulites in polymers.

James and McMillan [21] also studies phase separation in three glasses with composition of mole percent 30 Li_2O-70SiO_2 (glass 1), 30Li_2O-69SiO_2-1P_2O_5 (glass 2) and 31.5Li_2O-67.5SiO_2-1P_2O_5 (glass 3). Thin film transmission electron microscopy was used to determine size distribution, mean diameter, concentration and volume fraction of the particles as functions of time of heat-treatment at 550°C. The initial phase-separation was observed within a very short period, producing a high density of very fine particles. The tendency towards phase separation is greater in the glasses containing P_2O_5. In glass 2 the volume fraction of dispersed phase is much larger than in glass 1. The measured volume fractions of dispersed phase in the glasses are consistent with this phase having a composition approaching that of vitreous silica, and the continuous phases having a composition close to that of Li_2O-2SiO_2 but with some excess silica in solution. [In addition with the glass containing phosphate, the P_2O_5 appears to be distributed in the continuous lithia-rich phase and in some form of association with Li_2O.] The nature of this association may take the form of single molecules (probably 3Li_2O-P_2O_5) or small groups of molecules accommodated within the glass network of the continuous phase.

Dennis and Bradt [22] in their study of the microstructure and

reflectance of a $PbO\text{-}B_2O_3\text{-}SiO_2$ glass with crystalline opacified additions, observed that the reflectance of lead borosilicate glasses, which are opaque because of a fine droplet microstructure of immiscible liquids, can be enhanced. The reflectance maximum results from a balance of the effect of the large difference in refractive index of the crystalline opacifiers and the opacity caused by the droplet microstructure of the immiscible liquids. A fine-droplet structure is essential to the opacity in these systems and must be retained for maximum reflectance.

The effect of secondary phase separation on the apparent volume fraction of second-phase was examined by Shaw and Breedis [23] in the immiscible region of the $PbO\text{-}B_2O_3$ system. The volume fraction, V_2, of the PbO-rich phase agreed well with theoretical expressions relating V_2 to density and composition, except for $0.2 < V_2 < 0.5$. The discrepancy in this region was explained in terms of the peculiar shape of the immiscible phase boundary and the resulting mutual supersaturation of the immiscible phases with respect to each other.

Stooky [24] showed that the inclusion of a small amount (up to 0.05 percent) of cerium dioxide improved the photosensitivity of glasses containing copper as the photosensitive element. The valuable effect of cerium is due to the ease with which electrons are released by the reaction

$$Ce^{3+} + h\nu \rightarrow Ce^{4+} + e \quad ,$$

so that for the improved glasses the reaction can be represented by

$$Ce^{3+} + Cu^{+} + h\nu \rightarrow Ce^{4+} + Cu \quad .$$

In spite of the scientific and technological progress achieved during the past decade in the field of glass and glass-ceramics, the mechanism of crystallization in glass is not completely understood. Theoretical and experimental work still needed to have a complete understanding of the mechanism.

CHAPTER II

EXPERIMENTAL PROCEDURES

A. Glass Preparation

The glass samples were prepared from chemicals of analytical-reagent grade. Boron oxide was introduced in the form of boric acid. Phosphorus pentoxide was added as ammonium dihydrogen phosphate in order to avoid the hygroscopic and reactive phosphorus pentoxide. Cerium oxide was introduced as cerous oxalate. Other components were added as oxides. Lead-borate, lead-silicate, and cerium-phosphate glasses of molecular percentage compositions shown in Table 1 were prepared by melting 100-gram batches in alumina crucibles for two hours at 750°C, 850°C, and 1400°C respectively in a Globar furnace. To insure homogeneity, the crucibles containing the melt were shaken several times, and the subsequently solidified glasses were crushed and remelted. The glasses were refined at a temperature 200°C below the melting temperature several times. Finally the glass was cast in copper molds. The glasses were annealed at 400°C for the borates, at 400°C for the silicates, and at 600°C for the cerium phosphate. Disc-shaped samples 2.5 cm in diameter with different thicknesses were obtained.

B. Differential Thermal Analysis

Chemical reactions or structural changes within a crystalline

Table 1

Glass Composition in Mole Percent

Glass	Mole %				
	B_2O_3	SiO_2	PbO	P_2O_5	CeO_2
LB_o	72.5	--	27.5	--	--
LB_1	71.0	--	27.0	--	2.0
LB_2	66.0	--	25.5	--	8.5
LS_o	--	30.0	70.0	--	--
LS_1	--	29.2	70.7	--	0.1
LS_2	--	29.2	70.3	--	0.5
CP	--	--	--	79.0	21.0

or glassy substance are accompanied by the evolution or absorption of heat. The crystallization of a substance is exothermic, that is, the free energy of the regular crystal lattice is less than that of the disordered liquid state. Conversely, the melting of a crystal is endothermic. Differential thermal analysis (D.T.A.) is a technique for studying reactions or phase transformations, particularly at elevated temperatures. The material under test, in the form of a finely divided powder, is placed in a small platinum capsule. Adjacent to the test capsule is an identical one containing an inert powder, such as aluminum oxide, which exhibits neither endothermic nor exothermic effects over the temperature range in question. Thermo-couples embedded in the test substance and in the alumina powder are connected so that their e.m.f.s. are opposed. The net e.m.f. therefore reflects the temperature difference between the sample and the inert alumina reference. The two capsules are heated together at a nearly constant rate, and the differential temperature is plotted as the ordinate against the reference temperature as abscissa. Exothermic effects appear as peaks on the curve obtained, and endothermic ones as dips.

If a sample of a glass which devitrifies on heating is examined by D.T.A., at least one exothermic peak will be observed corresponding to the separation of a crystal phase. D.T.A. therefore offers a useful method of investigating the crystallization of glasses, and of determining the temperatures at which different crystals are formed. A typical D.T.A. curve, as seen in Fig. 6, shows a number of features during the crystallization of a glass.

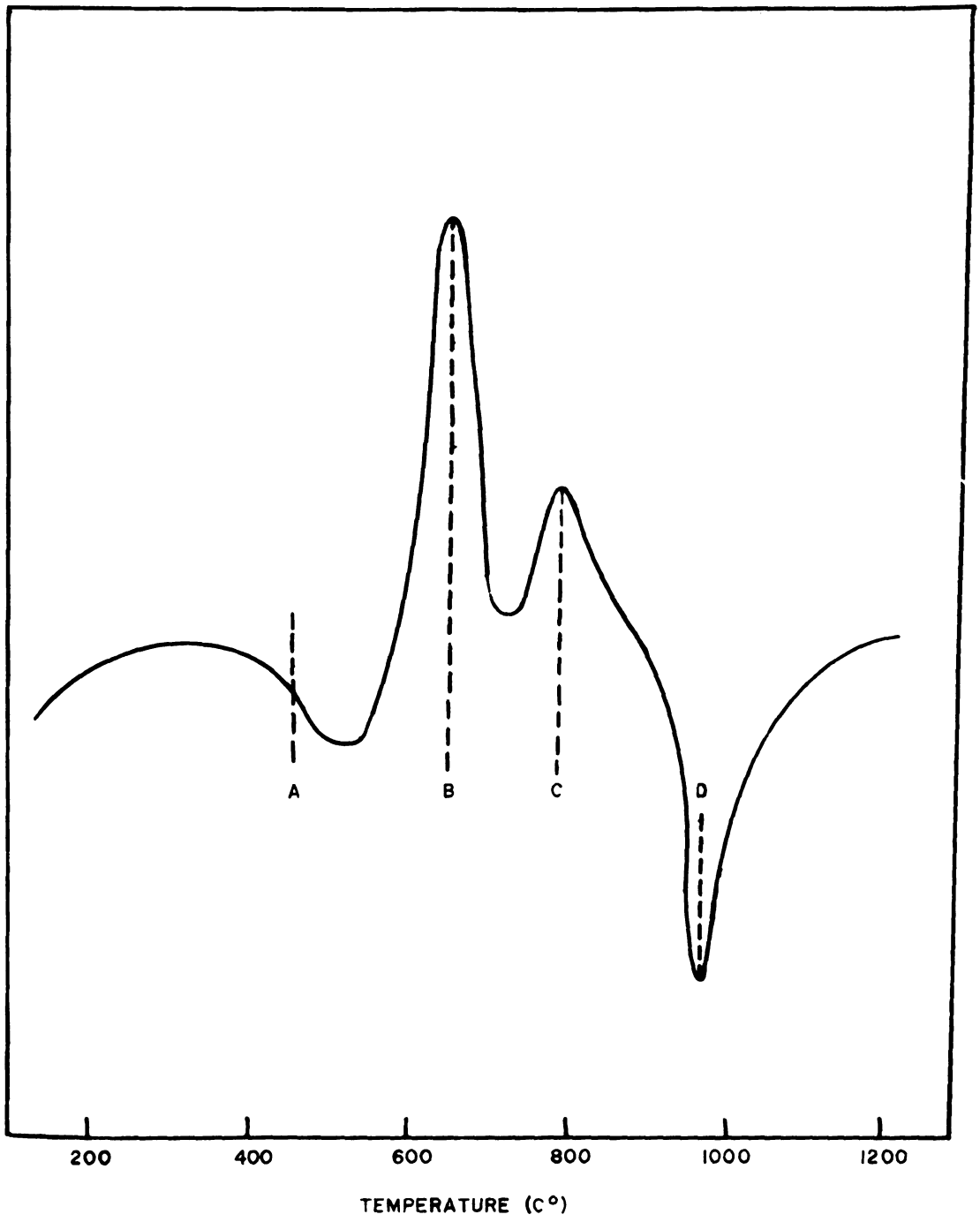
As the temperature is increased, there is observed in the D.T.A.

Fig. 6. Differential thermal analysis curve for a devitrifiable glass (McMillan [15]).

A: Annealing point.

B and C: Exothermic peaks due to formation of crystal phases.

D: Endothermic effect due to first melting.


A
B
C
D
200
400
600
800
1000
1200
TEMPERATURE (C°)

curve a dip due to a slight absorption of heat which occurs when the annealing point of the glass is reached. With further increase of temperature, one or more quite sharp exothermic peaks are observed, corresponding to the appearance of various crystal phases. At a still higher temperature, a marked endothermic effect occurs. It is due to the first melting of the crystalline phases. This D.T.A. curve can yield a great deal of information which is of assistance in preparing heat-treatment schedules for glass-ceramics, since it not only indicates the temperature ranges in which crystallization occurs, but it also shows the maximum temperature to which the glass-ceramic can be heated without deformation due to melting of crystal phases.

In the current investigation, the D.T.A. curves of all seven glasses were obtained by heating 100 milligrams of the glass powder in a platinum cup at a rate of 10C° per minute in R. Stone DS-2 pressure chamber and furnace D.T.A. apparatus.

C. Heat Treatment

Glass wafers 0.1 cm thick and 2.5 cm in diameter were cut with a Micromatic precision wafering diamond saw. The heat-treatment schedule for all glasses was based on a qualitative differential thermal analysis. The lead-borate wafers were heated at 450°C for 4 and 24 hours, the lead-silicate ones at 450°C for 2 and 14 hours, and the cerium-phosphate ones at 700°C for 2, 4, 5, 6, 7, 8, 12, 18, and 36 hours. A carbon cup was used as a container for heat treatment of these glasses in a Lindberg Hevi-duty electric furnace. After the desired heat-treatment was completed, the glass samples were quenched

in air, and mechanically polished to remove undesired surfaces and any contamination from the carbon cup.

D. Electron Microscopy

In electron-microscope examinations of glass-ceramics, one should be very careful in the sample preparation in order that the electron micrograph finally obtained not exhibit features which could be artifacts of the method. The first step in the technique involves careful polishing of the specimen followed by controlled etching. The object is to etch as slightly as possible consistent with revealing the structural features. Two percent hydrofluoric acid applied with gentle agitation is the most useful reagent. Buchi and Stewart [25] reported that the effect of etching is to reveal grain boundaries if these are present, and to accentuate the structural features of the glass-ceramic, since the various crystal phases--as well as the residual glass phase--etch at different rates. A replica of the etched surface is then prepared by co-evaporating carbon and platinum onto it in vacuum. The replica is floated off the specimen in dilute hydrofluoric acid, mounted on a grid, washed, and examined in the electron microscope.

Although this technique has provided a great deal of valuable information, it has certain shortcommings. Thus in the case of etched surfaces, the observed microstructure can depend on the precise etching treatment in certain circumstances. Replicas have limited application in revealing detail smaller than 50 to 100°A, since at these magnifications the microstructure may sometimes be confused with fine-scale detail in the carbon replicas themselves. Another limitation of the

replica technique is that one obtains a series of snapshots rather than a continuous record of the changes taking place. Hence it is not possible, for example, to follow the nucleation and growth stages of a particular crystal. Moreover, the technique does not have the power of distinguishing between glassy and crystalline phases, and reveals information only of the surface.

On the other hand, transmission electron microscopy in conjunction with electron diffraction provides the most powerful technique available to study phase separation and crystallization in glasses [15, 20, 21 and 26-28]. It provides a direct image of the microstructure and has the ability to distinguish glassy and crystalline phases by selected-area diffraction. It is particularly valuable in investigating the early stages of phase separation and crystallization. Progress of these processes can also be followed in the electron microscope by heat treating the specimen either by a hot-stage attachment, or by the electron beam itself. In the latter case, however, the temperature of the specimen is not known accurately.

To permit direct electron microscopy of glass and glass-ceramics, it is necessary to have very thin sections so that the electron beam is transmitted through the specimen. The differences between the electron scattering of various phases can then serve to provide an image or photograph correspnding with the microstructure of the material.

One technique has been to prepare a fine powder of the glass-ceramic. The powder that passes through a 400-mesh screen is then carefully dusted onto a specimen mounting screen which has first

been dipped into a dilute solution of formvar, and then dried. After dusting, the excess powder is brushed off. The mounting grid is introduced onto the stage of the electron microscope. The field of observation is then scanned until a wedge-shaped particle thin enough to transmit the electron beam is found. The disadvantage of this technique lies in the investigation of the microstructure of glass-ceramics. The crystalline phases physically separate out of the matrix, and may give a misleading picture.

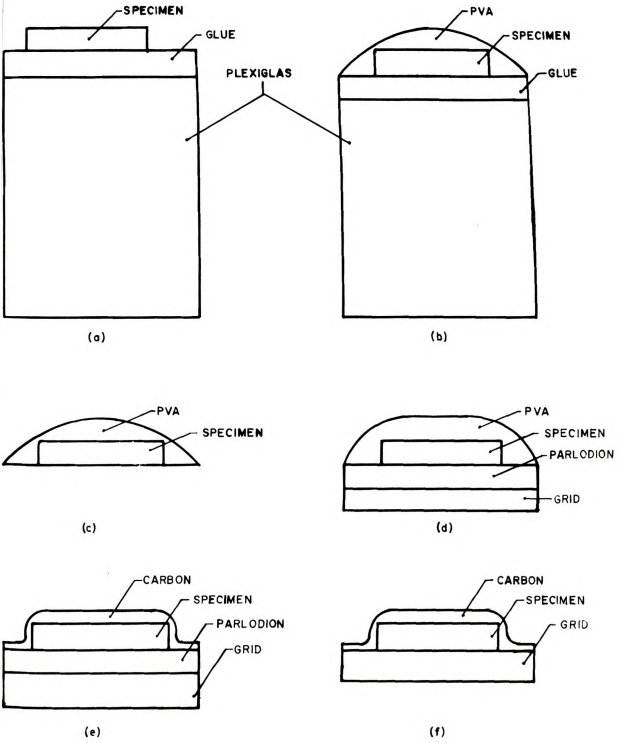
Another technique is mechanical polishing as developed by Doherty and Leombruno [26]. It can be summarized in the following basic steps:

1. Mechanically polishing one surface of a bulk specimen;
2. Gluing the polished surface of the specimen to a suitable substrate;
3. Grinding and polishing the opposite surface of the specimen to a thickness of 1000 Å;
4. Transferring the specimen to an electron-microscope grid.

The polished surface of the bulk specimen was glued to a Plexiglas mount with Varno-cement. The bulk specimen was then cut to a thickness of approximately 1/16 inch. A great deal of care was taken in the final stages of polishing. Polishing was complete when the edges of the specimen moved toward the center of the specimen.

The thinned specimen could not be removed from the mount by dissolving the glue because the expansion of the glue by absorption of solvent caused the specimen to break. A schematic representation of the alternative procedure developed is shown in Fig. 7. A film of polyvinyl alcohol -- which is soluble in water but not in ethylene dichloride--was placed on the thinned specimen (Fig. 7-b). The Plexiglas and the glue were then dissolved in ethylene dichloride, the

Fig. 7. Mounting procedure (Doherty and Leombrune [26]). For preparing thin glass foils by mechanical polishing.


SPECIMEN
GLUE
PLEXIGLAS
(a)
PVA
SPECIMEN
GLUE
(b)
PVA
SPECIMEN
(c)
PVA
SPECIMEN
PARLODION
GRID
(d)
CARBON
SPECIMEN
PARLODION
GRID
(e)
CARBON
SPECIMEN
GRID
(f)

specimen remaining on the P.V.A. (Fig. 7-c). The specimen then was cut into a size suitable for mounting on an electron-microscope grid. When the specimen was placed on the grid, and the P.V.A. was dissolved in water, surface-tension forces broke the specimen. Therefore a drop of Parlodion, which is soluble in amylacetate but not in water, was placed on the specimen. The specimen was then placed on the microscope grid (Fig. 7-d). The P.V.A. then was dissolved in water, the Parlodion preventing the breakage of the specimen. A film of carbon was evaporated on the specimen (Fig. 7-e) and the Parlodion subsequently was dissolved in amyl acetate. The carbon film was necessary to hold the specimen on the grid. The specimen was then ready for examination in the electron microscope (Fig. 7-e).

Seward III et al. [27] adopted the above technique for fused-silica studies. They observed an apparent substructure caused by the carbon film and as a result modified the procedure to eliminate the carbon layers. This procedure departs from the Doherty-Leombruno technique after the specimen, covered with P.V.A. film, has been cut into small sections. As shown in Fig. 8-e, a section of the specimen - Polyninyl alcohol composit is placed (P.V.A. side down) on a microscope grid, which is then placed, specimen side up, on a supporting screen in a Petri dish. The dish is gradually filled with distilled water to the level of the screen, after which surface tension draws the water to the height of the P.V.A. layer. The petri dish is then covered and left for 2 days while the P.V.A. layer dissolves.

These techniques are tedious. A much simpler technique, developed during the course of this work, is to glue the glass onto

Fig. 8 Specimen transfer procedure for mechanically thinned foils (Seward [27]).

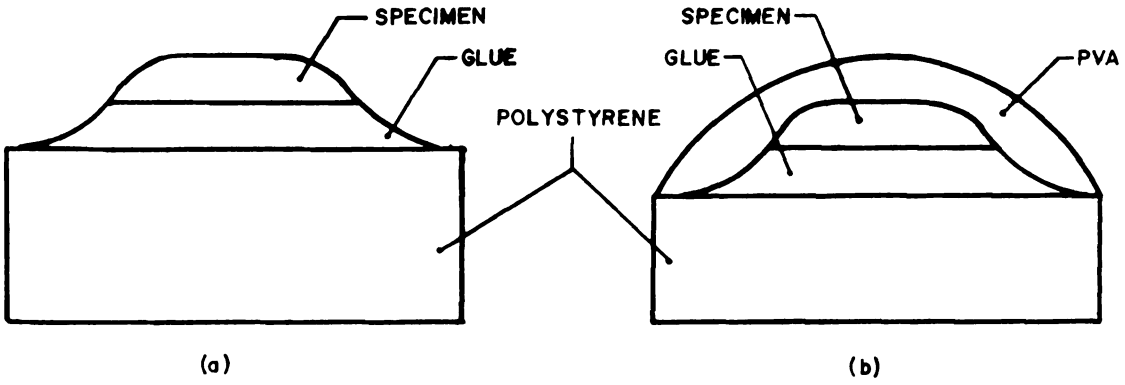
(a) Thinned sample glued to substrate.

