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A REVIEW OF PHASE SEPARATION IN BOROSILICATE GLASSES, WITH REFERENCE TO NUCLEAR FUEL WASTE IMMOBILIZATION

EXAMEN DE LA SÉPARATION DES PHASES DANS LES VERRES AUX BOROSILICATE QUANT À L'IMMOBILISATION DES DÉCHETS DE COMBUSTIBLE NUCLÉAIRE

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RÉSUMÉ

Dans ce rapport, on examine les renseignements sur les limites de miscibi-
lité des systèmes de formation des verres au borosilicate. Il comprend une
étude bibliographique ainsi qu'un compte rendu des travaux expérimentaux
exécutés dans le cadre du Programme Canadien de Gestion des Déchets de
Combustible Nucléaire. On y met en relief la mesure et description des
limites de miscibilité des systèmes (principalement quaternaires) à plu-
sieurs éléments et les effets des éléments individuels sur la manifestation
de la séparation des phases. Le comportement du système à plusieurs élé-
ments est lié à celui des systèmes (binaires et ternaires) plus simples.
On y examine également la manifestation possible de la séparation des
phases ainsi que sa suppression au cours du traitement des verres d'immobi-
lisation des déchets nucléaires.

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ABSTRACT

This report reviews information on miscibility limits in borosilicate
glass-forming systems. It includes both a literature survey and an account
of experimental work performed within the Canadian Nuclear Fuel Waste
Management Program. Emphasis is placed on the measurement and depiction of
miscibility limits in multicomponent (mainly quaternary) systems, and the
effects of individual components on the occurrence of phase separation.
The behaviour of the multicomponent system is related to that of simpler
(binary and ternary) glass systems. The possible occurrence of phase
separation, as well as its avoidance, during processing of nuclear waste
glasses is discussed.

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<u>CONTENTS</u>

1. INTRODUCTION

Amorphous phase separation occurs commonly in silicate and borosilicate glass-forming systems, including those with industrially important compositions. The phenomenon is also known as liquid immiscibility, unmixing, or (especially in the Soviet literature) liquation. Since it can profoundly affect glass properties, in particular durability towards dissolution in aqueous media, this phenomenon has been widely studied. A monograph edited by Mazurin and Porai-Koshits (1984) gives a comprehensive account of both scientific and technological aspects of phase separation. In addition, review articles have been published by Craievich et al. (1983), Charles (1973), James (1975), Pye (1977), Tomozawa (1979), Uhlmann and Kolbeck (1976) and Vogel (1977). More recent research activities have been reviewed by Tomozawa (1989). A very recent review by Jiang (1989) includes a useful tabulation of important events in the history of research into phase separation in glasses.

The purpose of this report is to review research on phase separation within the Canadian Nuclear Fuel Waste Management Program (CNFWMP), both in a scientific context and with reference to the possible occurrence of phase separation during processing of borosilicate glasses containing nuclear fuel recycle wastes. Borosilicate glasses have been investigated in many countries as waste forms for high-level radioactive wastes arising from nuclear fuel recycling, and full-scale vitrification plants are operating or under construction in France, Germany, the U.K., the U.S.A., India and Japan (Lutze 1988). It is therefore likely that borosilicate glasses would be used to immobilize wastes from possible future CANDU fuel recycle programs.

In this report emphasis is placed on depicting regions of immiscibility within multicomponent systems, and classifying the effects of various glass-modifying components, rather than on more profound theoretical aspects. Many hundreds of research papers have been written on phase separation in glasses. The literature cited here is representative of work published up to 1989, but it is far from being a comprehensive list.

2. DEFINITIONS AND EXPERIMENTAL PRINCIPLES

2.1 GENERAL DESCRIPTION OF THE PHENOMENON

The occurrence of phase separation is confined within a region of composition and temperature in the phase diagram known as the miscibility gap. In nearly all glass-forming melts, the composition range of the miscibility gap diminishes with increasing temperature. The temperature at which it disappears, i.e., above which all liquid compositions are homogeneous, is known as the consolute temperature, T_c. It is also possible for phase-separating liquid systems to have a lower consolute point, above which phase separation occurs but below which only one liquid occurs (Campbell and Smith 1951, Francis 1963). The classic example of this type of

behaviour is the nicotine-water system; the only glass-forming system in which it appears to occur is $Tl_2O-B_2O_3$ (Bouaziz and Touboul 1967, Mazurin and Porai-Koshits 1984).

The temperature below which any given composition becomes immiscible is called the critical miscibility temperature, T_b. The locus of T_b is known as the binodal; it is a curve (roughly an inverted parabola) in binary systems, and an n-dimensional surface in n-component systems at constant pressure. The form of the binodal in glass-forming oxide systems is discussed at length by Mazurin and Porai-Koshits (1984). Within the miscibility gap, tie lines connect coexisting compositions lying on the binodal. The experimental determination of miscibility limits and tie lines in glass-forming systems is discussed at the end of this section.

Phase separation is sometimes a stable phenomenon in the melt, e.g., in most of the alkaline-earth borate, silicate and borosilicate systems. In many technically important glasses, however, it is a metastable subliquidus process, i.e., T_b lies between the liquidus temperature, T_L, and the glass transition temperature, T_g.[*] In systems displaying stable immiscibility, there is normally a metastable extension of the miscibility gap below the liquidus. These concepts are illustrated in Figure 1.

In systems of n components, separation into as many as n liquids is theoretically possible at a given temperature and pressure (Campbell and Smith 1951, Francis 1963), but no more than two liquids have been demonstrated to occur in the systems discussed here. The possibility that a three-liquid region occurs in the sodium borosilicate system was discussed by Haller et al. (1970), but their proposal was not supported by other studies (Mazurin and Streltsina 1972, Srinivasan et al. 1971). Very recently, however, new evidence of three-liquid phase separation in this system has been reported (Fan and Chen 1989).

A phenomenon distinct from multi-liquid immiscibility is multiple phase separation promoted by changes in the boundaries of the miscibility gap with changing temperature (Porai-Koshits and Aver'yanov 1969). This may result in initial phase separation at one temperature, and subsequent further segregation of one or both of the initial phases at lower temperatures as the boundaries of the miscibility gap expand. This has been most

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[*]   The glass transition is a fairly sharp second-order phase transition below which a glass exhibits solid-like physical properties (e.g., thermal expansivitiy, heat capacity, electrical conductivity), and above which these properties have liquid-like values. There is no associated change in viscosity-temperature relationships, but the glass transition normally occurs at a viscosity of about 10^{12} Pa•s. Below the glass transition, the molecular structure of the glass is commonly considered to be "frozen"; it is thus a practical limit below which phase separation is not normally detected. The glass transition lies near the annealing point ($\eta = 10^{12.4}$ Pa•s). For a fuller discussion see Doremus (1973).
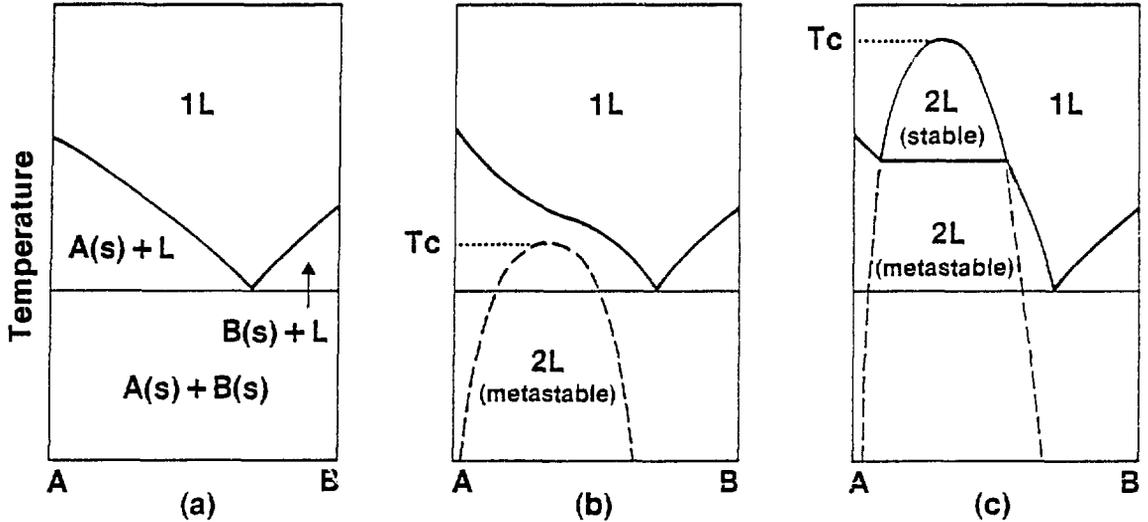
FIGURE 1: Schematic Phase Diagrams Illustrating Concepts of Liquid Immiscibility in a Binary System, A-B. (a) Simple eutectic with no immiscibility. (b) Like (a), but with a region of metastable immiscibility, bounded by dashed line, with consolute temperature T_c. The dashed line is the locus of T_b. Note the inflection in the liquidus curve, which is often an indicator of subliquidus immiscibility. (c) Like (a) and (b), but with a region of stable immiscibility extending above the horizontal portion of the liquidus. Dashed lines delineate the metastable extension of the miscibility gap. Note that only those portions of the metastable miscibility gap lying above the glass transition are experimentally accessible.

elegantly demonstrated for barium borosilicate glasses by Vogel (1977), and for complex titanosilicate glasses by Hayward et al. (1989). It has also been observed in a number of other systems, as discussed by Mazurin and Porai-Koshits (1984). Its occurrence in the $Na_2O-ZnO-B_2O_3-SiO_2$ system was discussed by Taylor and Owen (1981b).

Strictly speaking, phase separation of glasses, as opposed to supercooled melts (i.e., below T_g), may be thermodynamically possible, but is normally too slow to observe. Rather, the process of phase separation normally occurs in a liquid (either stable or supercooled), and a phase-separated glass is the product of cooling a phase-separated liquid. It is convenient, however, to speak of phase separation of a glass when comparing the properties of homogeneous and phase-separated glass samples of the same bulk composition.

The scale of phase domains within a phase-separated glass depends largely on the thermal history of the glass and the relationship between temperature and viscosity. The higher the viscosity, the slower is the rate of phase growth. Note, however, that the viscosity itself may also be strongly influenced by the onset of phase separation, as discussed by Tomozawa (1979). The influence of phase separation on physical properties is discussed in some detail by Shelby (1982, 1983), as well as the reviewers cited in the introduction.

Stable phase separation normally produces macroscopic domains, i.e., layers or droplets visible to the unaided eye. Subliquidus phase separation commonly produces phase domains in the 0.1- to 5-μm size range. On this scale, phase separation is usually detectable by visible opalescence in the glass, and is amenable to detailed microstructural study by scanning and/or transmission electron microscopy. Ultrafine phase separation, on a scale of nanometres, is often unavoidable even when a homogeneous melt is rapidly quenched through a subliquidus miscibility gap to temperatures below T_q. On this scale, phase separation is best detected by small-angle X-ray scattering (Mazurin and Porai-Koshits 1984, and references therein; Golubkov et al. 1977, Vasilevskaya et al. 1980), and its presence can sometimes be inferred from spectroscopic measurements (McMillan 1984a, 1984b, Ménassa et al. 1985b, White 1982). Although such heterogeneity on or near a molecular scale may affect the dissolution mechanism of a glass, our principal concern in this report is the more clearly defined phenomenon of phase separation on either a microscopic (> 100 nm) or a macroscopic scale.

2.2   DETECTION AND MEASUREMENT OF MISCIBILITY LIMITS

The visible opalescence in most phase-separated glasses is commonly used to plot the limits of miscibility on phase diagrams. A typical phase-separated glass appears bluish to milky white in reflected light, and reddish in transmitted light. If a glass changes from transparent to uniformly opalescent after heating at a given temperature, T_h, for duration t, this indicates that $T_h < T_b$. A series of heat treatments on selected glass compositions can thus be used to map T_b-composition relationships. Care is needed to assure that the opalescence is indeed caused by amorphous phase separation, rather than crystallization; this can be checked by a combination of electron microscopy (see below) and X-ray diffraction (Baylor and Brown 1976, Taylor and Owen 1981b, Zarzycki and Naudin 1971). Also, crystallization is often patchy or localized on the specimen surface.

If the refractive indices of the two phases are very similar, a glass may remain transparent after phase separation (Shartsis et al. 1958), but this situation is uncommon (e.g., Johnson and Hummel 1968). If suspected, it can be checked by electron microscopy. Much more common is the situation where the duration of heat treatment, t, is too short to allow sufficient development of phase separation for visible opalescence to occur. As a broad guide-line, heat-treatment times of less than 1 h are adequate for glasses with viscosities of 10^7 to 10^8 Pa·s (Mazurin and Porai-Koshits 1984). Typical values of t for borosilicate glasses of the types discussed

in this review are ~ 15 min near 900°C, 1 h near 800°C, and 16 h at 650 to
700°C. Heating times of many days often become necessary below 650°C, and
even then results may be inconclusive. For high-silica glasses, viscosi-
ties are high and heating times are correspondingly long. Other diffi-
culties in determining miscibility limits of high-silica glass composition
are discussed by Johnson and Hummel (1968). At high T_h values (above about
800°C for multicomponent borosilicates), care is also needed to distinguish
primary and secondary phase separation; rapid quenching and frequent
checking by microscopy are recommended.

Liquid immiscibility is a reversible phenomenon. A phase-separated glass
should become transparent again after heating for sufficient time at
$T_h > T_b$. In practice, this clearing phenomenon is often difficult to
observe because of crystallization. Some glasses, however, are amenable to
detailed study of the phase separation process close to the critical misci-
bility temperature (Johnson and Hummel 1968, Srinivasan et al. 1971, 1976).
The disappearance of opalescence in sodium borosilicate glasses at $T_h > T_b$
is discussed in detail by Alekseeva et al. (1977). For a detailed treat-
ment of light-scattering by phase-separated glasses, see Hammel and Ohlberg
(1965) and Andreev (1978).