(b) Coated with PVA.

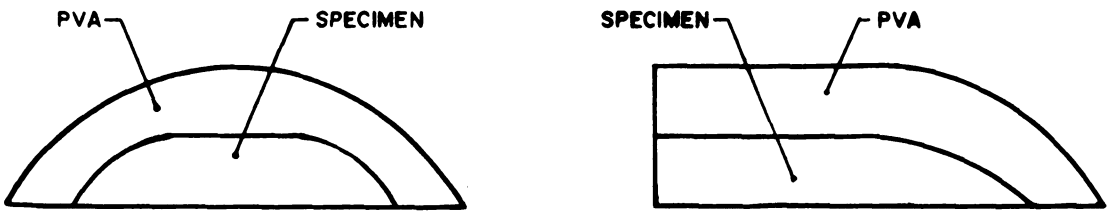
(c) Glue and substrate were dissolved in ethylene dichloride.

(d) Specimen - PVA composite was cut into sections.

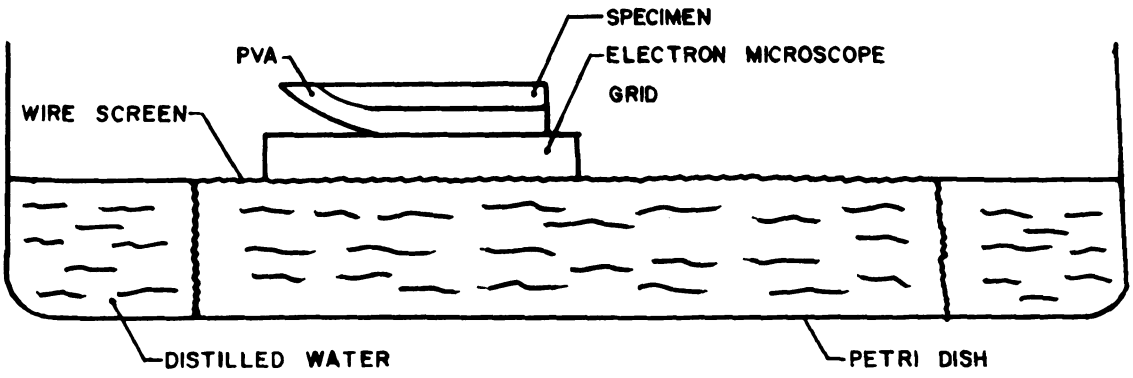
(e) Removal of PVA.


SPECIMEN
GLUE
POLYSTYRENE
SPECIMEN
GLUE
PVA

(a) (b)


PVA
SPECIMEN
SPECIMEN
PVA

(c) (d)


SPECIMEN
PVA
ELECTRON MICROSCOPE
GRID
WIRE SCREEN
DISTILLED WATER
PETRI DISH

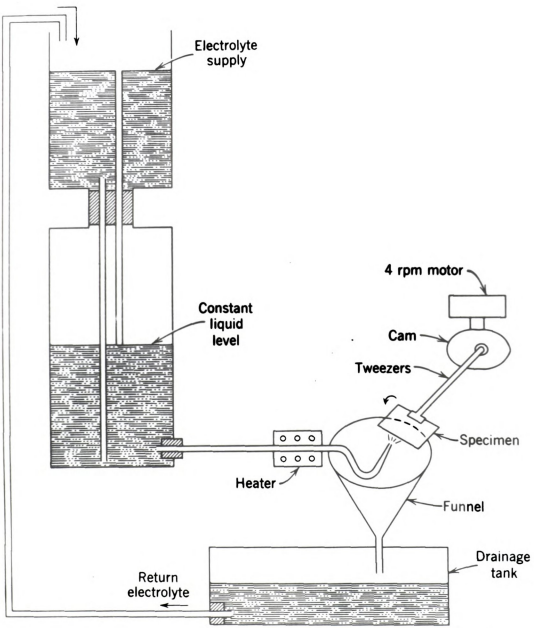
(e)

a metal substrate with beeswax. To apply the wax, the metal substrate was slightly heated. The other surface is ground and polished until the specimen is thin enough for observation by transmission electron microscope. The wax is then dissolved by immersion in acetone for 15 minutes. Alternatively the substrate can be slightly heated again; the specimen can then be easily removed and then washed in acetone. This technique is quite successful and does not take much time.

The last technique to be discussed here is chemical polishing. Washburn et al. [29] developed a chemical-jet-polishing technique to obtain foils $\sim$1000 Å thick directly from cleaved MgO crystals $\sim$1/4 mm thick. The method is illustrated in Fig. 9. The height of the specimen above the jet is such that break-away of the liquid is just prevented. The specimen is rotated about a vertical axis by an eccentric motor to produce a doughnut-shaped groove. As soon as the first hole appeared, polishing was stopped to obtain good thin edges. After washing thoroughly and drying by rinsing in alcohol and then ethyl ether, suitable specimens may be broken off with a needle.

On the other hand James and McMillan [28] developed a chemical thinning technique. Thin glass discs of uniform thickness of about 100 microns are first made by mechanical grinding. The surfaces of the plates are polished flat. Each disc is held near the rim by a pair of fine tweezers and, with the exception of a small region in the center of one side, the surfaces are covered with a thin coating of material inert to the chemical attack. This allows a shallow depression to be formed in the unprotected region when the disc is immersed in the thinning solution. The protecting medium is then

Fig. 9. Sketch of apparatus for thin foil preparation by chemical-jet-polishing technique (Washburn et al [29]).


Electrolyte supply
Constant liquid level
4 rpm motor
Cam
Tweezers
Specimen
Heater
Funnel
Drainage tank
Return electrolyte

dissolved away, but the disc is recoated around the rim to guard the edges from dissolution during the main thinning process. Thinning is continued with frequent agitation of the specimen in the solution until perforation occurs in the center of the disc. After washing in distilled water and methanol, and dissolving off the blanking medium, the perforated disc can be transferred to the electron microscope.

In the present investigations, the author used the chemical-jet-polishing technique developed by Washburn et al. [29] with slight modification. It was very successful for all glasses. An alternative chemical-polishing technique was also adopted from the work of James and McMillan [28]. Instead of dipping the sample it was suspended in the polishing solution with tweezers, a clamp, and a stand. The solution was agitated slowly with a magnetic stirrer. Sometimes the solution was also heated to produce ideal polishing conditions.

The polishing solutions for lead-borate and lead-silicate glasses containing cerium oxide, and for the cerium-phosphate glass, were [9 HNO_3 - 1 HCl - 90 H_2O], (1.5 HNO_3 - 0.5 HF - 98 H_2O] (volume percent) and [10 normal NaOH at 60°C followed by warm concentrated HNO_3]. These solutions have been found by trial and error. The operation is time consuming particularly for the cerium-phosphate glass.

All samples prepared either by mechanical or by chemical techniques showed interference fringes when observed in reflected light under an optical microscope as shown in Fig. 10.

All the electron-microscope observations were made with Hitachi-HU-11A electron microscope operated at 100 KV. The second condenser lens was defocused to diminish the heating of the specimen by the electron beam.

Fig. 10. Light optical photograph of cerium phosphate glass after thinning. The region showing fringes will be suitable for transmission electron microscopy.

E. X-ray Diffraction Analysis

Crystalline substances, as is well known, give sharp X-ray diffraction patterns which are a positive means of identifying crystals by comparison with standard data such as the A.S.T.M. Index. Glasses, on the other hand, show rather diffuse X-ray diffraction patterns with complete absence of sharp rings. X-ray diffraction analysis, therefore, provides an excellent means for investigating the crystallization of glasses. This technique is of great value in determining the sequence in which various crystals arise during the heat-treatment process. Specimens of the glass are subjected to the heat-treatment schedule, and are removed individually after predetermined time intervals. The specimens are cooled quickly to "freeze in" the conditions obtaining at the instant that they are removed from the furnace. They are then subjected to X-ray diffraction analysis. By this means, the complete crystallization process from the nucleation stage to the final crystallization stage can be followed, and the separation of different crystal phases can be correlated with the time-temperature schedule of the heat-treatment process and the corresponding electron-microscope micrographs.

The X-ray diffraction patterns for the powdered samples were obtained on a General Electric XRD-6 diffractometer with a copper target and a nickel filter. The diffraction intensity was recorded against 2θ, where θ is the Bragg angle.

CHAPTER III

RESULTS

1. Lead-Borate Glasses Containing Cerium Oxide

D.T.A. curves of lead-borate glass containing no cerium oxide, (LB_0), 2 mole percent cerium oxide (LB_1) and 8.5 mole percent cerium oxide (LB_2), are given in Fig. 11. In these plots the exothermic effects are recorded as peaks, and the endothermic ones as dips. endothermic effects were observed in all glasses over the temperature range 480°C to 515°C. They are associated with the annealing of these glasses. A broad weak exothermic peak was observed in the glass containing no cerium oxide, (LB_0), at 656°C. It is due to the crystallization of this glass, and disappears upon addition of cerium oxide.

The transmission electron micrographs of the annealed Ce_2O_3-free lead-borate glass (LB_0) are shown in Fig. 12. The effect of heat treatment on this glass at 450°C for 0, 4, and 24 hours are shown in Figs. 12A, (B) and (C) respectively. The Micrograph in Fig. 12-A suggests that glass-in-glass phase separation exists in the as-annealed sample. This suggestion is supported by the absence of the selected-area electron-diffraction micrograph of the phase-separated regions. The phase separation shows that nucleation had occurred during annealing. The dark, discrete, and approximately spherical globules are believed to be a lead-oxide-rich amorphous phase. The

Fig. 11. Differential thermal analysis curves for lead borate glasses.

LB_0 Containing no cerium oxide.

LB_1 Containing 2 mole percent cerium oxide.

LB_2 Containing 8.5 mole percent cerium oxide.

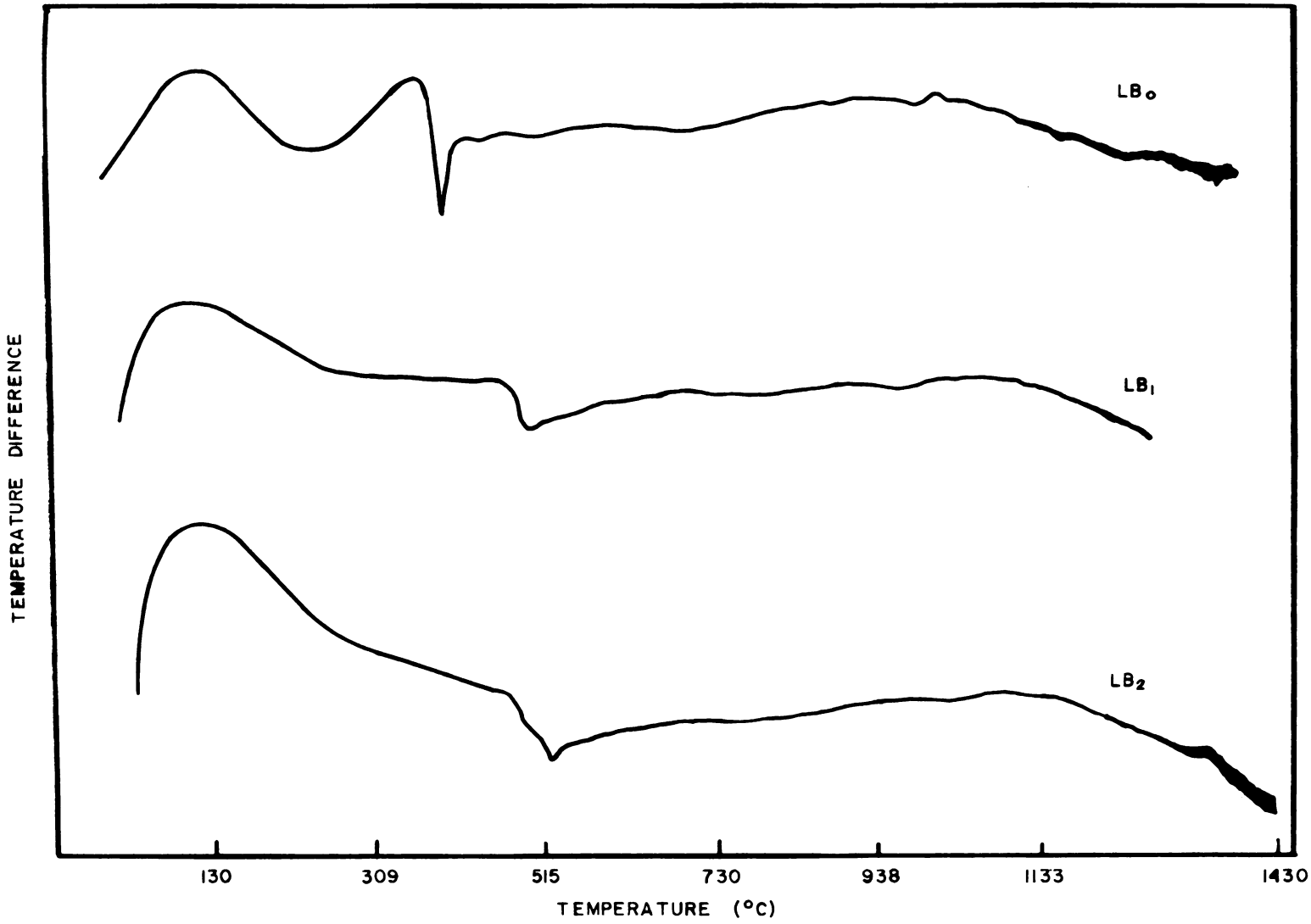
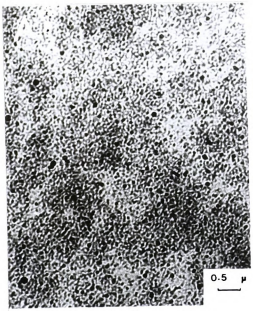

LB0
LB1
LB2
TEMPERATURE DIFFERENCE
130
309
515
730
938
1133
1430
TEMPERATURE (°C)

Fig. 12. Transmission electron micrograph of lead borate glass LB_0.

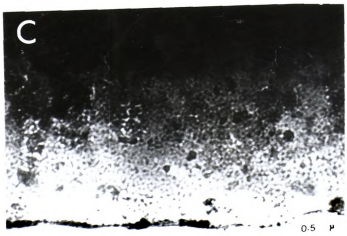
A. Annealed glass.

B. Heated at 450°C for 4 hours.

C. Heated at 450°C for 24 hours.


0.5 μ


0.5 μ


C
0.5 μ

lead-oxide-rich glassy phase slightly increases in size, and decreases in concentration, as a result of progressive heat treatment, as can be seen from the micrographs given in Fig. (12B and C).

The effect of cerium-oxide addition is illustrated in Fig. 13. When cerium oxide is added in 2 mole percent (Fig. 13-B) and 8.5 mole percent (Fig. 13-C), the average size of the separated particles increased and the particle concentration decreased.

The dispersed phases in the micrographs of Fig. 13 (B and C) are essentially of two types, those which are much darker than the continuous phase and those which are only slightly darker. This difference has been explained by James et al. [21] on the basis that the darker particles are near the surface of thin film, whereas the lighter ones are within the body of the film. An area of the thin sample where the dispersed particles were originally light in color, and became much darker by further thinning under the concentrated electron beam, is shown in Fig. 14.

The time dependence of the effect of heat treatment at 450°C on the lead-borate glass (LB_1) containing a low concentration of cerium oxide (2 mole percent) is illustrated in Fig. 15. The lead-oxide-rich amorphous phase (dark globules) has decreased in size, and a boron-oxide-rich phase starts to crystallize out on heating for 4 hours at 450°C (Fig. 15 B). On further heating for 24 hours at the same temperature, the amorphous phase almost disappears, and the crystalline boron-oxide-rich phase (elongated particles) keeps on growing (Fig. 15C). The crystalline nature of these particles is demonstrated by the selected-area electron-diffraction pattern.

The transmission electron micrographs given in Fig. 16 indicate

Fig. 13. Transmission electron micrograph of lead borate glasses.

A. Containing no cerium oxide.

B. Containing 2 mole percent cerium oxide.

C. Containing 8.5 mole percent cerium oxide.

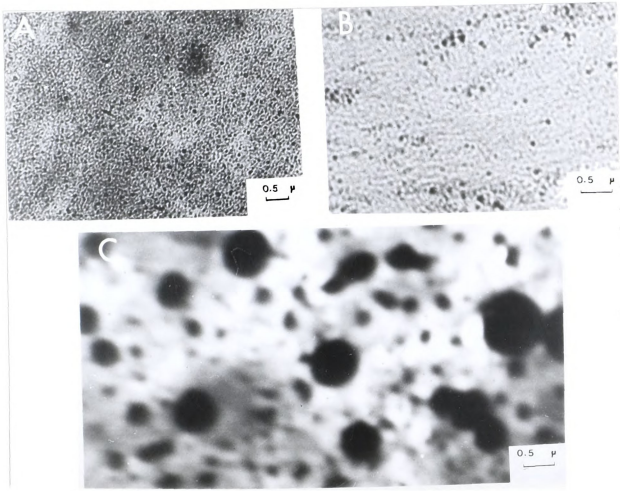

A
0.5 μ
B
0.5 μ
C
0.5 μ

Fig. 14. Transmission electron micrograph of lead borate glass beam heated.

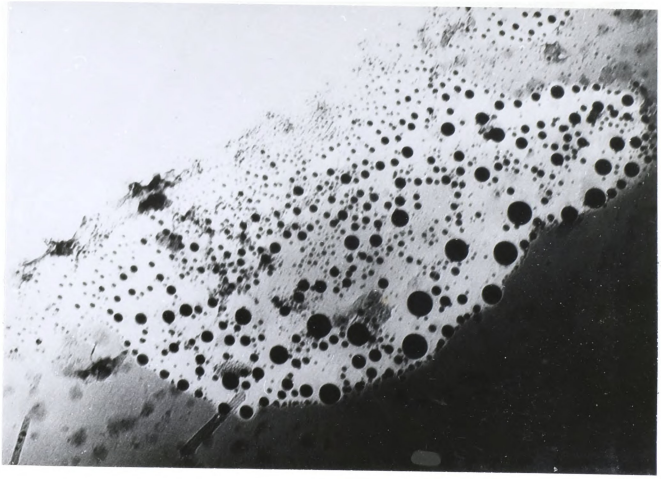


Fig. 15. Transmission electron micrograph of lead borate glass LB_1 containing 2 mole percent cerium oxide.

A. Annealed.

B. Heat treated at 450°C for 4 hours.

C. Heat treated at 450°C for 24 hours.

Diffraction pattern belongs to the selected area shown in C.

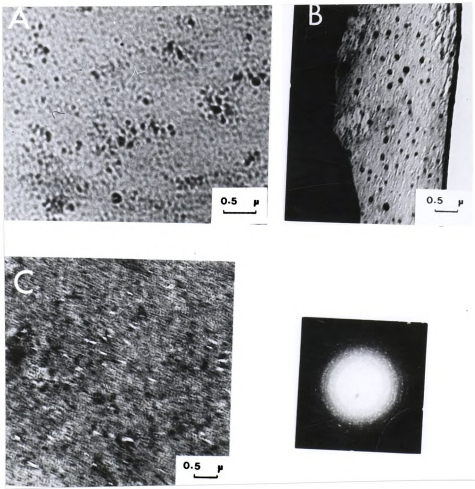
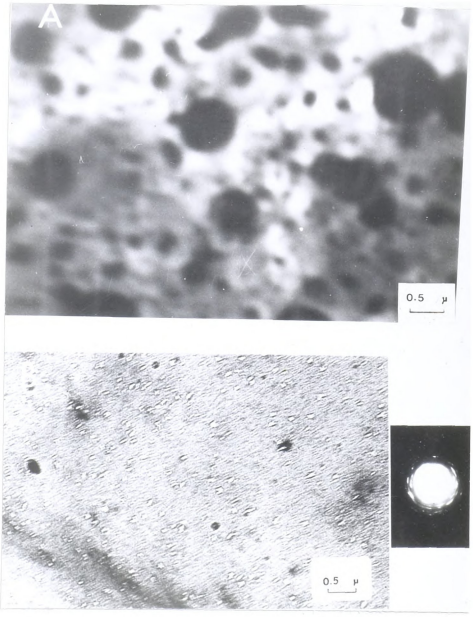

A
0.5 μ
B
0.5 μ
C
0.5 μ

Fig. 16. Transmission electron micrograph of lead borate glass LB_2 containing 8.5 mole percent cerium oxide.

A. Annealed.

B. Heat treated at 450°C for 24 hours.

Diffraction pattern belongs to the selected area shown in B.


A
0.5 μ
0.5 μ

the effect of heat treatment of the lead-borate glass (LB_2) containing a high concentration of cerium oxide (8.5 mole percent). The sample was heat treated at 450°C for 24 hours. The effect of the treatment was the same as that in the sample containing the low concentration of cerium oxide (Fig. 15C). The volume fraction of the elongated boron-oxide-rich crystalline phase (Fig. 16B) is higher than that observed in Fig. (15C). This increase suggests that the crystalline phase increases with increasing cerium-oxide content.

In Figs. 17, 18, and 19 are shown the X-ray diffraction powder patterns of glass LB_0 containing no cerium oxide, glass LB_1 containing 2 mole percent cerium oxide, and glass LB_2 containing 8.5 mole percent cerium oxide, each heat treated at 450°C for 24 and 170 hours, compared with those of the glass receiving no heat treatment other than annealing. It is clear from these figures that the crystalline phases previously observed by electron diffraction are too small in number to be detected by X-ray diffraction. One sharp peak does appear, however, at $2\theta = 27°$ in Fig. 19 in the case of the lead-borate glass containing 8.5 mole percent cerium oxide after heat treatment at 450°C for 170 hours. This finding suggests that the heat-treatment temperature lay in the nucleation region, and that in this system cerium oxide enhances crystallization.

2. Lead-Silicate Glasses Containing Cerium Oxide

D.T.A. curves of lead-silicate glasses are shown in Fig. 20. The annealing temperature for the base glass LS_0 is seen to be 460°C, for the low cerium-oxide-content glass LS_1 (0.1 mole percent) is 435°C. Exothermic peaks are observed at 585°C for glass LS_0, 570°C for glass LS_1, and 555°C for glass LS_2. The height of the exothermic

Fig. 17. X-ray diffraction powder patterns of lead borate glass LB_0 containing no cerium oxide.

1. As annealed.
2. Heat treated at 450°C for 24 hours.
3. Heat treated at 450°C for 170 hours.

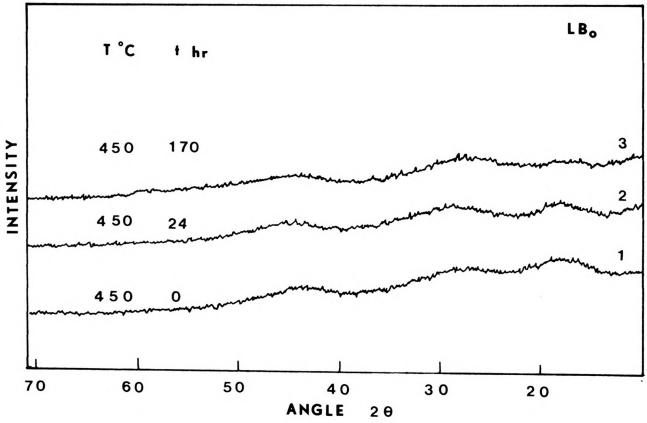

LB$_o$
T °C t hr
450 170
450 24
450 0
3
2
1
INTENSITY
70
60
50
40
30
20
ANGLE 2θ

Fig. 18. X-ray diffraction powder patterns of lead borate glass LB_1 containing 2 mole percent cerium oxide.

1. As annealed.
2. Heat treated at 450°C for 24 hours.
3. Heat treated at 450°C for 170 hours.

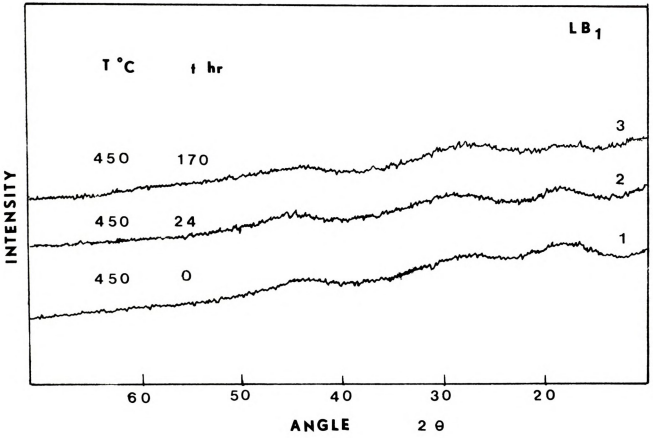

LB1
T °C
t hr
450
170
3
450
24
2
450
0
1
INTENSITY
60
50
40
30
20
ANGLE
2θ

Fig. 19. X-ray diffraction powder patterns of lead borate glass LB_2 containing 8.5 mole percent cerium oxide.

1. As annealed.
2. Heat treated at 450°C for 24 hours.
3. Heat treated at 450°C for 170 hours.

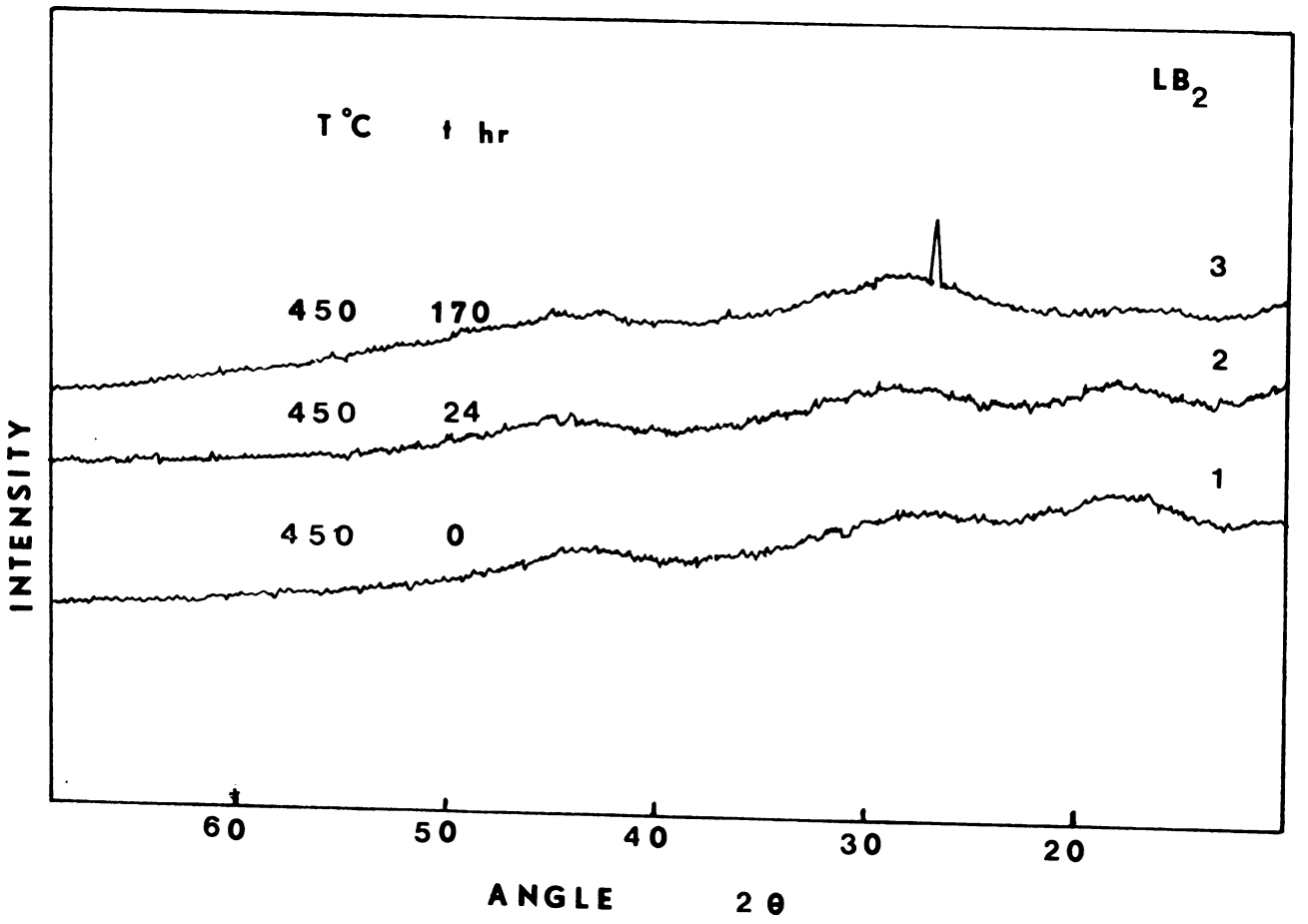
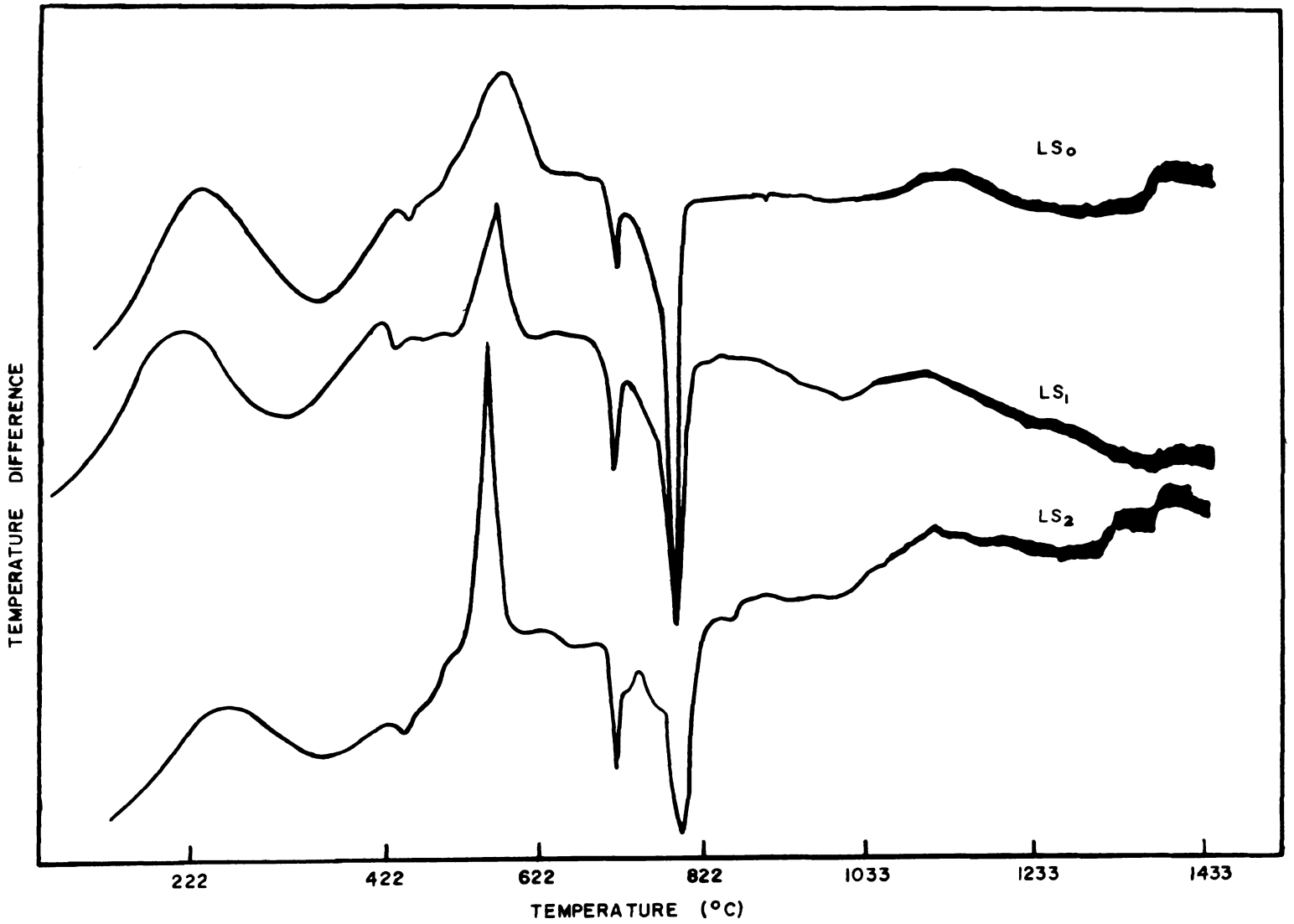

LB2
T°C t hr
450 170
3
450 24
2
450 0
1
INTENSITY
60
50
40
30
20
ANGLE 2θ

Fig. 20. Differential thermal analysis curves for lead silicate glasses.

LS_0 Containing no cerium oxide.

LS_1 Containing 0.1 mole percent cerium oxide.

LS_2 Containing 0.5 mole percent cerium oxide.


LS0
LS1
LS2
TEMPERATURE DIFFERENCE
222
422
622
822
1033
1233
1433
TEMPERATURE (°C)

peak increased markedly with increasing content of cerium oxide, but the width of the peak decreased. On the other hand, the endothermic reaction observed below 800°C (at 790°C) decreased in intensity as a result of addition of cerium oxide. The endothermic reaction observed at 720°C, on the other hand increased in intensity. The lower reaction is due to local eutectic melting crystals. The second reaction at 790°C corresponds to the liquidus.

The presence of two endothermic reactions and the broadness of the exothermic peak in LS_0 glass leads to the conjection that two crystalline compounds are precipitated as a result of heat treatment. Comparison with the work of McMillan et al. [30] suggests that the two compounds may be identified as lead metasilicate, and lead disilicate. This identification was verified by X-ray diffraction analysis.

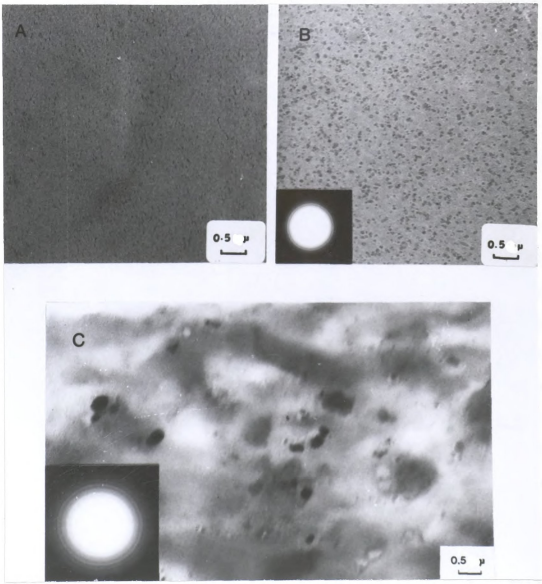
Transmission electron micrographs of Fig. 21 illustrate the effect of heat treatment of the annealed lead-silicate base glass LS_0 at 450°C for 0, 2 and 12 hours. As can be seen from this figure, two phases are present in the annealed glass that did not undergo any heat treatment (A). There is no crystalline regularity in the structure, as evidenced by the absence of sharp electron-diffraction lines. Therefore the two-phase structure must have arisin as a result of glass-in-glass phase separation. Heat treatment of this glass increased the size and decreased the concentration of the dark globules. These phases are crystalline, as shown by the selected-area electron-diffraction pattern (B). The crystallization increased with time (C). On the other hand, the addition of 0.1 mole percent cerium oxide to the annealed base glass has practically no effect on the phase separation or nucleation of this glass, as shown by the transmission

Fig. 21. Transmission electron micrograph of lead silicate glass LS_0.

A. Annealed glass.

B. Heated at 450°C for 2 hours.

C. Heated at 450°C for 12 hours.


A
0·5 μ
B
0.5 μ
C
0.5 μ

micrographs of Fig. 22 A and B. The glass-in-glass phase separation, however, has been slightly enhanced by the addition of 0.5 mole percent cerium oxide, (Fig. 22 C).

The effect of heat treatment on glasses LS_1 and LS_2 containing 0.1 and 0.5 mole percent cerium oxide is illustrated in Figs. 23 and 24. Heating the lead-silicate glass containing 0.1 mole cerium oxide percent at 450°C for 2 hours causes an increase in the phase separation, the dark lead-oxide-rich globules becoming more distinct, as shown in Fig. 23B. Further heating of this glass for 12 hours at the same temeprature increased the phase separation (Fig. 23C). These separated phases are presumed to be glass-in-glass phases, as indicated by the absence of sharp selected-area diffraction pattern. Comparison of the microstructure of the base glass LS_0 heated at 450°C for 2 hours shown in Fig. 21 B, with that of the glass LS_1 that experienced the same heat-treatment shown in Fig. 23 B indicates that crystallization observed in the base glass has disappeared as a result of 0.1 percent cerium-oxide addition. On the other hand, glass LS_2 containing 0.5 mole percent cerium oxide showed an increase in phase separation when heated at 450°C for 2 hours, as shown in Fig. 24 B. The globules are much larger in size than with the corresponding sample of glass LS_1 (Fig. 23 B). Further heating of LS_2 glass for 12 hours caused crystallization of this glass, as shown by the selected-area diffraction pattern of Fig. 24 D.

X-ray-diffraction powder patterns of the lead-silicate base glass LS_0 (containing no cerium oxide), lead-silicate glass LS_1 (containing 0.1 mole percent cerium oxide) and lead-silicate glass LS_2 (containing 0.5 mole percent cerium oxide) are shown in Figs. 25, 26,

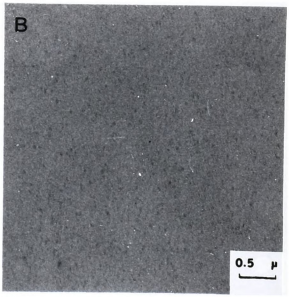
Fig. 22. Transmission electron micrograph of lead silicate glasses.