As studies progress from binary through ternary to multicomponent systems,
detailed mapping of miscibility gaps requires the preparation and study of
rapidly increasing numbers of glass compositions. This often constrains
research to narrow ranges of composition. Predictive methods, coupled with
limited numbers of experiments, have been used successfully to delineate
miscibility gaps in a number of multicomponent silicate systems, as dis-
cussed in Section 5 (Kawamoto and Tomozawa 1981a, 1981b, 1981c; Kawamoto
1985). This approach depends in part on the fact that, theoretically, one
phase is pure silica at absolute zero temperature. The method has not yet
been extended to include borosilicate systems, where the situation is com-
plicated by B_2O_3 in the silica-rich phase, although it appears to have been
used successsfully to describe a complex situation in the $Li_2O-Al_2O_3-SiO_2$
system (Kawamoto 1985).

Electron microscopy has found widespread use in the detection and study of
phase separation, and is reviewed extensively in Mazurin and Porai-Koshits
(1984) and elsewhere. Many early transmission electron microscopy (TEM)
studies of heterogeneity in glasses were plagued by artifacts of sample
preparation, especially in purported cases of segregation on a 10- to
100-nm scale (Mazurin and Porai-Koshits 1984). Nonetheless TEM techniques,
especially replication methods coupled with controlled etching, have
yielded much information on glass microstructure. Good examples include
the detailed studies by Moriya et al. (1967), Burnett and Douglas (1970),
Baron and Wey (1973) and several papers in the volume edited by Porai-
Koshits (1969). An interlaboratory comparison of direct and replica TEM
techniques for examining phase-separated glasses has been reported by Sakka
(1983).

Scanning electron microscopy (SEM) was first applied to phase-separated
glasses by Makishima and Sakaino (1970) and Elmer et al. (1970). This
technique has lower resolution than TEM, making segregation on a scale

below 0.1 μm difficult to detect. Its principal advantage lies in ease of
sample preparation. This usually consists of freshly fracturing a speci-
men, then lightly etching the fracture surface with water or dilute acid to
induce surface relief by differential etching of the two phases, and final-
ly mounting the sample and applying a thin conductive coating of gold or
carbon. The use of SEM to distinguish between primary and secondary phase
separation is described succinctly by Clemens et al. (1981). Other
examples of detailed SEM studies include Baylor and Brown (1976), Taylor
and Owen (1981b), Taylor et al. (1983b), and Hayward et al. (1989).

In a binary system, determination of the binodal curve that bounds the
miscibility gap defines coexisting compositions as well as miscibility
limits. In ternary and more complex systems, however, the added composi-
tional degrees of freedom mean that tie lines as well as miscibility limits
must be determined to fully define the phase relationships. Furthermore,
as discussed in Section 6, tie-line orientation is free to change with
varying temperature in such systems.

In systems that separate cleanly into layers in the melt, tie lines can be
determined directly by chemical analysis, but this is not normally possible
with extremely viscous glass-forming melts. Partial segregation allows
tie-line orientations (but not coexisting compositions) to be determined;
an early example is given by Morey and Ingerson (1937). If separated
domains are too small for conventional chemical analysis, but exceed a few
micrometres, they are amenable to electron-beam microanalysis (Scholes and
Wilkinson 1970, Scholes 1973). This technique is especially useful for
studying partition of minor components (> 1 mol%) between the phases,
although quantitative data are difficult to obtain (Ehrt et al. 1977,
Taylor and Owen 1980, Ménassa et al. 1985a, Vogel 1977). Microanalysis of
glasses using scanning transmission electron microscopy allows improved
spatial resolution (~ 10 nm) over SEM and other electron-beam techniques
(Bando et al. 1980, 1981).

Phase compositions can be deduced from leaching studies, in which leachate
compositions are dominated by the less durable phase. Difficulties with
this approach arise from partial dissolution of the more durable phase and
reprecipitation of silica, as summarized by Mazurin and Streltsina (1972)
and in Mazurin and Porai-Koshits (1984). The silica precipitation also has
a profound effect on the properties of porous glasses (Mazurin and Porai-
Koshits 1984). Glass-transition temperature measurements have been used
successfully to deduce tie-line orientations in the sodium borosilicate
system (Mazurin and Streltsina 1972); this approach has been assessed
further by Mazurin and Roskova (1982). A variety of other physicochemical
approaches to tie-line determination are reviewed in Mazurin and Porai-
Koshits (1984).

3. PHASE SEPARATION IN BOROSILICATES

When a borosilicate glass undergoes phase separation, it usually forms one
phase rich in silica and a second one enriched in most of the other compo-
nents. The latter is usually much more easily dissolved in aqueous media

than either the silica-rich phase or the homogeneous glass. The proportions of the two phases are determined (using the lever rule) by the position of the glass composition on a tie line within the miscibility gap, possibly modified by kinetic factors or secondary phase-separation during cooling. Depending on these proportions, a phase-separated glass may have either a continuous network or dispersed droplet microstructure. Tomozawa (1979) recognized three microstructural types (A, B, and C), subdividing the droplet type according to whether the dispersed phase is more or less durable towards aqueous dissolution than the matrix:

A. In Type A both phases have interconnected, continuous structures. This commonly occurs when the volume fractions of the two phases lie between about 0.25 and 0.75.

B. In Type B the more durable phase is dispersed as discrete particles in a continuous matrix of the less durable phase. This is usually, but not exclusively, observed when the latter exceeds about 0.75 volume fraction (Mazurin and Porai-Koshits 1984).

C. In the Type C microstructure the less durable phase is dispersed in a continuous matrix of the more durable phase, i.e., the converse of Type B.

Scanning electron micrographs illustrating these three types of microstructure, and other features discussed above, are presented in Figure 2.

The durability of a glass towards aqueous corrosion usually deteriorates upon separation to a Type A or B microstructure, because the less durable phase is continuous in both cases; whereas formation of a Type C microstructure often has little effect on durability (Tomozawa and Takamori 1977, Tomozawa 1979). With some compositions, however, phase separation can markedly improve durability because dissolution of the more durable (matrix) phase is now rate-controlling (Danilova et al. 1972, Taylor et al. 1987). Variation of microstructure with composition in sodium borosilicate glasses has been discussed at some length by Baron and Wey (1973) and Taylor et al. (1983b), and many other papers include microstructural information. In addition to the sources cited above, basic studies of the effects of phase separation on aqueous dissolution include publications by Howell et al. (1975), Makishima et al. (1979), Tomozawa and Takamori (1977) and Tomozawa et al. (1980).

Microstructures of Type A have received most attention because these have the greatest technical importance. Type A microstructures are also of theoretical interest because they sometimes arise from a spinodal mechanism of phase separation (see Andreev 1978, Cahn and Charles 1965, Cook 1970, Hammel 1965, Haskell 1973, and the reviews cited in Section 1).

Spinodal phase separation is a process of progressive development of compositional fluctuations, rather than nucleation and growth of a distinct phase. It is theoretically possible in a situation where the second derivative of the Gibbs energy of mixing of a system, with respect to composition, is negative. In contradistinction, the boundaries of phase
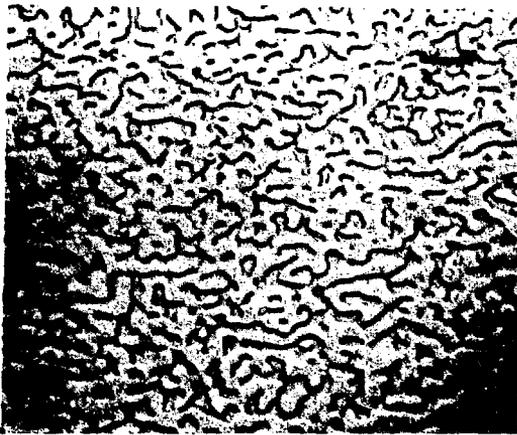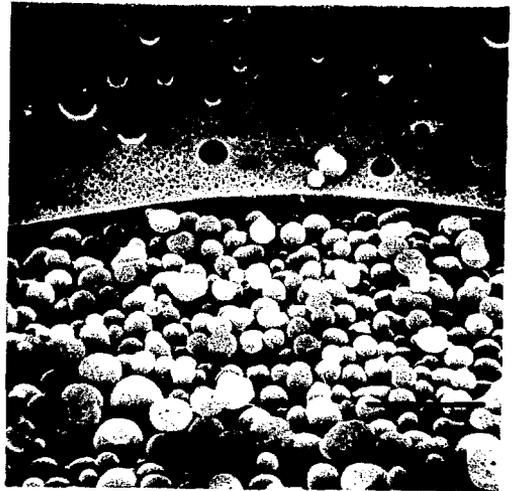
(a)

(b)

(c)

(d)

FIGURE 2: Examples of Scanning Electron Micrographs Showing the Micro-
structure of Phase-Separated Borosilicate Glasses, from Taylor
et al. (1987) and Taylor and Owen (1981b). (a) Typical Type A
interconnected microstructure. Composition (mol%)
$5.5Na_2O \cdot 31.5B_2O_3 \cdot 63SiO_2$, heated at 660°C for 16 h, fractured and
etched with water. Bar = 1 μm. (b) Type C microstructure,
$3.5Na_2O \cdot 32B_2O_3 \cdot 64.5SiO_2$, heated at 660°C for 16 h, fractured,
and etched with water. Bar = 2 μm. (c) Stable immiscibility
(light and dark regions; dark circles are gas bubbles) in a
glass of composition $2Na_2O \cdot 14ZnO \cdot 16.5B_2O_3 \cdot 67.5SiO_2$, air-quenched
from 1300°C melt, fractured, and etched with 2% HF. Bar = 100μm.
(d) Enlargement of a portion of (c), showing secondary phase
separation that occurred in both primary phases during quench-
ing. Upper area shows Type C droplet microstructure in silica-
rich matrix; lower area shows larger Type B droplet microstruc-
ture in Zn/B-rich phase. Bar = 5 μm.

separation are defined by the intersection of the common tangent to two minima or inflections in the Gibbs energy surface (Pye 1977). The spinodal region is thus a restricted region within the whole miscibility gap, as discussed in the references cited above. Spinodal phase-separation is usually associated with a Type A microstructure. The converse is not true, however, and other formation and growth processes can give rise to highly interconnected microstructures (Uhlmann and Kolbeck 1976).

Leaching a glass with Type A microstructure, usually done with dilute acid, removes the more soluble alkali- and/or boron-rich phase, leaving behind a microporous, high-silica material. The pore size distribution can be controlled by variation of the time and temperature of heat treatment in the phase-separation step prior to leaching, and by variation of the leaching process itself. The porous glass may be useful as it stands, or it can be converted by appropriate heating to a consolidated high-silica glass (Vycor) whose direct formation by conventional melting would require extremely high processing temperatures. This process was patented by Hood and Nordberg in 1938. Various actual and potential uses of phase-separated glasses are discussed by Mazurin and Porai-Koshits (1984).

4. RELEVANCE TO NUCLEAR WASTE GLASSES

Porous glasses have been considered as precursors to a Vycor-like "stuffed glass" material for immobilizing high-level radioactive waste (Macedo et al. 1979, Simmons et al. 1979). To manufacture this material, it is proposed that radioactive wastes would first be loaded into a porous glass by soaking the glass in a waste solution. After washing the outermost layer, the glass would then be dried by slowly heating to about 700°C, then consolidated (as in the Vycor process) by further heating at 900°C, thereby encapsulating the waste in a high-silica glass matrix. This concept is basically sound, and preliminary results are promising, but further development and evaluation remains to be done, as discussed by Ewing (1988).

Although phase separation may thus be a useful phenomenon in nuclear fuel waste immobilization, the main concern in the CNFWMP is that it may reduce the durability of borosilicate waste glasses towards leaching and dissolution in groundwater. This concern is heightened by the fact that most metal oxides, and hence most fission products, tend to partition into the more soluble, (alkali + boron)-rich phase (Ehrt et al. 1977, Ménassa et al. 1985a, Taylor and Owen 1980, Taylor et al. 1986). It is therefore a phenomenon to avoid, if possible, by appropriate choice of glass composition (Uhlmann 1977, Engell and Roed 1982). A comprehensive review of waste glass properties, including a discussion of phase separation and emphasizing the importance of controlling composition to avoid it, was published recently by Lutze (1988).

Engell and Roed (1982) have investigated the occurrence of phase separation in glasses related to two compositions (ABS-39 and ABS-41) that were being considered for immobilization of Swedish nuclear fuel waste. Like most nuclear waste glasses, these are sodium borosilicate compositions modified

by a large number of additional oxide components. These include univalent and divalent metal oxides introduced to adjust the glass melting properties, as well as fission-product oxides and other waste components arising from corrosion and chemical treatments in the recycle plant. In most simulated waste glasses, compositions are simplified to avoid the use of expensive (e.g., platinum metals) or radioactive components (e.g., technetium, promethium, and some of the actinides).

Engell and Roed (1982) demonstrated that both the ABS-39 and ABS-41 compositions lie outside the miscibility gap at 600°C, and so are not expected to phase-separate during glass processing. The ABS-41 composition lies closer to the immiscibility boundary than ABS-39, because of partial substitution of Li_2O for Na_2O and ZnO for Al_2O_3 and Fe_2O_3 (see below). Addition of up to 20 wt.% of simulated fission products caused a slight contraction of the miscibility gap (i.e., a reduced tendency to phase-separate) for ABS-41, and a more pronounced contraction for ABS-39.

The main approach to experimental work on phase separation in the CNFWMP has been to determine systematically the influence of individual oxide additives or substituents on the behaviour of sodium borosilicate glasses (Ménassa et al. 1985a, 1985b; Taylor and Owen 1980, 1981a, 1981b; Taylor et al. 1983a, 1983b, 1984, 1986). Our work thus complements the more pragmatic approach of Engell and Roed (1982). When this work commenced, miscibility-gap measurements had already been published for many binary and ternary silicate systems, and provided a vital basis for understanding the behaviour of multicomponent systems.

5. BACKGROUND ON BINARY AND TERNARY BORATE AND SILICATE SYSTEMS

Perhaps the earliest observation of immiscibility in glass-forming systems was by Guertler (1904), who reported its occurrence in divalent metal borate systems. Liquid immiscibility in a variety of binary and ternary silicate melts was reported by Greig (1927), although it had previously been inferred by petrologists to be an important process in the formation of certain igneous rocks. Greig showed that many systems of the Type MO-SiO_2 have stable miscibility gaps in the high-silica region of the phase diagrams. He also recognized the possible occurrence of metastable immiscibility in the system BaO-SiO_2. The thermodynamic basis of metastable immiscibility was brought to light by Roy (1960), although the phenomenon had long been employed in the Vycor process (Hood and Nordberg 1938). Since Greig's pioneering work, miscibility gaps in many silicate systems have been mapped.