A. Containing no cerium oxide.

B. Containing 0.1 mole percent cerium oxide.

C. Containing 0.5 mole percent cerium oxide.


A
0.5 μ


B
0.5 μ

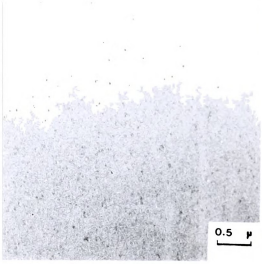

C
0.5 μ

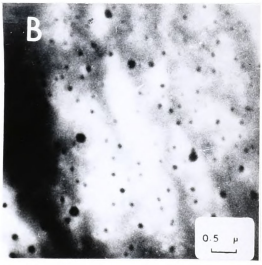
Fig. 23. Transmission electron micrograph of lead silicate glass LS_1 containing 0.1 mole percent cerium oxide.

A. Annealed.

B. Heat treated at 450°C for 2 hours.

C. Heat treated at 450°C for 12 hours.


0.5 μ


B
0.5 μ

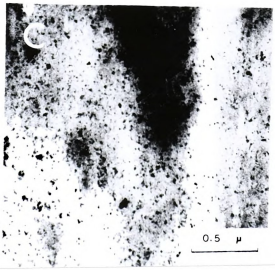

C
0.5 μ

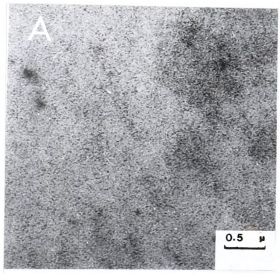
Fig. 24. Transmission electron micrograph for lead silicate glass LS_2 containing 0.5 mole percent cerium oxide.

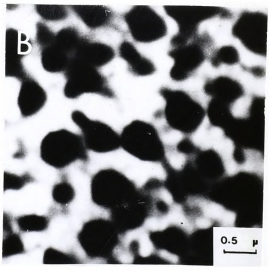
A. Annealed.

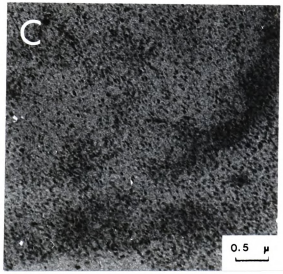
B. Heat treated at 450°C for 2 hours.

C. Heat treated at 450°C for 12 hours.

D. Diffraction pattern belongs to the selected area shown in C.


A
0.5 μ


B
0.5 μ


C
0.5 μ

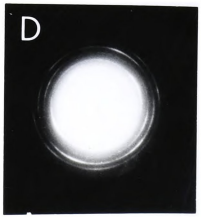

D

Fig. 25. X-ray diffraction powder patterns of lead silicate glass LS_0 containing no cerium oxide.

1. As annealed.
2. Heat treated at 450°C for 12 hours.
3. Heat treated at 450°C for 170 hours.

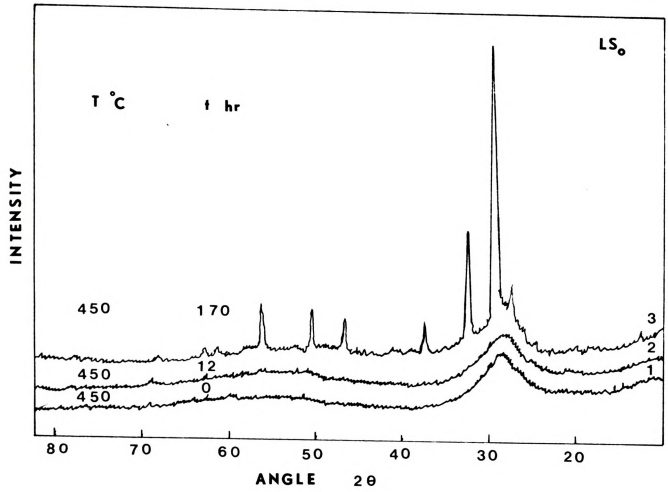

LS$_o$
T °C
t hr
INTENSITY
450
170
3
2
450
12
1
450
0
80
70
60
50
40
30
20
ANGLE 2θ

Fig. 26. X-ray diffraction powder patterns of lead silicate glass LS_1 containing 0.1 mole percent cerium oxide.

1. As annealed.
2. Heat treated at 450°C for 12 hours.
3. Heat treated at 450°C for 170 hours.

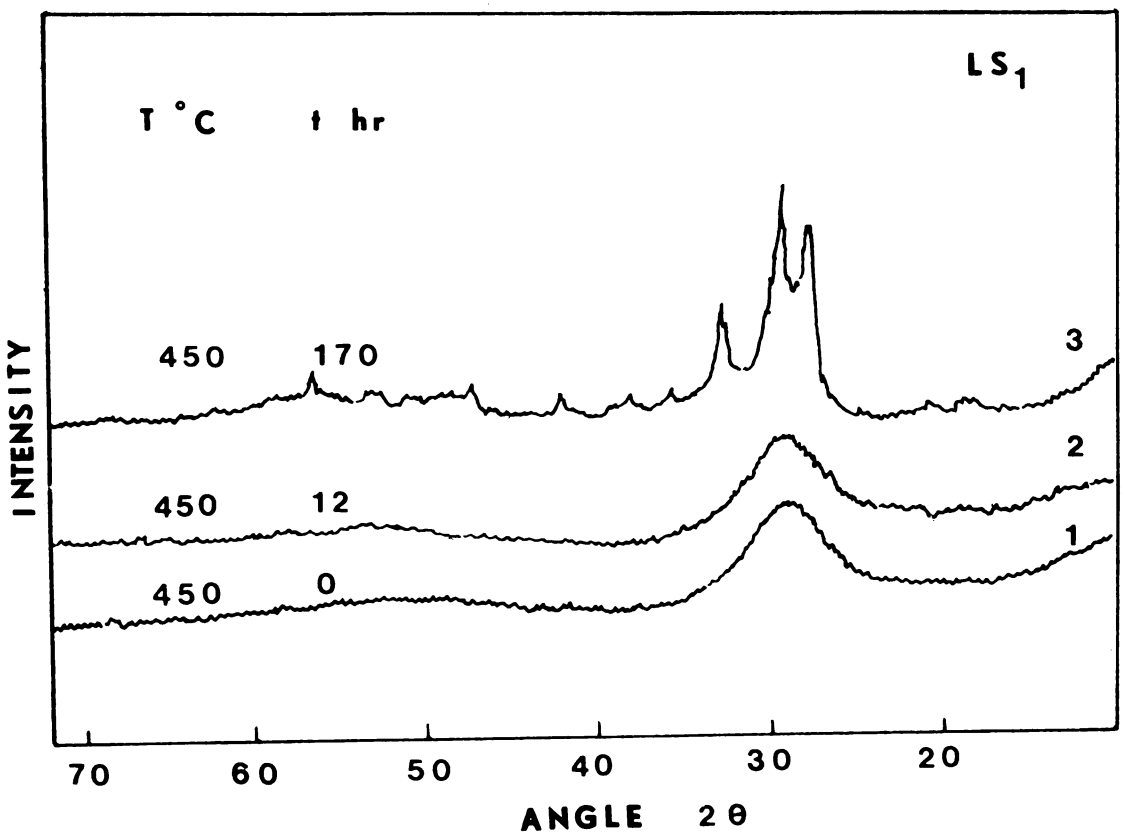
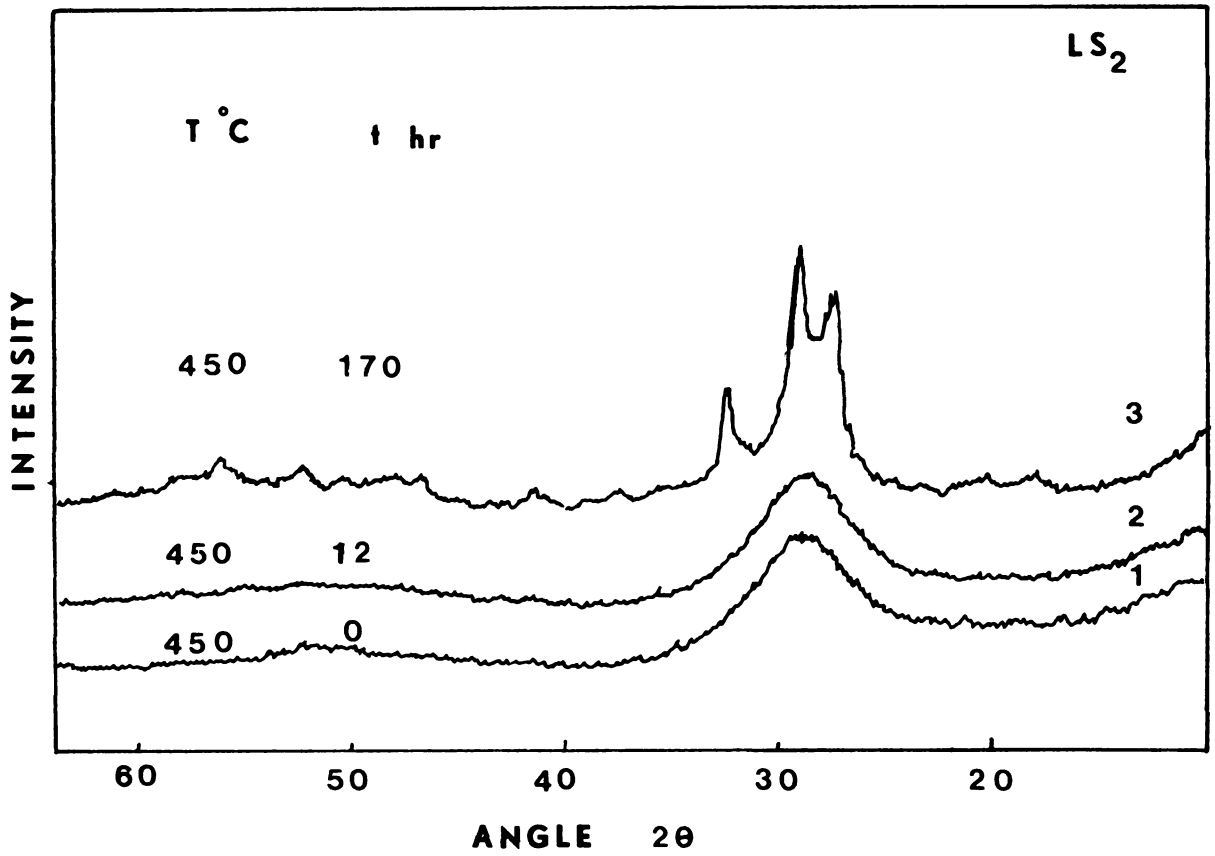

LS1
T °C t hr
450 170
3
450 12
2
450 0
1
INTENSITY
70 60 50 40 30 20
ANGLE 2θ

Fig. 27. X-ray diffraction powder patterns of lead silicate glass LS_2 containing 0.5 mole percent cerium oxide.

1. As annealed.
2. Heat treated at 450°C for 12 hours.
3. Heat treated at 450°C for 170 hours.


LS2
T °C
t hr
450
170
3
450
12
2
1
450
0
INTENSITY
60
50
40
30
20
ANGLE 2θ

and 27 respectively. These patterns are of the glasses when heat treated at 450°C for 12 and 170 hours, compared with those of the glasses as annealed. A broad peak was observed in all samples, even those heat treated for 12 hours. When the glasses were heat treated at 450°C for 170 hours, whenever the crystals precipitated in the glass grew and showed sharp diffraction peaks. Identification of these patterns shows that lead disilicate and lead metasilicate crystals precipitate in the glass upon heat treatment. Comparison of the intensities of the largest peaks shows that the eutectic composition increases with increasing cerium-oxide content.

3. Cerium-Phosphate Glass

A DTA record of cerium-phosphate glass of composition 21 mole percent cerium oxide and 79 mole percent phosphorus pentoxide during heating from room temperature is given in Fig. 28. A shallow dip occuring over the temperature range 600 to 650°C is associate with annealing of this glass. A well-defined broad exothermic peak observed at about 850°C is due to the crystallization of the glass. The presence of two endothermic reactions observed at 1050 and 1180°C suggests that the broad exothermic peak may be due to precipitation of more than one crystalline phase.

The transmission electron micrograph of the annealed cerium-phosphate glass, together with the selected-area diffraction pattern are given in Fig. 29. The absence of structures in the pattern suggests that the glass did not phase-separate during annealing. On heating the glass at 700°C for two hours, no obvious change in the microstructure was observed by the transmission electron microscopy, as shown in Fig. 30. The electron-diffraction pattern of the selected

Fig. 28. Differential thermal analysis curve for cerium phosphate glass.

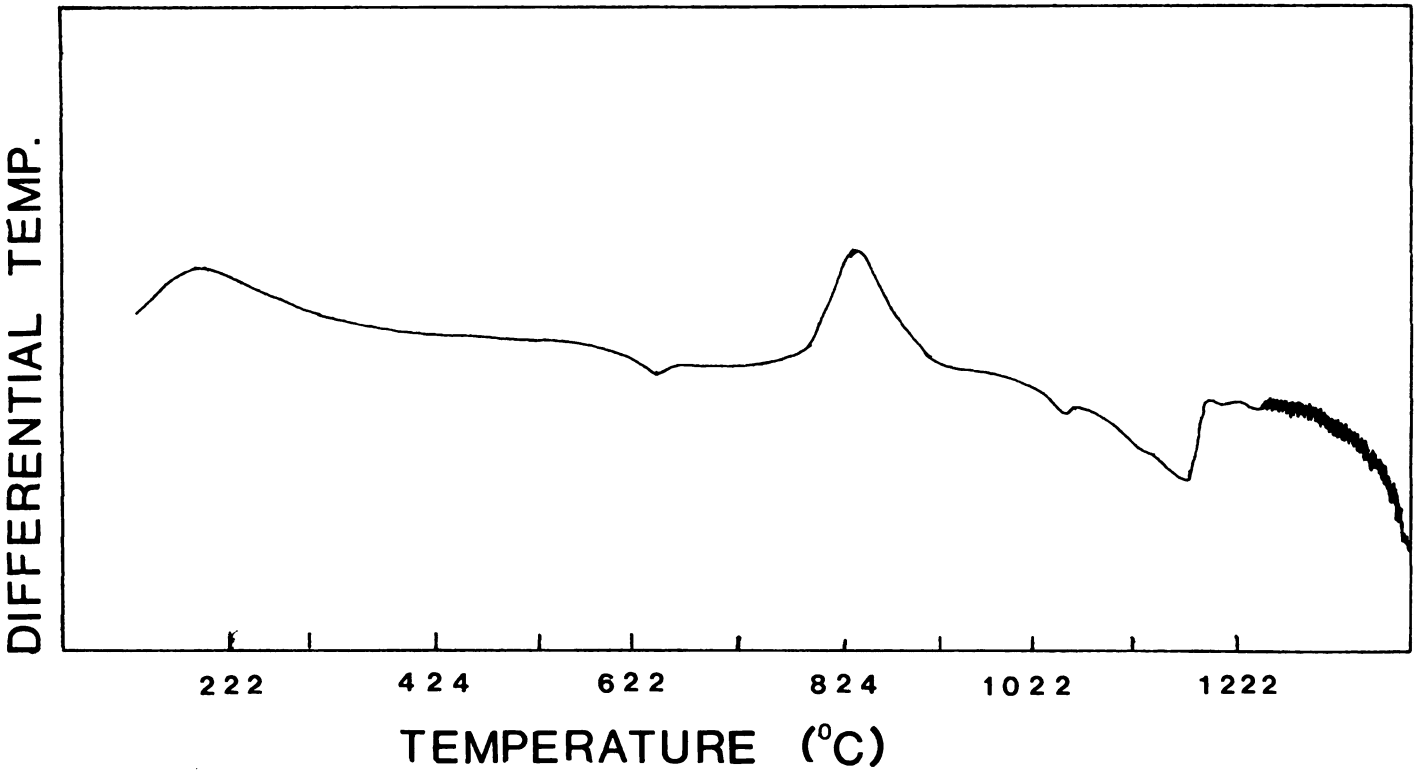

DIFFERENTIAL TEMP.
222
424
622
824
1022
1222
TEMPERATURE (°C)

Fig. 29. Transmission electron micrograph of cerium phosphate glass as annealed.

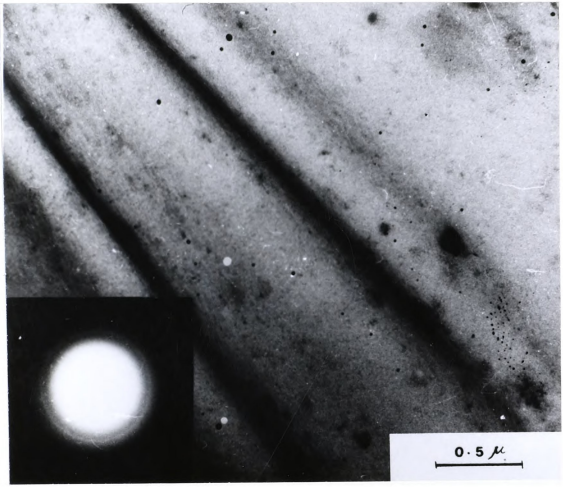
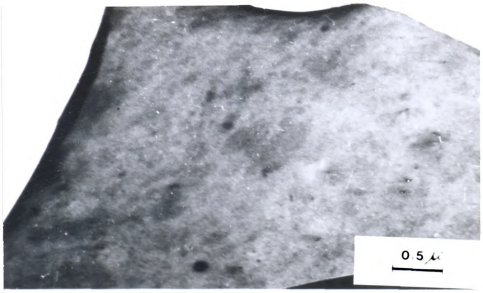
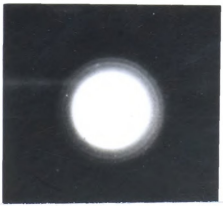

0·5 μ

Fig. 30. Transmission electron micrograph of cerium phosphate glass heat treated at 700°C for 2 hours.


0.5 μ



area shows sharp lines, however. These lines have been identified as the diffraction pattern from cerium-oxide crystals present in the glassy matrix. Heating the specimens at the same temperature for 4 hours gives visible cerium-oxide nuclei, shown as dark spherical regions in the transmission electron micrograph presented in Fig. 31. The selected-area diffraction pattern of this sample is exactly the same as that shown in Fig. 30. When the glass was heated at 700°C for 5, 6, and 7 hours, the dark regions observed in Fig. 31 grew continuously with time as illustrated in Figs. 32, 33, and 34 respectively. The structure of the glass heat treated for 8 and 12 hours at 700°C is presented in Fig. 35. The electron-diffraction pattern shown is for heat treatment of 12 hours. After 8 hours, the regions surrounding the cerium oxide look like dark globules, which can be identified as the cerium-oxide-rich glass phase. This analysis is based on the fact that the 12 hour heat treatment causes these globules to shrink to the crystalline cerium oxide that appears as dark spots in the electron micrograph. The shrinkage was demonstrated by the two micrographs of Fig. 36. Electron micrograph A of Fig. 36 is that of cerium-phosphate glass heat treated at 700°C for 8 hours. When heated by the electron beam, the dark globules shrank as shown in Fig. 36 B. On the other hand, when the glass is heated at the same temperature (700°C) for 18 hours, cerium-oxide crystals grew as shown in Fig. 37. The light regions in the matrix that start to appear are believed to be phosphorus-oxide-rich glass. The effect of further heating the glass for 36 hours is illustrated with the micrograph of Fig. 38. It shows that as the number of the dark spherical regions decreases slightly and there size increases, the light regions get

Fig. 31. Transmission electron micrograph of cerium phosphate glass heat treated at 700°C for 4 hours.

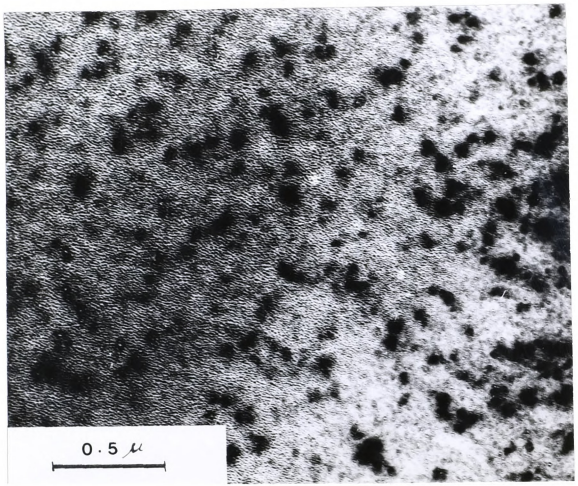

0·5 μ

Fig. 32. Transmission electron micrograph of cerium phosphate glass heat treated at 700°C for 5 hours.

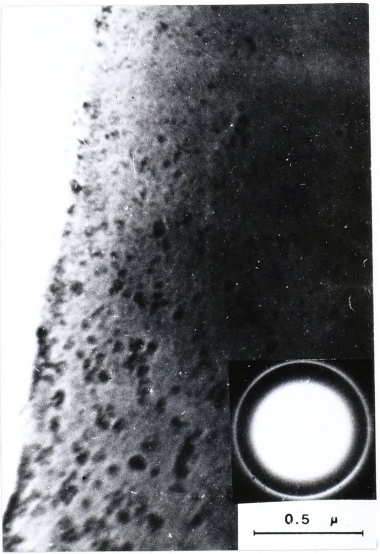

0.5 μ

Fig. 33. Transmission electron micrograph of cerium phosphate glass heat treated at 700°C for 6 hours.

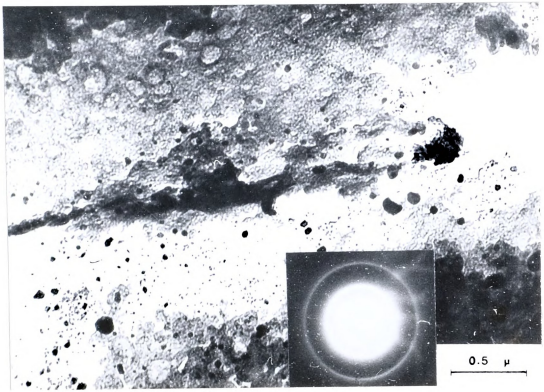

0.5 μ

Fig. 34. Transmission electron micrograph of cerium phosphate glass heat treated at 700°C for 7 hours.

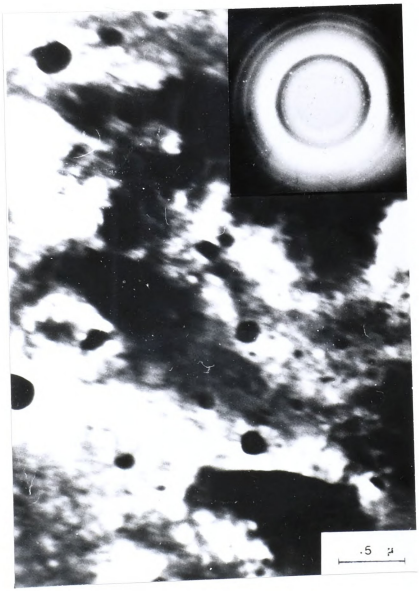
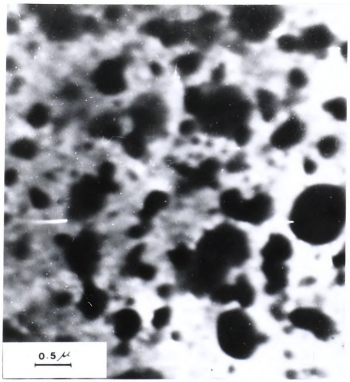

.5 μ

Fig. 35. Transmission electron micrographs of cerium phosphate glass.

Upper - Heat treated at 700°C for 8 hours.

Lower - Heat treated at 700°C for 12 hours.


0.5 μ

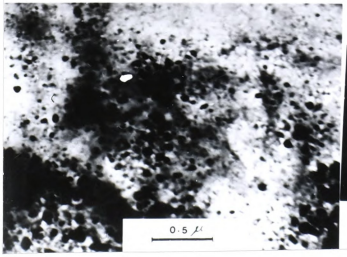

0.5 μ

Fig. 36. Transmission electron micrographs of cerium phosphate glass.

A. Heat treated at 700°C for 8 hours.

B. The same area in A after heating by the electron beam.

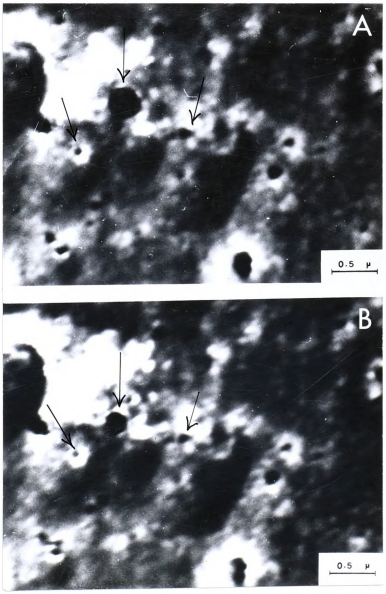

A
0.5 μ
B
0.5 μ

Fig. 37. Transmission electron micrograph of cerium phosphate glass heat treated at 700°C for 18 hours.

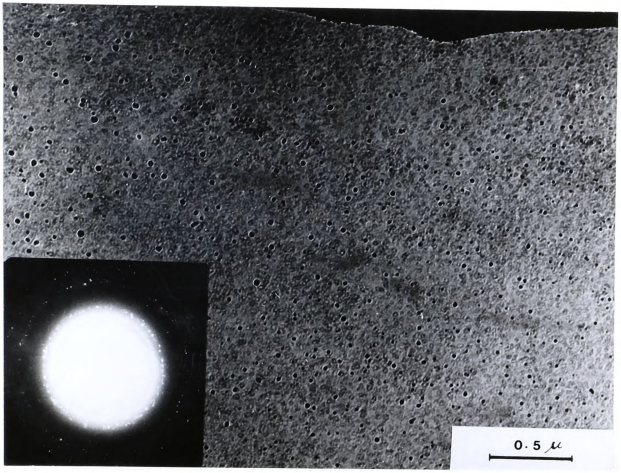
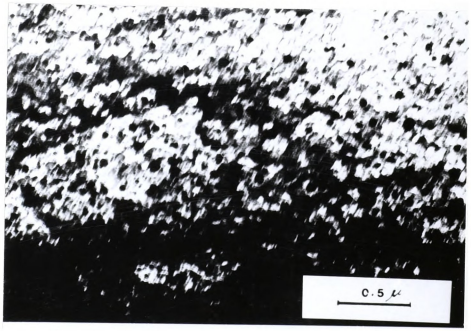

0·5 μ

Fig. 38. Transmission electron micrograph of cerium phosphate glass heat treated at 700°C for 36 hours.


0.5 μ

lighter, more numerous, and bigger.

In Fig. 39 are shown the X-ray-diffraction powder patterns of two samples heat treated at 700°C for 12 and 36 hours, compared with that of the glass that underwent no treatment except annealing. From this figure it is obvious that crystalline phases observed by electron diffraction are too small in number to be detected by X-ray diffraction. When this glass is heated at a higher temperature -- 815°C -- for 40 hours, however, several diffraction peaks were observed. Direct comparison with the diffraction pattern of ceric-oxide powder shows that the crystalline phase in glass is ceric oxide, as shown in Fig. 40. Further heating of cerium-phosphate glass at the same temperature for 240 hours shows that crystalline phases other than ceric oxide are precipitating. Identification of these diffraction patterns shows that cerium phosphate and phosphorus crystals precipitate when the sample is heated for a longer time, as shown in Fig. 40.

Fig. 39. X-ray diffraction powder patterns of cerium phosphate glass.

As annealed.

Heat treated at 700°C for 12 hours.

Heat treated at 700°C for 36 hours.

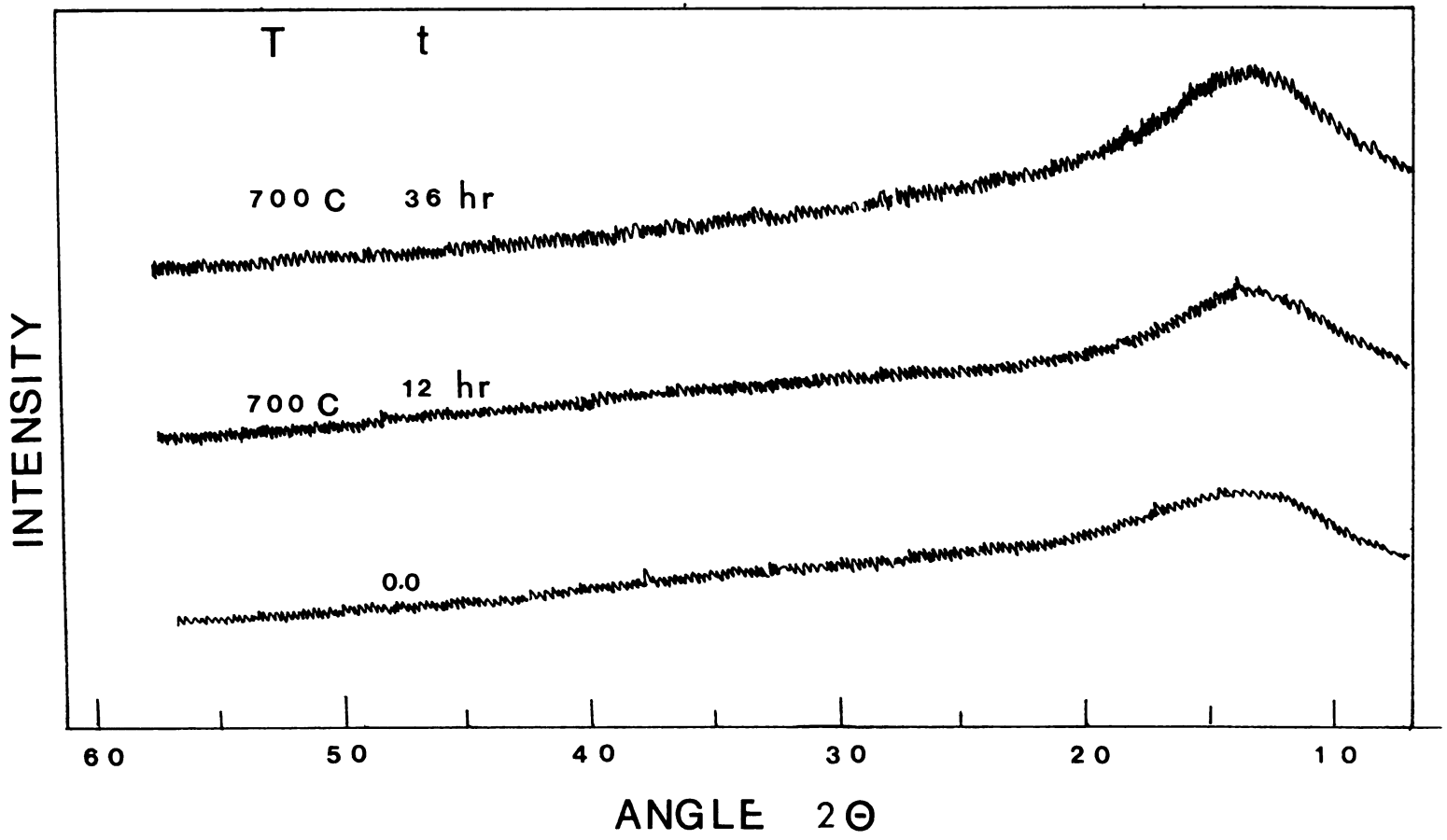
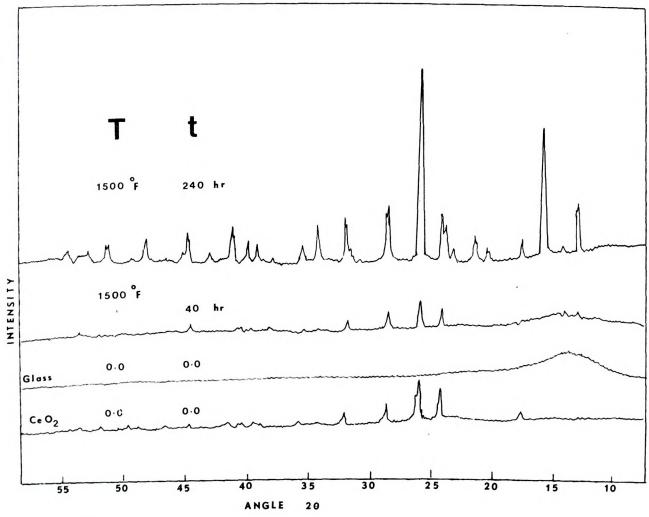

T t
700 C 36 hr
700 C 12 hr
0.0
INTENSITY
60
50
40
30
20
10
ANGLE 2Θ

Fig. 40. X-ray diffraction powder patterns of cerium phosphate glass heat treated at 815°C for different periods of time and that of polycrystalline ceric oxide.


T t
1500 °F 240 hr
1500 °F 40 hr
Glass 0·0 0·0
CeO2 0·0 0·0
INTENSITY
55 50 45 40 35 30 25 20 15 10
ANGLE 2θ

CHAPTER IV

DISCUSSION

The development of a new area of glass technology, the production of glass-crystalline materials, became possible because of the discovery of the catalytic crystallization method, in which the growth of crystals starts simultaneously from a larger number of nuclei which are uniformly distributed in the preshaped glass article.

Gibbs [31] made theoretical investigations of the process of nucleus formation, based on thermodynamic considerations, and concluded that the growth of the new phase B at the expense of the initial phase A is possible if these phases are not in equilibrium with respect to each other.

As mentioned before, phase separation occurs in glass as a consequence of the incompatibility between different types of network-forming structure groups present in glass. McMillan [15] suggested two reasons for this incompatibility. The first reason is based on geometrical differences between the principal network-former and the foreign ones. Some ions, moreover, tend to change their coordination number with changing temperatures. These geometrical differences cause distortion in the chemical bonds of the principal network-former groups and as a result phase separation occurs so that the network may exist in an undisturbed form in one phase, the network of the other

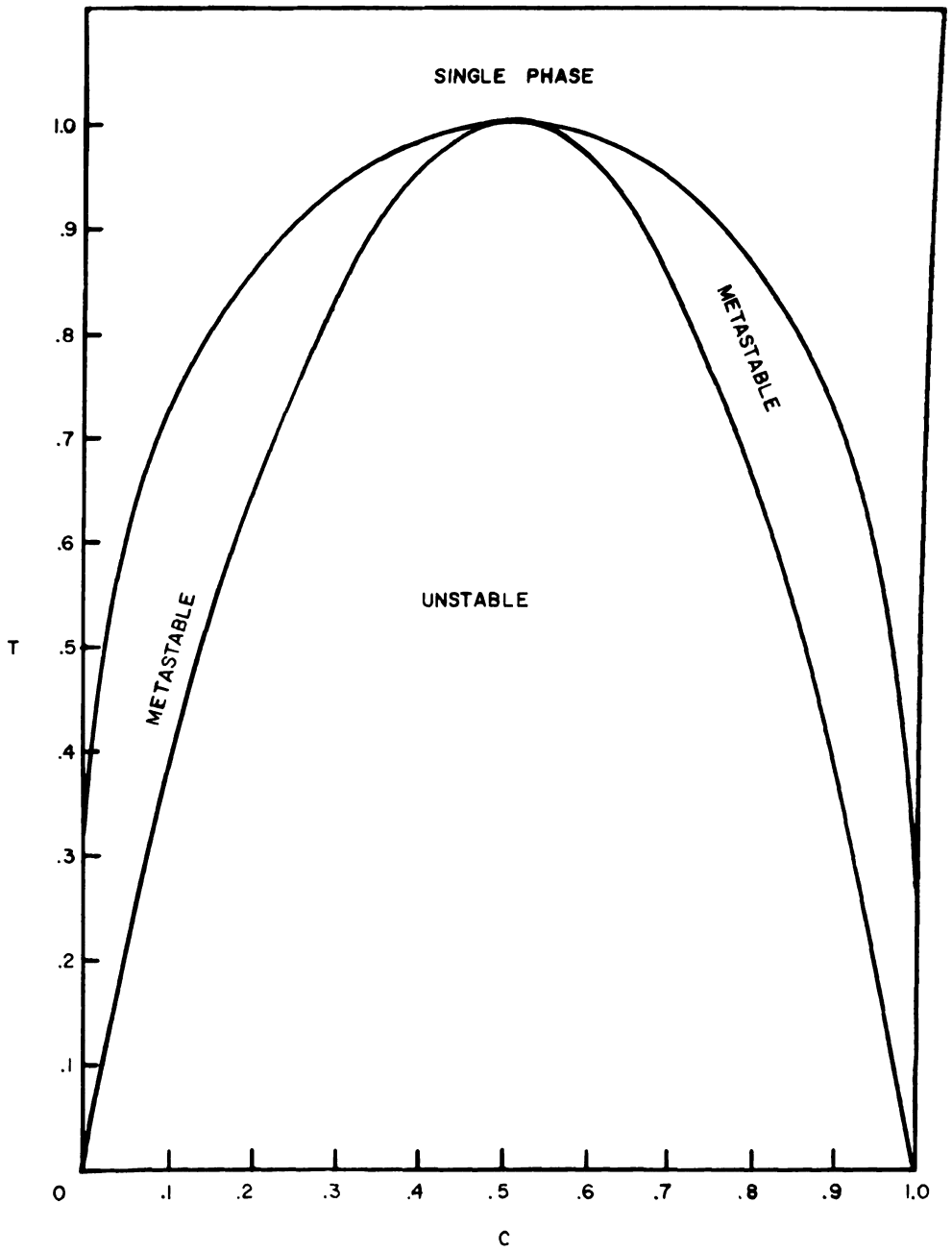
groups existing in the other phase. The second basic reason for incompatibility between different network-forming oxides is the differences between the charges associated with the network-forming cation. This difference could lead to instability.

Another way of understanding the problem of the phase separation in glass and the effect of nucleating agents is to consider the effect on the immiscibility boundary. It has a close relationship to the morphology of the separated phases. When a specimen is heat-treated inside the immiscibility boundary, an interconnected structure is obtained. The mechanism of formation of this structure is not clearly understood, since such a structure can result either by spinodal decomposition, or simply by coalescence of the growing precipitates.

Gibbs [32] in his classic treatment of heterogeneous equilibria, derived a necessary condition for the stability of a fluid phase: the chemical potential, G, of a component must increase with increasing density of that component, C. For a two-component system this condition reduces the condition to $(\partial^2 G/\partial C^2)_{T,p} > 0$. If this condition is not met, the solution is unstable with respect to continuous changes in composition. The limit of metastability, where $\partial^2 G/\partial C^2 = 0$, is called the spinodal.