The influence of glass-modifying components on the extent of miscibility gaps in silicate melts can be discussed in terms of the polarizing power of the modifier cation. This is a function of its charge, Z, and radius, R, and has been variously expressed as Z/R, Z/R^2, and $Z/(R+R_0)^2$, where R_0 is the radius of the O^{2-} ion (Mazurin and Porai-Koshits 1984, Ch. II). It has long been known that cation polarizing power affects a number of melt properties, including immiscibility (Dietzel 1942, Warren and Pincus 1940,

Galakhov and Varshal 1969). In general, the greater the polarizing power, the stronger is the attraction between the cation and non-bridging, negatively charged oxygens, and the greater is the tendency towards clustering of these species and hence phase separation. Up to a point, the greater the polarizing power of the cation, the more extensive is the miscibility gap in terms of both composition and temperature. Examples involving monovalent and divalent cations are shown in Figure 3, which is taken from Kawamoto and Tomozawa (1981a). This relationship breaks down with the most polarizing species, e.g., Al^{3+}, which substitute in the silicate structure in a network-forming rather than network-modifying role. Furthermore, formation of $AlO_{4/2}$ groups promotes delocalization of negative charge from one silicate non-bridging oxygen to four aluminate bridging oxygens, and therefore diminishes the electrostatic forces that promote phase separation. In the case of Ti^{4+}, four-coordination (network-forming) is believed to be favoured at high temperatures, e.g., in silicate melts, but six-coordination is preferred at lower temperatures (McMillan 1979).
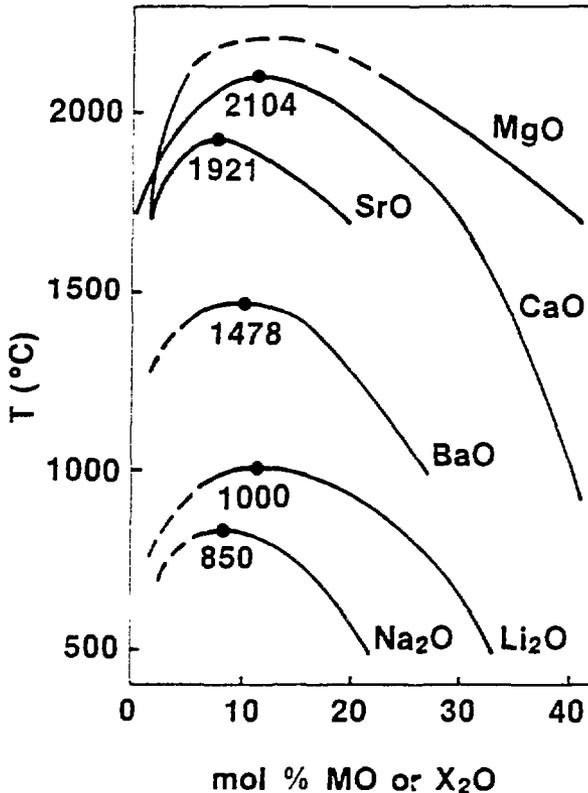

FIGURE 3: Miscibility Limits in Systems MO-SiO_2 and X_2O-SiO_2, Showing Increasing Extent of Miscibility Gap with Increasing Polarizing Power (Increasing Charge and/or Decreasing Radius) of M^{2+} or X^+ (from Kawamoto and Tomozawa 1981a)

The similar form of miscibility gaps in various systems of the Types X_2O-SiO_2 and MO-SiO_2 has been used by Kawamoto and Tomozawa (1981a, 1981b, 1981c) to predict miscibility limits within ternary systems, X_2O-MO-SiO_2 and X_2O-$X_2'O$-SiO_2. In each case, the miscibility gaps in the binary systems are the ends of a smooth, continuous band of immiscibility extending through the ternary system, as shown in Figure 4. Note, however, that the variation of T_c with substitution of X' for X is not linear (Kawamoto and Tomozawa 1982). Earlier calculations of miscibility limits in the Li_2O-BaO-SiO_2 system were published by Charles (1967). One of the most thorough and technically important experimental studies of a system of this Type was the investigation of the Na_2O-CaO-SiO_2 system by Burnett and Douglas (1970). Several investigators have also reported more limited studies of the effects of adding small quantities of a third component to a phase-separating binary glass (Moriya 1970, Tomozawa and Obara 1973, Topping and Murthy 1973).

Water is a special example of an oxide of a univalent element. Tomozawa and Capella (1983) have recently reported a small-scale (5 to 20 nm) microstructure in hydrated silicate glasses. They describe this as a silica-gel/water phase separation phenomenon. It is not clear how this relates to more conventional phase separation in glass. It may well have some relevance to the ion-transport behaviour of hydrated gel layers on corroding glass surfaces.
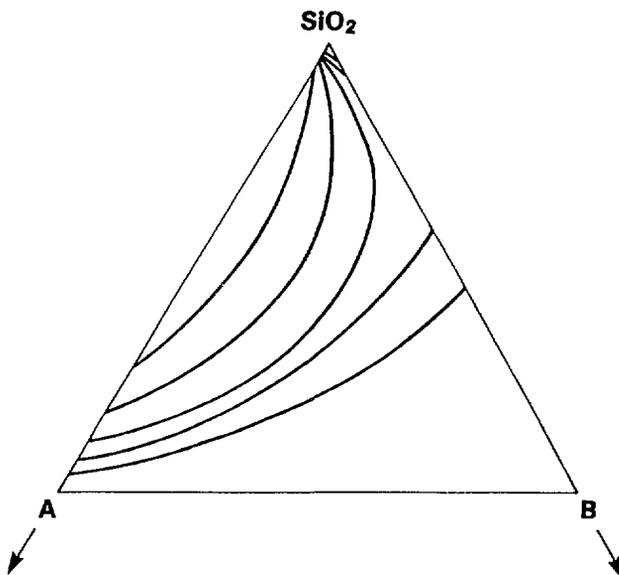

FIGURE 4: Typical Form of the Miscibility Gap in a Ternary System, A-B-SiO_2, Where A and B are both Glass-Modifying Oxides, X_2O or MO. The consolute temperature in the binary system A-SiO_2 is higher than that in the system B-SiO_2. Contours expanding out from the A-SiO_2 edge of the diagram represent miscibility limits at progressively lower temperatures. For specific examples, see Kawamoto and Tomozawa (1981a), Mazurin and Porai-Koshits (1984), and references they cite.

Many investigators have described approaches to modelling immiscibility in silicate systems. This subject has been reviewed by Mazurin and Porai-Koshits (1984) and Tomozawa (1979); representative papers include Barron (1981), Charles (1969), Haller et al. (1974), Jiang et al. (1982), Nakagawa and Izumitani (1972a), Strnad and Strnad (1978) and Tomozawa (1986). In an interesting recent development, McGahay and Tomozawa (1989) have used Debye-Hückel electrolyte solution theory to quantify the relationship between cation polarizing power and miscibility limits; in particular, the theory was successful in predicting critical temperatures of binary silicate systems. For a recent discussion and a particularly striking demonstration of the universal form of miscibility gaps in binary silicate systems, see Ding and Jiang (1989) and Jiang (1989). For a more general discussion of the various forms that miscibility gaps may take in ternary systems, the monograph by Francis (1963) is recommended.

Liquid immiscibility, both stable and metastable, occurs in many binary borate as well as silicate systems. Reported phase separation in the alkali borate systems, however, has been disputed for all except the lithium system (Shaw and Uhlmann 1968, Golubkov et al. 1977), and controversy on this topic still persists (Tomozawa 1989 and references therein). In general, immiscibility in borate systems is less well known than in silicate systems, although its occurrence has been known since Guertler's 1904 paper. The known miscibility gaps resemble those in the silicate systems, in that they lie close to the glass-former (in this case, B_2O_3) edge of the phase diagram, and their extent varies with the polarizing power of the modifier cation (Hageman and Oonk 1987, Mazurin and Porai-Koshits 1984). Miscibility gaps in ternary borate systems with two glass modifiers (as opposed to ternary borosilicate systems) are likely to have a similar form to those in corresponding silicate systems, but they have received much less experimental attention. Jiang et al. (1982) have calculated miscibility limits in some ternary borate systems.

The binary system B_2O_3-SiO_2 is interesting, because it consists of two glass-network-forming oxides. There is some controversy about the behaviour of this system. Charles and Wagstaff (1968) and Pichavant (1978) each reported an extensive metastable miscibility gap, with consolute temperature estimates of 520 and 560°C, respectively. Vasilevskaya et al. (1980) observed some nonuniformity in B_2O_3-SiO_2 glasses with a domain diameter of 2 to 3 nm, but they concluded that this was not a phase-separation phenomenon. Similarly, Kawamoto et al. (1983) concluded that phase separation does not occur above the glass transition in this system. This controversy is relevant to a precise understanding of the behaviour of borosilicate glasses with extremely low concentrations of Na_2O or other glass modifiers. It has little impact on the behaviour of glasses with fairly high modifier concentrations, which are of interest in the present context. One consequence of a true miscibility gap in the B_2O_3-SiO_2 system, however, could be the occurrence of three-liquid regions in ternary and more complex borosilicate systems, but probably only at temperatures below T_c for the B_2O_3-SiO_2 system ($\leq$ 560°C).

6. ALKALI BOROSILICATE SYSTEMS

Because of its technical importance, the miscibility gap in the system
$Na_2O-B_2O_3-SiO_2$ has been studied in great detail, and provides a sound basis
for discussion of more complex systems. The original patent for the Vycor
process was granted to Hood and Nordberg in 1938, but detailed understand-
ing of the phase-separation behaviour of the sodium borosilicate system was
not possible until the advent of electron microscopy.

Four detailed studies of miscibility limits in the sodium borosilicate
system were published between 1969 and 1972 (Galakhov and Alekseeva 1969,
Haller et al. 1970, Srinivasan et al. 1971, Mazurin and Streltsina 1972).
Although they differ in some details, they present together a fairly
detailed picture of the miscibility gap and tie lines therein. A refined
determination was reported by Alekseeva et al. (1977). Numerous other
papers deal with certain details of this system, as reviewed by Mazurin and
Porai-Koshits (1984). In addition, a monograph on this system has been
published (in Spanish) by Rincón and Durán (1982).

Miscibility limits in the sodium borosilicate system, as assimilated by
Mazurin and Porai-Koshits (1984) from several sources including the studies
cited above, are shown in Figure 5. The principal feature is an elongated
dome of immiscibility near the $B_2O_3-SiO_2$ edge of the phase diagram. Above
about 725°C, this dome is an island, separate from a second small region of
immiscibility contiguous with the Na_2O-SiO_2 binary miscibility gap. At
lower temperatures these regions coalesce and the dome expands to composi-
tions with progressively higher Na_2O and B_2O_3 contents. The maximum extent
of the observable miscibility gap is about 16 mol% Na_2O, at 550°C. The
region of observable immiscibility, as outlined in Figure 4, can be regard-
ed as the region of composition within which phase separation is likely to
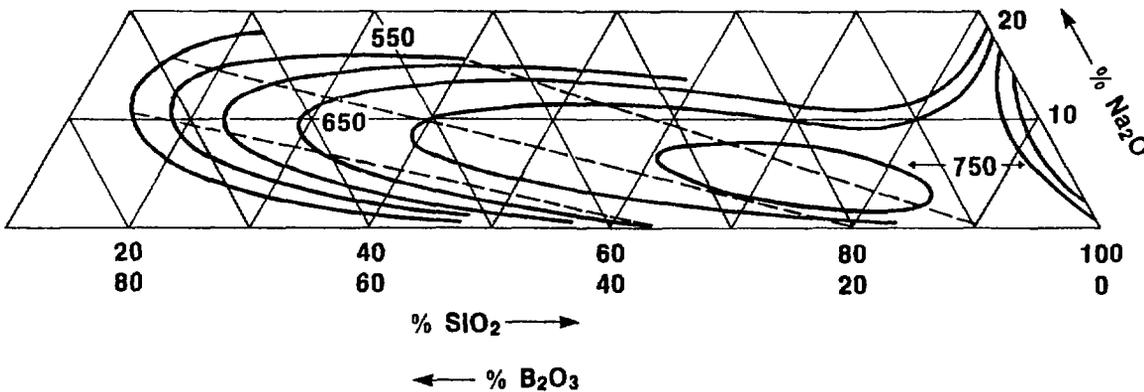be a concern in glass processing.

FIGURE 5: Miscibility Limits in the $Na_2O-B_2O_3-SiO_2$ System. Dashed lines
show three representative tie lines, two based on measurements
at 500°C, and one at 550°C. This figure is derived from Mazurin
and Porai-Koshits (1984).

The orientation of tie lines, linking coexisting compositions delineated by
the contours in Figure 5, has been the subject of much discussion (Mazurin
and Porai-Koshits 1984, Tomozawa 1979, Taylor et al. 1983b, Galakhov and
Alekseeva 1969, Haller et al. 1970, Srinivasan et al. 1971, Mazurin and
Streltsina 1972). Although interpretations differ in detail, there is gen-
eral consensus that the tie lines link compositions rich in Na_2O and B_2O_3
to others rich in SiO_2, as shown in Figure 5. It should be noted that, in
any system of three or more components, tie-line orientations are free to
change with varying temperature. This is discussed for the sodium boro-
silicate system by the authors cited above; the actual degree of rotation
of the tie lines appears to be small in this case. The phenomenon has been
clearly demonstrated in the system $BaO-B_2O_3-SiO_2$ (Aver'yanov et al. 1979,
M. Tomozawa and V. McGahay, pers. comm.). The interesting possibility that
a three-liquid phase-separation region exists in the sodium borosilicate
system, as proposed by Haller et al. (1970), is discussed briefly above.
This possibility is open for all systems of three or more components.

Miscibility limits in the other alkali borosilicate systems, $X_2O-B_2O_3-SiO_2$
(X = Li, K, Rb, Cs), have received less attention than in the sodium sys-
tem, but all have been delineated (Mazurin and Porai-Koshits 1984, Taylor
and Owen 1981a, Sastry and Hummel 1959, Galakhov and Alekseeva 1968, Voldan
1977, Galakhov et al. 1981, Voldanova 1982). Figure 6 compares reported
miscibility limits in the five systems. As expected from the preceding
discussion of silicate and borate systems, the extent of the miscibility
gaps increases in the order Cs < Rb < K < Na < Li. For the larger cations
(K, Rb, Cs), only a small portion of the miscibility gap emerges above the
glass-transition surface in the phase diagram. Limited information on
mixed-alkali borosilicate glasses (Taylor and Owen 1980) indicates a
monotonic progression in critical miscibility temperature, T_b, upon
substitution of one alkali for another in a given composition, as shown in
Figure 7. Thus, the miscibility gap in the $Na_2O-B_2O_3-SiO_2$ system expands
upon substitution of Li_2O for Na_2O, and contracts upon substitution of the
other alkali oxides. A more detailed study of this phenomenon in the case
of Li_2O was reported by Alekseeva and Galakhov (1976).