Cahn [33] developed a theory for phase separation by spinodal decomposition in isotropic systems. He found that in the metastable region on a phase diagram, which is between the spinodal and the phase boundary illustrated in Fig. 41, a finite fluctuation is required to render the solution unstable. This fluctuation is called a nucleus, and the work of forming such a nucleus is a measure of the metastability

Fig. 41. Phase diagram of a regular solution showing the equilibrium phase boundary and the spinodal (Cahn [33]). The unstable region is the spinodal.


SINGLE PHASE
METASTABLE
METASTABLE
UNSTABLE
T
C
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0

of the phase.

Cahn [33] examined the essential difference between his mechanism and nucleation and growth. In the latter mechanism, the new phase starts from small regions which proceed to grow in extent. At any time the structure consists of two phases, and in each region the compositions are either those of one phase or the other. In the spinodal mechanism, the composition changes gradually in both directions from the average. In the early stages the entire composition range between the composition extremes exists within the sample. The spread in composition increases with time. It has been found [33] that this kind of growth is thermodynamically impossible except in an unstable region. It may happen that a shift of the immiscibility boundary brings about favorable and more thermodynamically stable compositions. On the other hand, it is possible also that nucleating agents might affect the kinetics of phase separation without shifting the immiscibility boundary, through change in the viscosity of the glass by providing numerous hetergeneous nucleating sites.

In part A of this chapter the merits of the thin-foil preparation techniques, transmission electron microscopy, X-ray diffraction, and differential thermal analysis will be discussed. In part B the preparation of the new cerium-phosphate glass will be discussed. Part C will be concerned with the discussion of the present results of the effect of cerium-oxide addition on the microstructure of lead-borate and lead-silicate glasses. Part D will treat the effect of the heat treatment on the microstructure of cerium-phosphate glass. In part E the role of cerium oxide as a nucleating agent in different

host-glass matrices will be discussed.

A. Merits of Experimental Techniques

As mentioned earlier, both mechanical polishing and chemical polishing were used to prepare thin foils of the sample materials for observation under the transmission electron microscope. A powder technique was chosen for preparation of one sample only (cerium phosphate), and then was abandoned because the crystalline phases separate physically from the matrix, and the specimen does not give a true picture of the structure.

The mechanical-polishing technique developed by Doherty and Leombruno [26] and modified by Seward III et al. [27] is successful, particularly after modification in the present investigation. The major changes were to shorten the specimen-preparation time from 24 hours in the work of Doherty et al [26], and 2 hours in the work of Seward III et al. [27], to only one-half hours. This technique is particularly successful in highly-crystallized glasses. It is also a good technique for soft glasses (lead-borate and lead-silicate), but requires more attention in polishing hard glasses (cerium-phosphate). Although the techniques have been modified to shorten the time required for preparation of thin foil, it is still tedious and time-consuming compared with the chemical-polishing techniques. In this technique, moreover, washing and handling the thin foil requires much more care than the other techniques.

In case of chemical polishing, two methods previously described were adopted for the present investigation. The first method

developed by James et al. [28], and modified in the present work, is ideally suited for hard glass (cerium phosphate). It produces many large thin areas, and the sample is polished equally from both sides so that the thin foil obtained is from the internal region of the bulk glass. In this case it is very easy to wash, handle, and chip the thin area. Unfortunately this method did not work as well for the soft glasses (lead-borate and lead-silicate), because the edges get rounded very fast. It is a fairly fast method. The second method developed by Washburn et al. [29], and adopted in the present work, is very successful for any glass, partially or completely-crystallized glass, soft or hard. In the case of the relatively hard slide glass as presented in appendix C, the method was ideal and very fast. It is necessary, however, to polish the glass sample from both sides in order to obtain a thin specimen near the center of the bulk sample. It is not always possible to polish an area on one side and then polish exactly the corresponding area from the other side. This method is faster than the mechanical polishing technique but much slower than the method developed by McMillan [28] and modified in the present investigation. In this method, moreover only one hole, with thin areas near the hole, is produced. Therefore the investigation is limited to working with a small region of the specimen after each polishing.

A powder technique can be used to prepare thin foils of cerium-phosphate glass ceramic. The disadvantage of this method is that the crystallites in the sample physically separate out of the glass matrix, and the electron micrograph will not be representative of the structure of the specimen. Nevertheless, in samples containing

glasses only, the method can be used successfully.

Reproducibility of some of these methods is illustrated in Figs. 48 and 49 in Appendix A. Equivalence of the mechanical and the chemical polishing techniques is demonstrated by Figs. 50 and 51 in Appendix A. These two figures indicate that these two techniques can be replaced by one another, for example in samples with high percentage of crystals the mechanical polishing will be more suited.

X-ray diffraction is very useful in identifying the separated crystalline phases in the heat-treated glasses, and has been used extensively by various researchers. This technique, cannot however, detect a crystalline phase when its concentration in the glassy matrix is small.

Qualitative thermal analysis in the present investigation serves two purposes. The first is to find the proper annealing temperature of the glasses. A dip in the DTA curve occurs at its lower-temperature end. It is associated with the annealing temperature, is always distinct, and can be easily identified. The second purpose is to find whether the glass wil be able to crystallize when heat treated, and to determine the heat-treatment temperature schedule. This method also gives qualitative information on the number of the precipitated phases in the heat-treated glass. In Fig. 20, which is the DTA curve for lead-silicate glasses, there exist two pronounced sharp exothermic peaks which are associated with the crystallization of the glass. These two peaks are a good indication that two crystalline phases may precipitate when the glass is heat treated. Analysis of the results obtained from both X-ray and electron-diffraction

studies of these glasses shows that there are actually two crystalline phases, namely 2 PbO · SiO_2 and PbO · SiO_2, in the glass when heat treated at 450°C for 2 and 12 hours. Thus DTA is seen to be an important tool and an essential technique in these studies.

B. Cerium-Phosphate Glass Preparation

Cerium-phosphate glass of molecular percentage composition 21 CeO_2 and 79 P_2O_5 was prepared for the first time during the course of the present investigation. The cerium oxide and phosphorus oxide can be added as different compounds, according as the cerium ions are to exist in glass as ceric ions (Ce^{4+}) or as cerous ions (Ce^{3+}). To prepare glasses under normal melting conditions, cerium oxide can be introduced as cerous oxalate, and the phosphorus can be added as P_2O_5. In case of glasses in which the ratio Ce^{3+}/Ce^{4+} is to be greater than one, the phosphorus oxide should be added as ammonium phosphate, and melting should be carried out in an inert atmosphere. In glasses where the ratio Ce^{3+}/Ce^{4+} is to be less than one, however, the cerium oxide is added as CeO_2, and phosphorus oxide is added as P_2O_5. An oxidizing compound should be added to the batch to help in oxidizing most of the cerous ions to ceric ions. The advantageous feature of this glass is that the ratio of cerous to ceric ions is controllable. This ratio affects the optical, electrical, and magnetic properties of the resulting glass.

Since the physical properties of this glass were not investigated during the course of this work, the ratio Ce^{3+}/Ce^{4+} is not of particular interest in the present investigation. To make the glass, cerium

oxide was added as cerous oxalate, and phosphorus oxide was added as ammonium dihydrogen phosphate. Decomposition of the oxalate and phosphate radicals, together with the evolution of gases as a result of the decomposition, helped in mixing the components. Melting was conducted in alumina crucibles in air. Corrosive action of P_2O_5 on platinum precluded the use of platinum crucibles for making this glass. Further, platinum acts as a good nucleating agent, and it may distort the development of the microstructure of the cerium-phosphate glass.

The glass was originally colorless owing to the reducing action of the ammonium ions that keeps part of the cerium ions in the cerous form. When the glass was crushed and remelted (to insure homogenity), it turned yellow, owing to the oxidation of most cerous ions to ceric.

The cerium-phosphate glass did not break during the cutting of 0.1-mm thick glass wafers with a diamond saw. Crushing the glass, however, proved to be most difficult. The glass is chemically durable. Of the reagents tested, concentrated hydrofluoric acid and sodium hydroxide were the only two reagents that attacked it.

C. Cerium Oxide As a Nucleating Agent in Glass-Ceramics

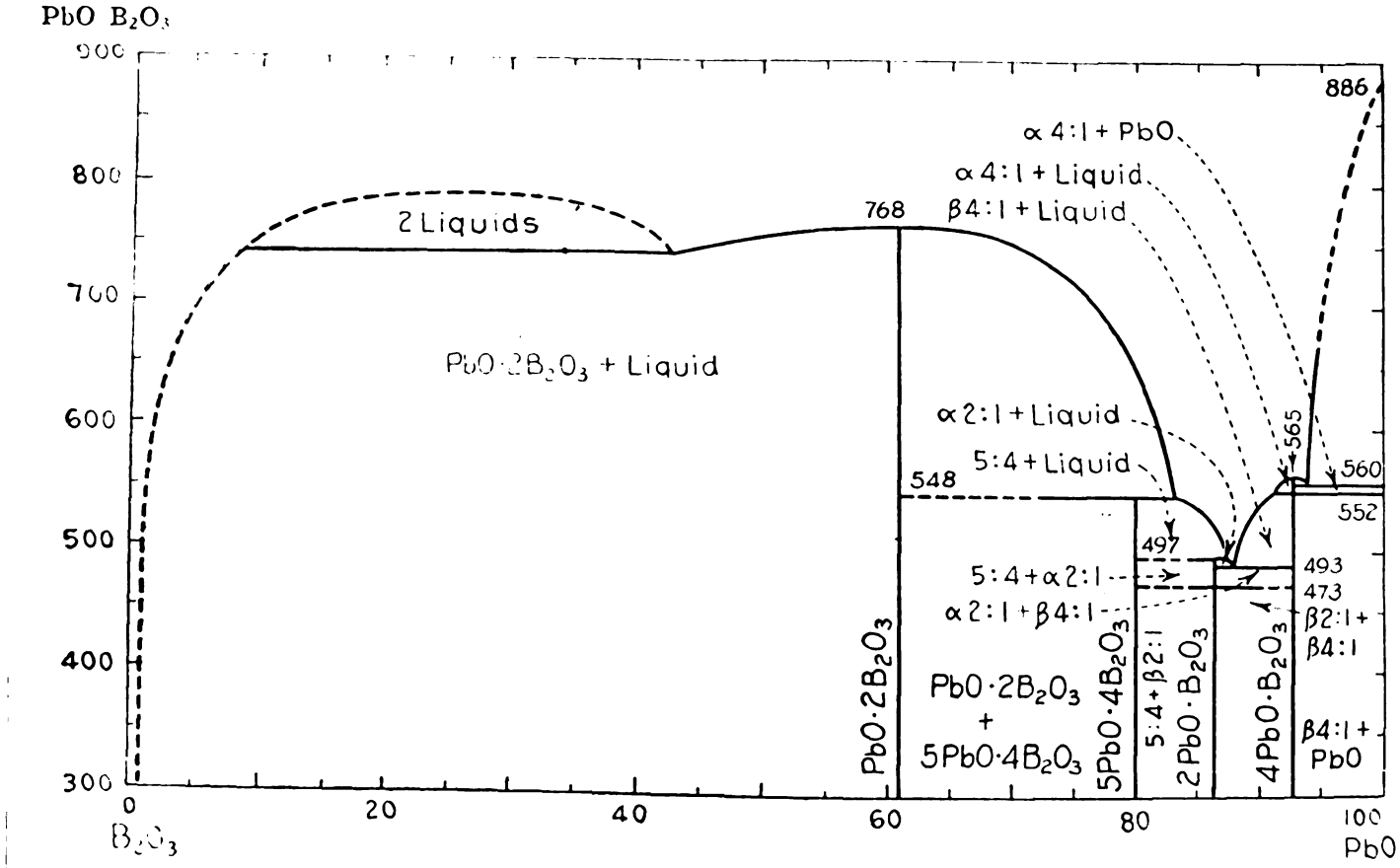
Transmission electron microscopy and electron-diffraction techniques have proved to be powerful tools in investigating phase separation and crystallization in glasses and glass-ceramics. In investigations of the function of nucleating agents, it is advantageous to work at first with simple binary glass systems rather than with complex commercial compositions. Further, in binary oxide glass systems, it is

helpful to choose oxides of elements which have large difference in the atomic number. Then the large difference in electron absorbance of these elements will provide the necessary contrast in the transmission electron micrograph. The systems PbO - B_2O_3 and PbO - SiO_2 fulfill these requirements, the high atomic number of Pb(Z_{pb} = 82) providing the necessary contrast with that of the glass matrix (Z_{Si} = 14, Z_B = 5 and Z_O = 8).

The phase-equilibrium diagram of the lead-borate system obtained by Geller and Bunting [34] is shown in Fig. 42. It comprises a narrow two-liquid region between approximately 9 and 43 wt% PbO, the rather flat upper limit of this area at 785°C being determined by temperatures of demixing in the liquid state. However, there were uncertainties as to the position of the dome of the demixing curve. This entire curve was redetermined by Zarzycki and Naudin [35], and was found to agree very well with the results of Geller and Bunting [34]. The composition of lead-borate glasses of the present investigation lay under the dome, and these glasses should separate to two liquidlike phases upon heat treatment.

The electron micrographs presented in Figs. 12(A), (B) and (C) show the effect of heat treatment on the lead-borate glass containing no cerium. It is quite obvious that glass-in-glass phase separation occurred during annealing, and that it progressed during heat-treatment of the glass. The absence of a sharp electron-diffraction pattern confirmed the existence of glass-in-glass phase separation. On the other hand, when cerium oxide was added to the base glass the average size of the precipitated glass phase increases, whereas the total number of the particles decreased, as shown in Figs. 31(A), (B) and (C). In a

Fig. 42. Equilibrium phase diagram of $PbO-B_2-O_3$ system Geller et al [34].


PbO B_2O_3
900
800
700
600
500
400
300
0
20
40
60
80
100
B_2O_3
PbO
2 Liquids
$PbO \cdot 2B_2O_3$ + Liquid
768
886
α 4:1 + PbO
α 4:1 + Liquid
β 4:1 + Liquid
α 2:1 + Liquid
5:4 + Liquid
548
565
560
552
497
493
473
5:4 + α 2:1
α 2:1 + β 4:1
β 2:1 +
β 4:1
β 4:1 +
PbO
$PbO \cdot 2B_2O_3$
+
$5PbO \cdot 4B_2O_3$
$PbO \cdot 2B_2O_3$
$5PbO \cdot 4B_2O_3$
5:4 + β 2:1
$2PbO \cdot B_2O_3$
$4PbO \cdot B_2O_3$

solution which undergoes phase separation, two basic stages of development may be distinguished. The first stage is the nucleation-and-growth stage. In this stage concentration fluctuations due to the incompatibility of the triangular boron oxide and the tetrahedral PbO--which partially assumes network-forming position--produce nuclei of the new phase, which grow from the supersaturated matrix. The second stage is one of coalescence, which begins when the particles formed reach an appreciable size, and the degree of supersaturation of the matrix has become slight. The smaller particles tend to dissolve, the larger ones growing at their expense. Concentration fluctuations play a negligible part in this second stage. The overall effect of the coarsening of the precipitate is to reduce the total surface energy of the dispersed phase. The two phases that separated in this system consist of lead-oxide-rich glass (appearing as dark globules) and boron-oxide-rich glass (as a matrix depleted of lead oxide). This analysis shows that cerium oxide enhances the glass-in-glass phase separation in this system.

As stated earlier, when the lead-borate glass containing 2 mole percent cerium oxide was heat treated at 450°C for 4 and 24 hours, another light-color phase precipitated in the glass matrix. The selected-area electron-diffraction pattern shows that this boron-oxide-rich phase is crystalline. Analysis of the electron-diffraction pattern shows that this phase is boron oxide (B_2O_3). It is also obvious that the lead-oxide-rich glassy phase disappears as the boron oxide crystallizes out and forms a homogeneous glassy phase. From the phase-equilibrium diagram shown in Fig. 42 and the electron-diffraction analysis, it can be concluded that the background glassy dark phase is of the composition ($PbO - 2B_2O_3$). Since cerium oxide enhances phase separation

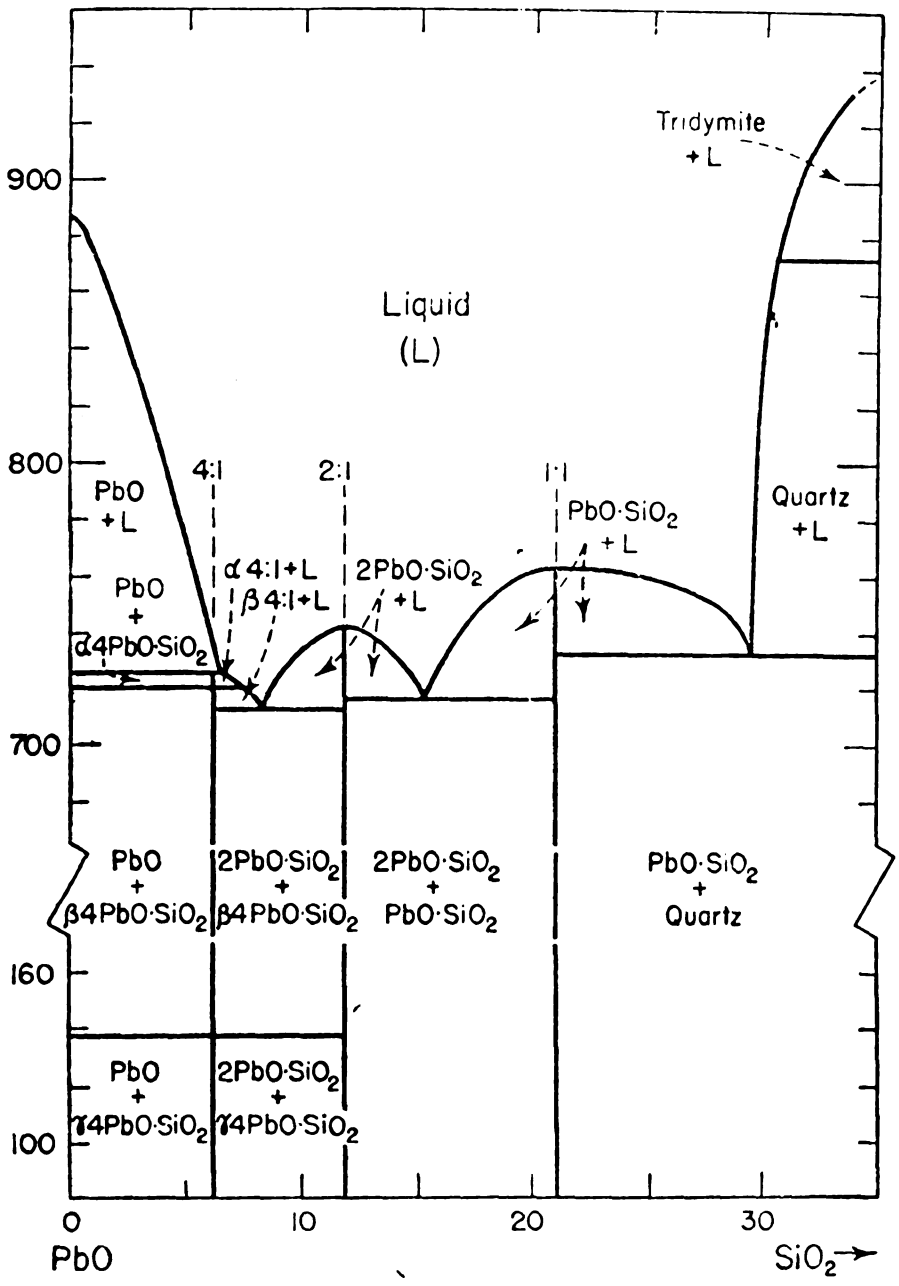
in lead-borate glass, it appears that cerium ions assume network-modifying positions and break up the structure, making it more susceptible to phase separation and crystallization.