7. DIVALENT METAL BOROSILICATE SYSTEMS

Just as the $MO-B_2O_3$ and $MO-SiO_2$ binary systems have large miscibility gaps,
above the liquidus in most cases, so are the miscibility gaps in the ter-
nary systems, $MO-B_2O_3-SiO_2$, much more extensive than those in the $X_2O-B_2O_3-$
SiO_2 systems. Stable miscibility limits for five such systems (M = Mg, Ca,
Ba, Zn, Pb), as compiled by Voldan (1977), are shown in Figure 8, together
with data for M = Sr from Baylor and Brown (1976). Again, we find that the
extent of the miscibility gap increases with the polarizing power of the
cation, M^{2+}: Pb $\simeq$ Ba < Sr < Ca < Mg $\simeq$ Zn.

Isotherms within these miscibility gaps have yet to be determined in most
cases, but a detailed study of the barium system has been reported (Levin
and Cleek 1958). The miscibility gap extends as a stable feature from the
$BaO-B_2O_3$ binary almost to the $BaO-SiO_2$ binary, before submerging beneath
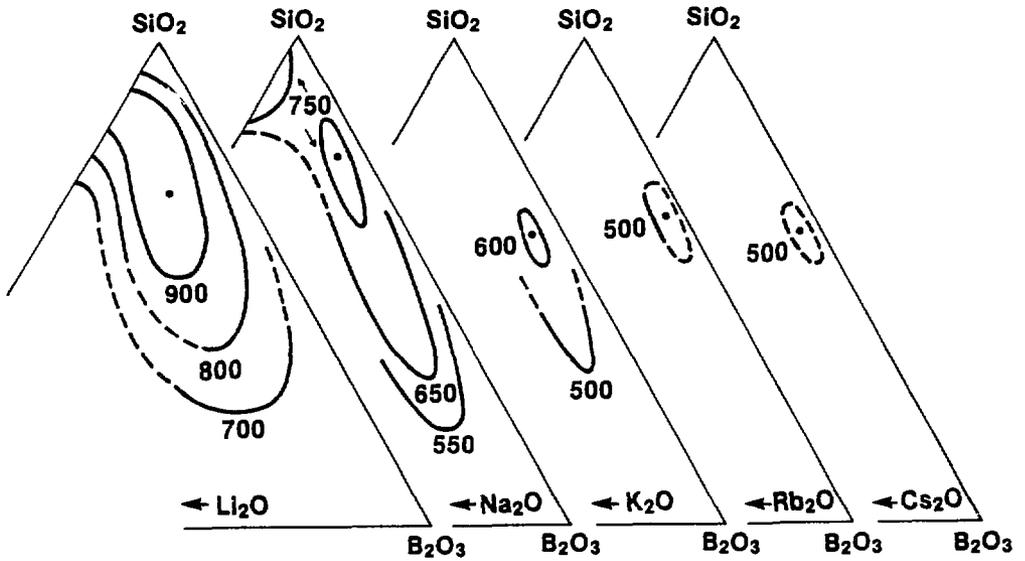
FIGURE 6: Comparison of Miscibility Limits in the Five Alkali Borosilicate Systems, as Compiled by Mazurin and Porai-Koshits (1984)
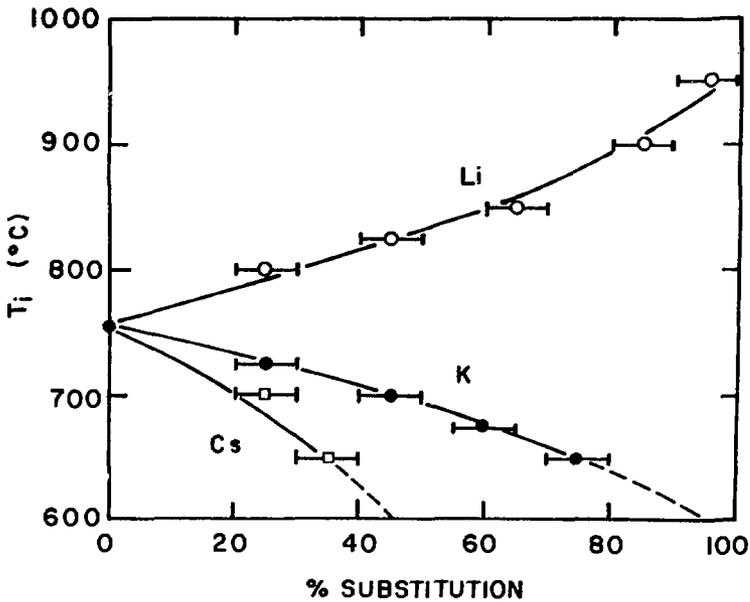

FIGURE 7: Measured Variation of Critical Miscibility Temperature, T_b, with Substitution of Li_2O, K_2O or Cs_2O for Na_2O in a Glass of Composition (mol%) $5Na_2O-23B_2O_3-72SiO_2$, from Taylor and Owen (1980)
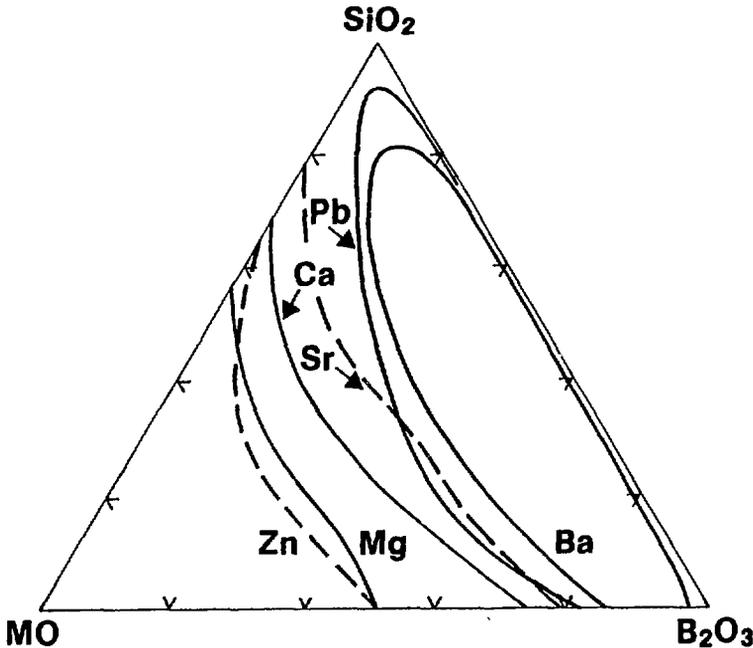
FIGURE 8:   Limits of Stable Immiscibility (Molar Scale) in the Systems MO-
            B_2O_3-SiO_2, M = Mg, Ca, Sr, Ba, Pb, Zn. Note that, for M = Ba,
            and presumably also for M = Pb, a metastable extension of the
            miscibility gap reaches the MO-SiO_2 edge of the phase diagram
            (see Figure 9). The MO-poor edge of the miscibility gap is
            shown only for M = Ba; in all cases, it is very close to the
            SiO_2-B_2O_3 edge of the diagram. (As compiled by Mazurin and
            Porai-Koshits (1984) with Sr data added from Baylor and Brown
            (1976)).

the liquidus. The consolute temperature, T_c, in the BaO-B_2O_3 binary is
1225°C, while the BaO-SiO_2 system has a metastable T_c of about 1430°C. The
dome of immiscibility extends smoothly between these limits (Figure 9).