The phase-equilibrium diagram of the lead-silicate system as obtained by Geller, Creamer and Bunting [36] is given in Fig. 43. A eutectic is observed in the range from approximately 12 to 21 weight percent SiO_2. The eutectic temperature is approximately 718°C. Below this temperature two phases of the composition $2PbO \cdot SiO_2$ and $PbO \cdot SiO_2$ are present. Therefore it is expected that these two compounds will crystallize when the lead-silicate glass containing between 12 and 21 weight percent SiO_2 is heated at temperatures below 718°C. The lead-silicate glass of the current investigation contains approximately 18 weight percent SiO_2.

In the DTA curve for the lead-silicate glass containing no cerium oxide (LS_0) shown in Fig. 20, the exothermic peak observed at 570°C is seen to be a broad asymmetric peak. This broadening suggests that there may be more than one phase crystallizing in this temperature region. The presence of two endothermic peaks at 710°C and 765°C also indicates that there are more than one crystallizing phase. The lower endothermic reaction observed at 710°C perhaps represents formation of local eutectic, in view of the fact that the eutectic temperature in the phase diagram shown in Fig. 42 of the composition range 12 to 21 weight percent SiO_2 occurs at 718°C. The phase diagram shows that the composition of the eutectic is 66.7% $PbO \cdot SiO_2$ - 33.3% $2PbO \cdot SiO_2$ and that of the crystallized glass is 33.3% $PbO \cdot SiO_2$ - 66.7% 2 $PbO \cdot SiO_2$. Therefore, when the glass (LS_0) is completely crystallized, 16.6% of 2 $PbO \cdot SiO_2$ and 33.3% of $PbO \cdot SiO_2$ will form the eutectic composition, and the remaining 50.1% will

Fig. 43. Equilibrium phase separation of $PbO-SiO_2$ system Geller et al [36].

$PbO–SiO_2$


Tridymite
+L
900
Liquid
(L)
800
4:1
2:1
1:1
PbO
+L
PbO·SiO2
+L
Quartz
+L
α4:1+L
β4:1+L
2PbO·SiO2
+L
PbO
+
α4PbO·SiO2
700
PbO
+
β4PbO·SiO2
2PbO·SiO2
+
β4PbO·SiO2
2PbO·SiO2
+
PbO·SiO2
PbO·SiO2
+
Quartz
160
PbO
+
γ4PbO·SiO2
2PbO·SiO2
+
γ4PbO·SiO2
100
0
10
20
30
PbO
SiO2→

be $2PbO \cdot SiO_2$. The X-ray and electron diffraction pattern of the crystallized lead-silicate glass shows that $PbO \cdot SiO_2$ and $2PbO \cdot SiO_2$ precipitate when the glass is crystallized upon heat treatment. Moreover, adding cerium oxide to the base glass increases the amplitude ratio of the low-temperature endothermic peak to the high-temperature one in the DTA curves. It should be noted that addition of cerium oxide is at the expense of the silica. Therefore one should expect that the eutectic content will increase as the $PbO \cdot SiO_2$ content decreases with increasing cerium oxide. This shift supports the suggestion that the low-temperature endothermic peak is due to local eutectic melting.

Transmission electron micrograph of Fig. 21A shows that glass-in-glass phase separation occurred during annealing of the lead-silicate glass containing no cerium oxide (LS_0). Heat treatment of this glass caused the precipitation of crystalline lead disilicate and lead metasilicate as shown in Figs. 21B and 21C. The precipitated compounds were detected by analyzing the electron diffraction pattern and were confirmed by X-ray diffraction line profiles given in Figs. (25, 26 and 27). It is believed that phase separation and crystallization occurred in this glass as a result of the incompatibility between different types of network-forming structural groups, namely the silica and lead oxide. This incompatability is a result of the difference between the charge of the principal network-forming ion (silicon) and that of the other ion (lead), which can either enter the network or assume a modifying position. This difference can lead to instability. Also, phase separation occurs in this system because the lead ion is highly polarizable, and the Pb-O distance is 2.3 $\mathring{A}$, much larger than the Si-O distance of 1.6 $\mathring{A}$.

Addition of 0.1 mole percent cerium oxide to the base glass did not affect the structure, but addition of 0.5 mole percent slightly increased glass-in-glass phase separation, as shown in Fig. 22. This effect can be explained on the following basis: In the silicate system, glasses containing a high proportion of PbO (up to 77 molecular percent) are possible. In such glasses a continuous network SiO_4 tetrahedra cannot be present. A portion of the lead-oxide goes into network-forming positions, and the rest fits into network-modifying positions. In the latter the lead ions provide large numbers of non-bridging oxygens between adjacent SiO_4 tetrahedra. Hence the structure will be loose. It appears that when cerium oxide is added in low concentration (0.1 mole percent), the cerium ions assume network-forming positions and reduce markedly the number of the nonbridging oxygens. This reduction probably tightens the structure, and increases slightly the stability of the system. For this reason the phase separation previously observed in the base glass did not change. On the other hand, when the cerium-oxide content was increased to 0.5 mole percent, the phase separation was slightly enhanced. This observation can be explained by the idea that when cerium-oxide content was increased, cerium ions assumed network-modifying positions because of the lack of nonbridging oxygen in the structure. The increase in the number of the modifying ions loosens the structure and causes instability. This idea is based on the fact that in the current investigation lead-silicate glass containing more than 0.5 mole percent Ce_2O_3 could not be prepared.

When the glasses containing cerium oxide were heated at 450°C for 2 and 12 hours, a lead-oxide-rich glassy phase separated out. This phase, owing to stronger electron absorption, appear as dark globules

in the electron micrographs of Figs. 23 and 24. Hence it is plausible that cerium ions always associate themselves with the lead ions, inasmuch as the voids created by the presence of lead ions in the network-forming position are large enough for the cerium ions to fit into.

Addition of cerium oxide to lead-silicate glass did not enhance phase separation in annealed glass, as shown in Fig. (22). Upon heat treatment, however, as can be seen in Figs. 21, 23 and 24, cerium-oxide addition does enhance phase separation. The phase separation observed in Fig. 24B, (0.5% CeO_2) is more significant than that observed in Fig. 23B (0.1% CeO_2) and in Fig. 21B (0.0% CeO_2). In this system, cerium ions tend to associate with the lead-oxide-rich region that is causing phase separation. The role of cerium ion in enhancing phase separation in lead-silicate glasses is similar to its role in lead-borate glasses.

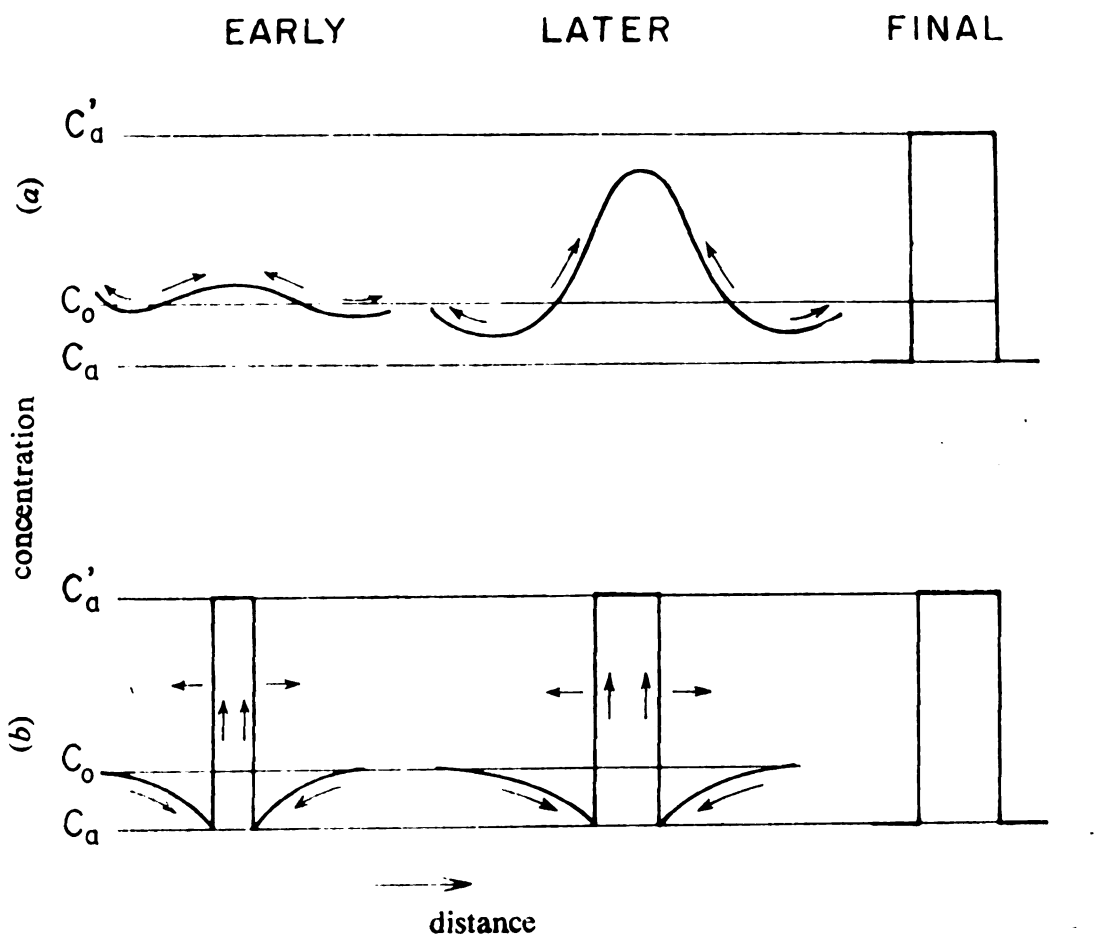
D. Crystallization of Cerium-Phosphate Glass

The DTA results for the cerium phosphate glass, as mentioned earlier, showed that when the glass is heated, more than one crystalline phase will precipitate out. The X-ray diffraction pattern of the heat-treated glass contained numerous sharp peaks (Fig. 40). Analysis of this diffraction pattern showed that ceric-oxide, cerium-phosphate, and phosphorus crystals precipitate out when the glass is heated at 815°C for 240 hours. A close examination of the DTA results seen in Fig. 28 reveals three endothermic reactions at 1050, 1122, and 1180°C. The DTA thus can yield the number of the compounds which will precipitate out when the glass is heat treated, and the X-ray diffraction can identify them.

In a two-phase system, separated particles increase indefinitely in size by growth and coalescence (until, theoretically, only one particle is left) in order to reduce the interface area. Cahn [37] considered a system with two species of atoms to explain the dynamics of initial clustering. He argued that if the preference for like members is small, then the clusters have no permanence. They form and disappear at random, and any concentration gradient that might be set up vanishes. The system then forms one phase. When the preference for like species is great enough that the flux of individuals is against the concentration gradient, a spontaneous separation into two phases occurs. The system is then within the spinodal shown in Fig. 41. The atoms sense the depleted zone and move away from it, building a new cluster a short distance away. This process leads to a rapid and simultaneous formation of extremely small clusters arranged approximately periodically in space. The concentration of the two phases varies continuously with time, a diffuse interface being present in the initial stages, and sharpens progressively as the separation proceeds (Fig. 44 A). To this mechanism Cahn [34] has given the name "spinodal decomposition." Between these two extremes -- when the attraction for like species is insufficient to cause a flux up the concentration gradient, but strong enough for a large supercritical cluster to retain the atom -- lies the classical case of nucleation and growth. In the vicinity of a growing particle the matrix concentration is reduced, and feeding of the particle occurs by normal diffusion down the concentration gradient (Fig. 44 B). This leads to particles randomly distributed in space, the interface being sharp from the beginning.

From the above argument, it is clear that spinodal decomposition

Fig. 44. Schematic evolution of concentration profiles to illustrate the differences between (a) spinodal decomposition and (b) the nucleation and growth mechanism (Cahn [40]).


EARLY
LATER
FINAL
(a)
C_a'
C_o
C_a
concentration
(b)
C_a'
C_o
C_a
distance

upon heat treatment at 700°C does not occur in the cerium-phosphate glass prepared during the course of this work. The essential characteristic of spinodal decomposition is the diffusion up the concentration gradient (uphill diffusion). It is quite obvious that depleted zone (light contrast) surrounds the separated spherical phases (dark contrast) as shown in Fig. 37. Thus phase separation in this system occurs through conventional nucleation by ceric-oxide nuclei which separates first as a crystalline phase (Fig. 30 and 31). The cerium-oxide-rich glassy phase finds a ceric-oxide nucleus to be a suitable zone to separate around, as shown in Figs. 31 to 35.

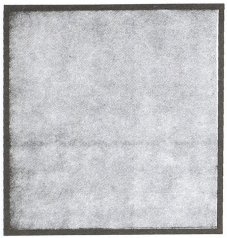
The cerium-phosphate glass contains both cerous and ceric ions. It is believed that the cerium ions enter the glass structure partially as network-modifying ions, and partially as network-forming ions. It appears that the cerous ions assume the forming positions, and the ceric ions fit in the modifying sites. This assignment is based on the observation that ceric-oxide crystals precipitated out in the early stages of heat treatment. McMillan [15] has shown that oxides of modifying ions separate out upon heat treatment of the glass. As mentioned before, ceric oxide crystallizes out in the early stages of heat treatment. Cerium-oxide-rich glassy phases separate around these crystals. This glass can be seen as dark spherical globules in the electron micrograph shown in Fig. (31). These globules are assumed to glassy phases because they shrink on further heating. This effect is illustrated in Fig. 35. Confirmation is provided in Fig. (36), the electron micrograph of cerium-phosphate glass heated at 700°C for 8 hours, compared with the micrograph of the same specimen after heating by the electron beam (Fig. 36 B). It is clear that the dark phase

shrank when beam-heated. The process of shrinking was observed under the microscope. After ceric oxide has crystallized out, further heat treatment precipitates phosphorus (orthorhombic). This surprising result was established by careful analysis of electron and X-ray diffraction patterns of glasses heat-treated for 18 hours at 700°C. Prolonged heat treatment for 36 hours at 700°C crystallizes $CePO_4$ (hexagonal) out of the system. This observation that the cerium occurs in the cerous form points out that ceric ions were present in the network-modifying positions and cerous ions were in the network-forming positions. The precipitation of phosphorus may be explained in the following way: ceric ions, while precipitating as CeO_2, acquired some of the oxygen ions present in the network. This process depletes oxygen from the network. As a result phosphorus, which is in excess of that required for forming $CePO_4$, precipitates out.

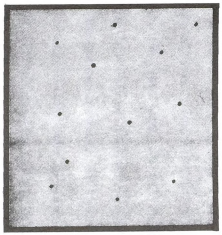
From the above results it is possible to propose a tentative model for nucleation and growth of crystals in cerium-phosphate glass of composition 79 mole percent phosphorus pentoxide and 21 mole percent cerium oxide when heated at 700°C for different periods of time. This model shown in Fig. (45), suggests that nucleation and growth of crystals progress in the following steps during heat-treatment:

1. Cerium oxide dispersed in the glass matrix precipitates first.
2. Cerium-oxide-rich glass phase separates around cerium-oxide nuclei on further heating.
3. The cerium-oxide-rich glass phase regions shrink in size, and the ceric-oxide crystals grow larger.
4. Further heating causes the precipitation of a phosphorus-rich

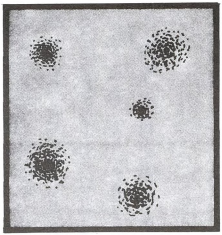
Fig. 45. Model for nucleation and growth of crystals in cerium phosphate glass of composition 79 mole % P_2O_5 - 21 mole % CeO_2.



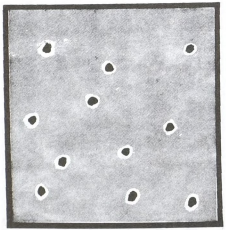
Glass



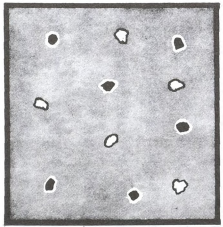
CeO_2 Separation



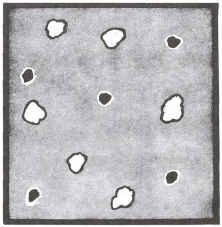
CeO_2 rich glass phase separation around CeO_2 particles



CeO_2 crystallization



Phosphorous rich glass separating from matrix



CeO_2 and phosphorous rich crystals in glass

phase together with the cerium crystalline phases.

E. Role of Cerium Oxide as a Nucleating Agent in Different Host Glasses

It is hard to generalize and propose wide-ranging theories to explain the process of phase separation, nucleation, and crystallization in glasses. In classical theory of crystallization of glass, the nucleating agent precipitates out as a crystalline phase and acts as a nucleus around which the glass phase crystallizes into stable compounds. McMillan [38] suggests, however, that glass-in-glass phase separation might be an essential step in the formation of a fine-grained microstructure. Tomozawa [39] recently reported that nucleating agents such as TiO_2 and ZrO_2 do not enhance phase separation in alkali-silicate glass, but rather may suppress it drastically. He also reported that low concentrations of P_2O_5 have no tendency to promote phase separation in alkali-silicate glasses. The present work suggests that the effect of the nucleating agent on the phase separation and crystallization depends strongly on the host-glass matrix and its composition.

In the three glass systems studies, cerium-phosphate, lead-silicate, and lead-borate, the crystallization mechanisms depended on the host-glass matrix. In case of cerium-phosphate glass, ceric-oxide crystals separate and act as nucleation sites as in classical nucleation. The large content of cerium oxide in this glass increases the concentration of the non-bridging oxygen. The loose structure is therefore in a highly unstable state. However, if the cerium-oxide content is decreased, the structure will be more stable. This reduction can be achieved by separating out the extra cerium oxide on

heat treatment. Lead-borate glass is phase-separated into two immiscible liquids, one rich in lead oxide and the other in boron oxide. Boric-oxide glass is built up of BO_3 triangles. On adding lead oxide to the glass, boron changes its coordination from 3 to 4, and the lead ions assume both network-modifying and network-forming positions. Most of the oxygen ions added to the system through lead-oxide addition serve first to four-coordinate the boron ions. The excess oxygen ions, if any, will break the network structure. In the current case the content of lead oxide is only 25.5 - 27.5 mole percent; therefore the concentration of the nonbridging oxygen ions is low. Addition of cerium oxide introduced more oxygen ions, increasing the concentration of the nonbridging oxygen ions and promoting the instability of the glass system. On heat treatment of such a glass two amorphous phases do separate. In lead-silicate glasses, the mechanism of phase separation and crystallization is similar to that of the lead-borate glasses. In this case, however, silicon is originally four-coordinated, and most of the oxygen ions introduced to the system by addition of lead oxide are used to break the silicon-oxygen-bonding. The concentration of the nonbridging oxygen is high owing to the large concentration of lead oxide in this system. This situation is highly unstable and any small driving force will promote glass-in-glass phase-separation.

In lead-borate glasses, addition of cerium oxide enhanced phase separation even in the annealed condition. In the lead-silicate glasses, however, the addition of cerium oxide did not show a significant effect on phase separation in the asannealed condition. This absence of effect can be attributed to the fact that phase separation

occurred in the lead-silicate glass composition used in the asannealed condition as a result of the instability of the structure. The role of cerium oxide in promoting this phase separation in the annealed lead-silicate glasses could not be detected in view of the already existing and pronounced phase-separation. However, during nucleating heat-treatment in both lead-borate and lead-silicate glasses, cerium-oxide additions enhanced phase separation and crystallization.

In lead-borate and lead-silicate glasses, although a lead-oxide-rich glassy phase separates, the first crystalline phase that forms is usually the major constituent that is present in the system. In the case of lead-borate glasses, boron-oxide crystals precipitated out on prolonged heat treatment. In the case of lead-silicate glasses, lead disilicate and lead metasilicate crystallized out. In cerium phosphate, however, P_2O_5 maintains the network structure until most of the ceric oxide is crystallized out.

The present investigation has shown that the role of cerium oxide, in promoting phase separation, nucleation and crystallization strongly depends on the host-glass matrix.

CHAPTER V

CONCLUSIONS

1. Cerium oxide enhances phase separation and crystallization in the lead-borate glass of the compositions studied. In mole percent they are 66 - 72.5 B_2O_3; 25.5 - 27.5 PbO; 0, 2, and 8.5 CeO_2.
2. Cerium oxide does not enhance phase separation in the lead-silicate glass in the annealed condition. However, the addition of cerium oxide enhances phase separation during the heat treatment in the nucleation-temperature range. In mole percent the composition studied are 29.2 - 30 SiO_2; 70 - 70.7 PbO; 0, 0.1 and 0.5 CeO_2.
3. A good-quality cerium-phosphate glass containing 21 mole percent cerium oxide can be prepared.
4. Progress of nucleation, phase separation, and crystallization of cerium-phosphate glass in the nucleating-temperature region consists of the following steps:

   a. In early stages of heat treatment, ceric-oxide crystals separate and act as nucleation sites as in classical nucleation.

   b. Cerium-oxide-rich glass phase separates from the matrix glass around the crystalline ceric-oxide particles.

   c. Ceric-oxide crystals grow by using cerium oxide present in

the glassy phase that surrounds them.

d. The rest of the matrix tends to crystallize phosphorus and cerium phosphate on prolonged heat treatment.

5. Cerium oxide is an effective nucleating agent in promoting phase separation and crystallization in lead-borate and lead-silicate glasses. In the cerium-phosphate glass containing both cerium and phosphorus, nucleation due to cerium is more effective than that due to phosphorus.

6. A fine-grained glass-ceramic, which is optically transparent, can be obtained by heat-treating the cerium-phosphate glass in the nucleating-temperature range.

7. Although differential thermal analysis is not in itself a complete means to explore the crystallization possibilities of glasses, it serves as a guide in the preparation of heat-treatment schedules. It gives information about the number of precipitating phases in glass when heated. The amplitude ratios of the peaks (and dips) give information about the relative amounts of the phases separating as seen in lead-silicate results.

8. The chemical jet-polishing technique developed by Washburn et al. [29] is suitable for preparing thin foils of glasses for transmission electron microscopy. Foils of hard glasses can be prepared by dipping in chemical-polishing solutions as described by McMillan [30]. Mechanical polishing serves to supplement the chemical-polishing technique for the preparation of thin foils of highly crystallized glass-ceramics, or to provide an alternative method.

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APPENDICES

APPENDIX A

Reproducibility of the Techniques for
Preparing the Glasses and the Thin Foils

a. Reproducibility for the Glass Preparation

The structure and the properties of a certain glass depend strongly on the method of preparation, the raw materials, the crucible material, and the thermal history (melting and annealing temperatures). Therefore, to check the reproducibility of the glass-preparation methods under the laboratory conditions specified in Chapter II, two batches of lead-borate glasses of the same composition containing cerium oxide were prepared under identical conditions. These batches had the same thermal history. Foils from both the glasses were prepared by the chemical jet-polishing technique. The electron micrographs of these glasses are shown in Fig. 46. The reproducibility of the preparation of this borate glass is evidenced by the similarity between the micrographs (Fig. 46).

Similar checks were carried out for the lead-silicate glasses containing cerium oxide. Specimens prepared from two different mother glasses of the same composition showed similar structures in the electron micrographic observations (Fig. 47).

Fig. 46. Transmission electron micrographs of lead borate glass containing cerium oxide obrained from different mothers of the same composition and thermal history.

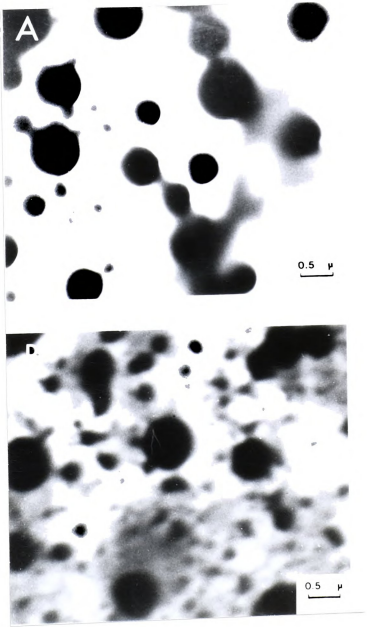
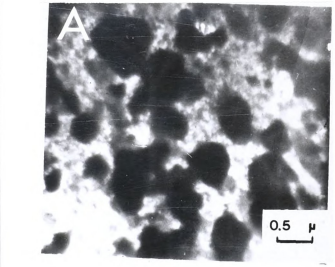
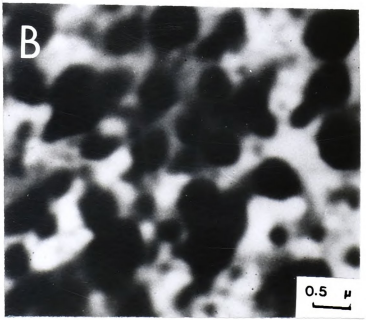

A
0.5 μ
B
0.5 μ

Fig. 47. Transmission electron micrographs of lead silicate glasses containing cerium oxide obtained from different mothers of the same composition and thermal history.


A
0.5 μ

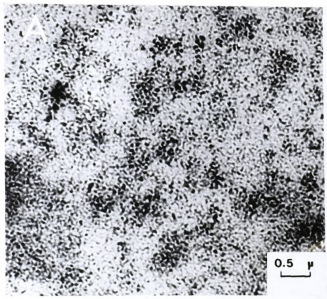

B
0.5 μ

b. Reproducibility for the Thin-foil Preparation

To check the reproducibility of the chemical jet-polishing technique, thin foils of two lead-borate glass samples obtained from the same mother glass were prepared by chemical jet-polishing. The similarity of the microstructures shown in Fig. 48 demonstrates the reproducibility of the chemical jet-polishing technique. The electron micrographs of two lead-silicate glass samples containing cerium oxide obtained from the same mother prepared by mechanical polishing are shown in Fig. 49. The similarity of the microstructures demonstrates the reproducibility of the mechanical-polishing technique.

The mechanical and the chemical thinning techniques were compared for two glass systems to show the equivalency of the methods. The electron micrographs of two lead-silicate glass foils containing 0.1 mole percent cerium oxide obtained from the same mother glass are shown in Fig. 50 for specimens by chemical and mechanical polishing techniques. There is no obvious difference between these two micrographs. Similar results are found for cerium-phosphate foils from the same mother glass prepared by chemical thinning and by mechanical thinning. The equivalence of the chemical jet-polishing and the mechanical polishing techniques for preparation of thin glass foils is demonstrated by these observations.

Fig. 48. Transmission electron micrographs of two lead borate glasses obtained from the same mother glass. Thin foil was prepared by chemical jet-polishing method.


A
0.5 μ

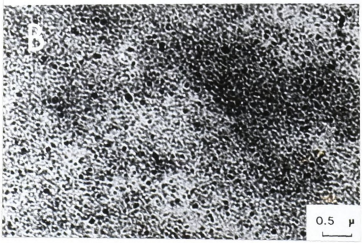

B
0.5 μ

Fig. 49. Transmission electron micrographs of two lead silicate glasses containing cerium oxide obtained from the same mother glass.
Thin foil was prepared by mechanical polishing.

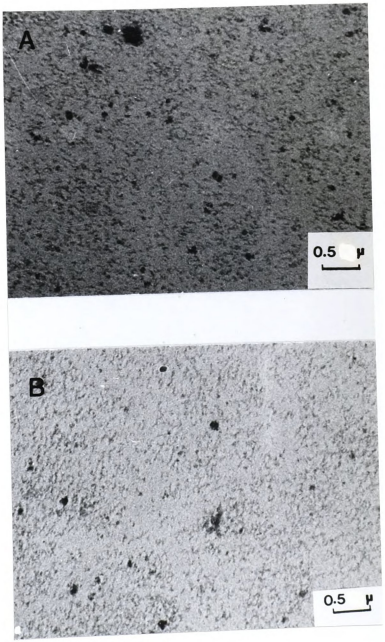

A
0.5 μ
B
0.5 μ

Fig. 50. Transmission electron micrographs of two lead silicate glasses containing 0.1 mole percent cerium oxide obtained from the same mother glass prepared by:

A: Chemical polishing

B: Mechanical polishing.


A
0.5 μ


B
0.5 μ

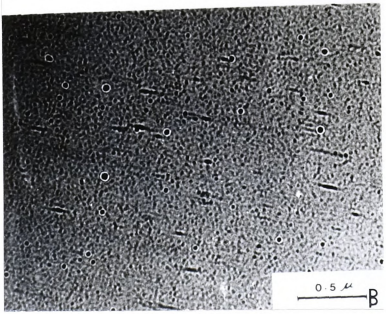
Fig. 51. Transmission electron micrographs of foils of cerium phosphate glasses obtained from the same mother glass and prepared by:

A: Chemical polishing

B: Mechanical Polishing.

These glasses have been heat-treated at 700°C for 18 hours.


0.5 μ
A


0.5 μ
B

APPENDIX B

Electron-Beam Heating

The phase separation and crystallization of glasses can be followed with the electron microscope by heating the thin foils with a concentrated electron beam. Two electron micrographs of cerium-phosphate glass directly heated by concentrated electron beam for different lengths of time are shown in Fig. 52. Glass-in-glass phase separation is observed in the microstructure of the thin foil heated for two minutes with the beam as shown in Fig. 52(A). The absence of sharp diffraction lines indicated that the phase-separated regions were amorphous. When the glass foil was heated for ten minutes, however, crystallization did take place as shown in Fig. 52(B) by the presence of the sharp lines.

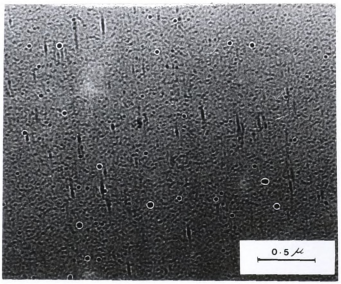
Beam heating of thin glass foils in the electron microscope provides a method for observing the progress of phase separation and crystallization of the glasses. The features observed in the beam heated foils of cerium-phosphate glass are similar to those in the thin foils prepared from heat-treated specimens. In localized beam heating, the temperataure of heat treatment cannot be readily measured, since only a very small portion of the specimen is heated. Much clearer understanding of the progress of phase separation and crystallization in this glass, as a function of heat-treatment

Fig. 52. Transmission electron micrographs of cerium phosphate glass heated by the electron beam for different lengths of time.

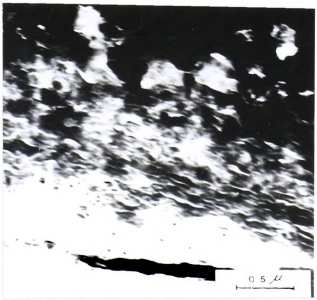
A: 2 minutes

B: 10 minutes

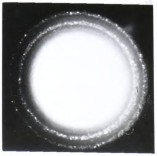
Diffraction pattern belongs to the selected area shown in B.



A



B



temperature, can be obtained by controlled experimentation with an electron microscope fitted with specimen-heating facilities.

APPENDIX C

Commercial Borosilicate Glass

The chemical jet-polishing technique was developed with commercial borosilicate glass of the molecular percentage composition 7 B_2O_3 - 92.5 SiO_2 - 0.5 PbO, obtained from "Curtin Scientific Company." This glass was chosen because it is available in the same size, thickness, and shape, as the specimens to be studied and is optically polished.

A DTA record for this glass during heating from room temperature is given in Fig. (53). The shallow dip occurring over the temperature range 530 to 560°C is associated with annealing of the glass. A very weak broad exothermic peak is observed at about 730°C. This peak is perhaps due to the crystallization of quartz (of McMillan et al [30]).

The transmission electron micrographs of Fig. (54) are those of borosilicate glass heated at 600°C for 0, 18, 44, 72 and 318 hours. The micrographs of the same glass heated at 650°C for 2, 15 and 24 hours are presented in Fig. (55). On heating commercial borosilicate glass at 600°C for 18 and 44 hours, phase separation developed (Fig. 54). On further heating for a total of 72 hours, the glass developed a high density of secondary phase-separated regions, their average size increasing and their concentration decreasing with time. These secondary

Fig. 53. Differential thermal analysis curve for commerical borosilicate glass.

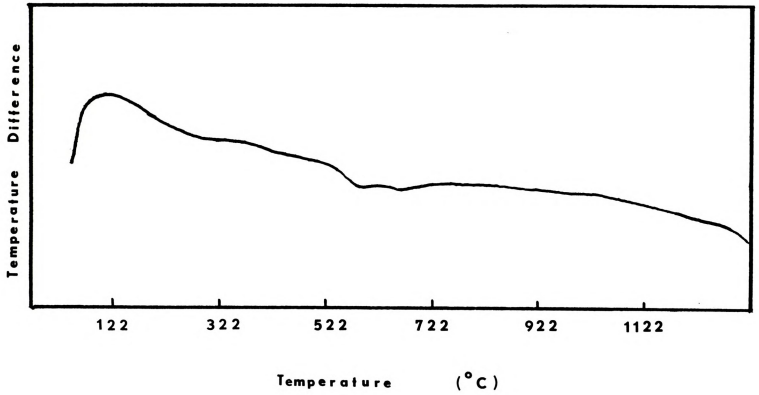

Temperature Difference
122
322
522
722
922
1122
Temperature (°C)

Fig. 54. Transmission electron micrographs of commercial borosilicate glass.

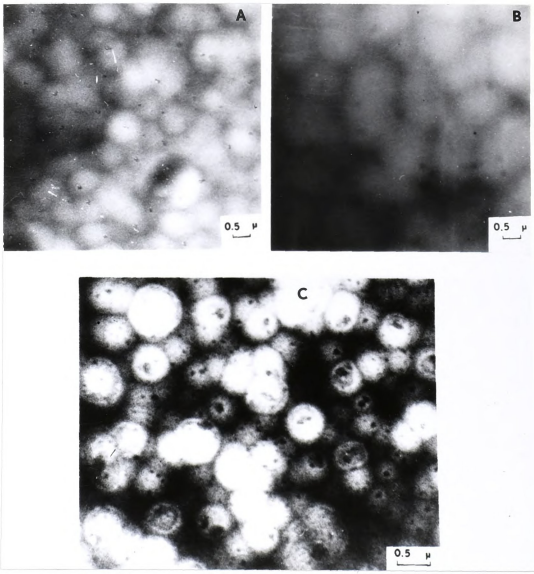
A: As annealed.

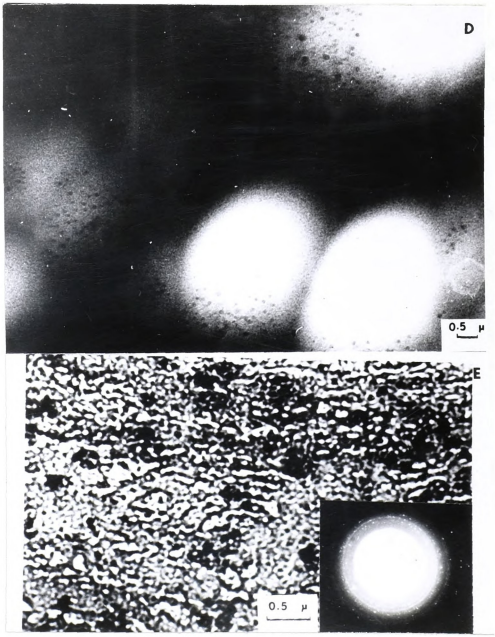
B: Heat treated at 600°C for 18 hours.

C: Heat treated at 600°C for 44 hours.

D: Heat treated at 600°C for 72 hours.

E: Heat treated at 600°C for 318 hours.


A
0.5 μ
B
0.5 μ
C
0.5 μ


D
0.5 μ
E
0.5 μ

phase-separated regions appear as dark globules in the light regions which have separated. These processes were the precursors to crystal nucleation and growth. Crystallization of this glass was observed in a specimen heat-treated for 318 hours at 600°C (as shown in Fig. 54(E)), whereas crystallization was observed in specimens heat-treated for 24 hours at 650°C as shown in Fig. 55(C). The crystallization at both heat-treatment was verified by selected-area electron-diffraction technique. This slide glass is transparent even after crystallization.

The glass was heated at two different temperatures for different lengths of time. In both cases, the micrographs showed that glass-in-glass phase separation preceeded crystallization. Secondary phase separation was observed in the glass samples heated at 600°C. When the glass was heated at 650°C the secondary phase separation was not so pronounced. In these electron micrographs the two separating phases have different contrast. The light area is assumed to be due to boron-oxide-rich phase, and the dark region is believed to be associated with silica-rich phase.

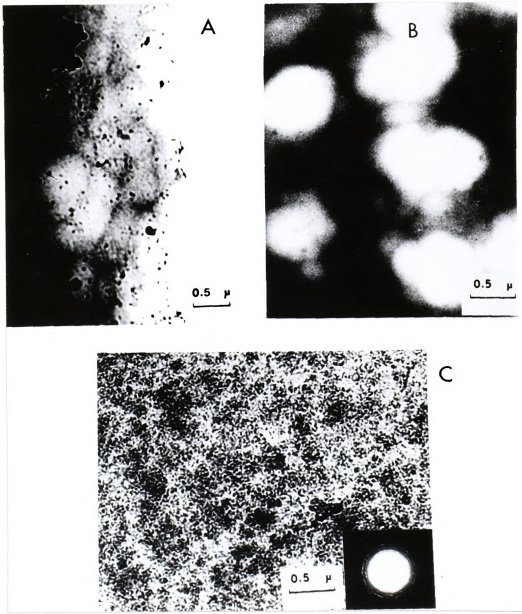
Although this borosilicate glass did not show a pronounced peak in the DTA curve, it did crystallize to a transparent glass-ceramic on heat-treating at 600°C for 318 hours and at 650°C for 24 hours. This suggests that in this system, controlled phase separation and nucleation can be achieved by heating the glass at 600°C. Faster crystallication, however, can be achieved by heating the glass at 650°C.

Fig. 55. Transmission electron micrographs of commercial borosilicate glass.

A: Heat treated at 650°C for 2 hours.

B: Heat treated at 650°C for 15 hours.

C: Heat treated at 650°C for 24 hours.


A
0.5 μ
B
0.5 μ
C
0.5 μ