In all of the MO-B_2O_3-SiO_2 systems summarized above, the miscibility gap is
bounded on one side by liquids rich in the network formers (B_2O_3 and SiO_2),
and on the other by liquids rich in the modifier (MO) - 50 mol% or more in
the case of MgO and ZnO.

Tie lines for a miscibility gap of this Type were first determined by Morey
and Ingerson (1937) for the calcium borosilicate system, and have since
been estimated for several of the other systems (Mazurin and Porai-Koshits
1984, Taylor and Owen 1981b). In all cases, tie lines tend to radiate from
the vicinity of the MO-B_2O_3 and SiO_2 extremities of the miscibility gap,
demonstrating that B_2O_3, as well as MO, tends to concentrate in the
modifier-rich phase. Examples with M = Ca and Zn are reproduced in
Figure 10. This tie-line orientation resembles that in the sodium boro-
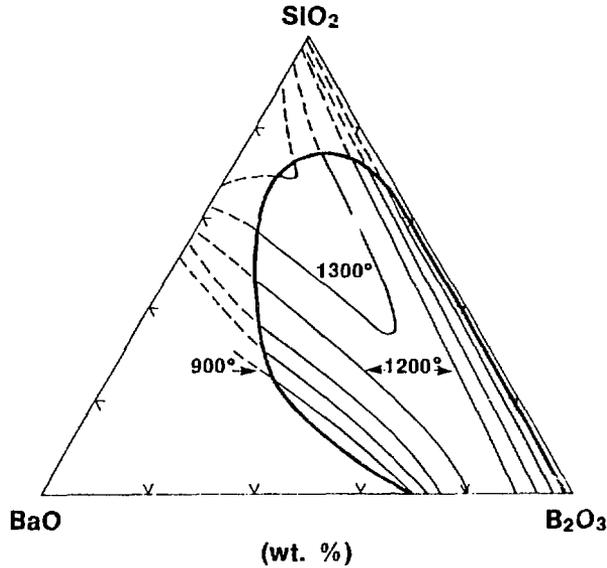silicate system, discussed in Section 6.

FIGURE 9: Miscibility Limits in the System $BaO-B_2O_3-SiO_2$, from Aver'yanov et al. (1979), after Levin and Cleek (1958). Bold line shows extent of stable miscibility gap. Narrower solid and dashed lines show stable and metastable limits, respectively, at temperatures from 900 to 1400°C.
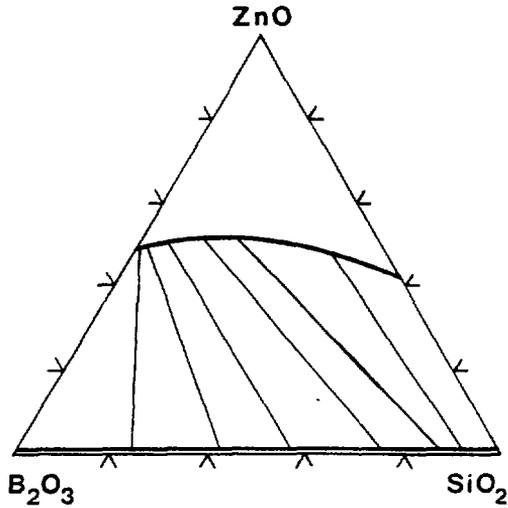

FIGURE 10: Estimated Tie Lines Connecting Coexisting Liquids (Weight Percent Compositions) in the Zinc Borosilicate System, Based on Microanalysis of Glass Samples Quenched from 1300°C Melts (Taylor and Owen 1981b). Tie line orientations in other MO-$B_2O_3-SiO_2$ systems are similar (Mazurin and Porai-Koshits 1984). Note that the tie line orientations can change with temperature (see Aver'yanov et al. 1979).

8. BOROSILICATE SYSTEMS CONTAINING BOTH X₂O AND MO

Zinc oxide was commonly included as a major component in early formulations of nuclear waste glasses in the CNFWMP and elsewhere, because it can both improve glass durability towards aqueous leaching and lower melt viscosity (Lutze 1988, Mendel 1977, Strathdee et al. 1979). For this reason, and because phase separation in most of the binary and ternary subsystems was already quite well understood, the quaternary system $Na_2O-ZnO-B_2O_3-SiO_2$ was chosen for detailed study (Taylor and Owen, 1981b).

Although T_g varies with composition, and generalizations must be made with caution, glasses with T_b < 550°C (within the range of borosilicate compositions usually considered for nuclear waste immobilization) are unlikely to undergo significant phase separation during waste processing. Specifically, cooling and annealing are the stages when phase separation is most likely to occur. In our experience with borosilicate glasses, phase separation is difficult to detect, either microscopically or by its influence on glass durability, at 550°C; this is consistent with other studies, in particular the work of Engell and Roed (1982). We therefore use the 550°C contour as a working definition of the limit of the miscibility gap. In many cases miscibility limits could not be measured experimentally below about 650°C, and 550°C limits can only be estimated.

8.1   THE SODIUM ZINC BOROSILICATE SYSTEM

Detailed mapping of miscibility limits in a four-component system requires the preparation and heat treatment of a large number of samples. Over 200 glasses were prepared and examined in the sodium zinc borosilicate study (Taylor and Owen 1981a). These spanned most of the compositions with T_b in the range 650-950°C, except for very high-silica compositions, which are difficult to prepare because of high liquidus temperatures and viscosities. Coverage of the high-boron portion of the phase diagram was also sparse, since this region is not of interest in the waste management context (Lutze 1988); boron-rich sodium borosilicate glasses have poor resistance to aqueous leaching and corrosion (Adams and Evans 1978). Miscibility limits were determined at 650, 800 and 950°C. The results are best illustrated by cross sections through the quaternary phase diagrams at various B:Si ratios, as shown in Figure 11.

Note that the diagrams in Figure 11 are not true pseudo-ternary sections, because the tie lines do not lie within the planes of the diagrams. Thus, the diagrams represent miscibility limits only, and not coexisting compositions (see Francis 1963, pp. 21-24 and 103-118).

Figure 11 shows that miscibility limits are rather insensitive to variation of SiO_2/B_2O_3 weight ratios between 1 and 5. At 950°C, the miscibility gap is a low dome, extending up to about 6 wt.% Na_2O, contiguous with the zinc borosilicate ternary miscibility gap (Ingerson et al. 1948, Marinov and Popinova 1977, Taylor and Owen 1981b). As the temperature is decreased this dome expands and bulges toward the sodium borosilicate face of the phase diagram, which it intersects below 755°C, the consolute temperature
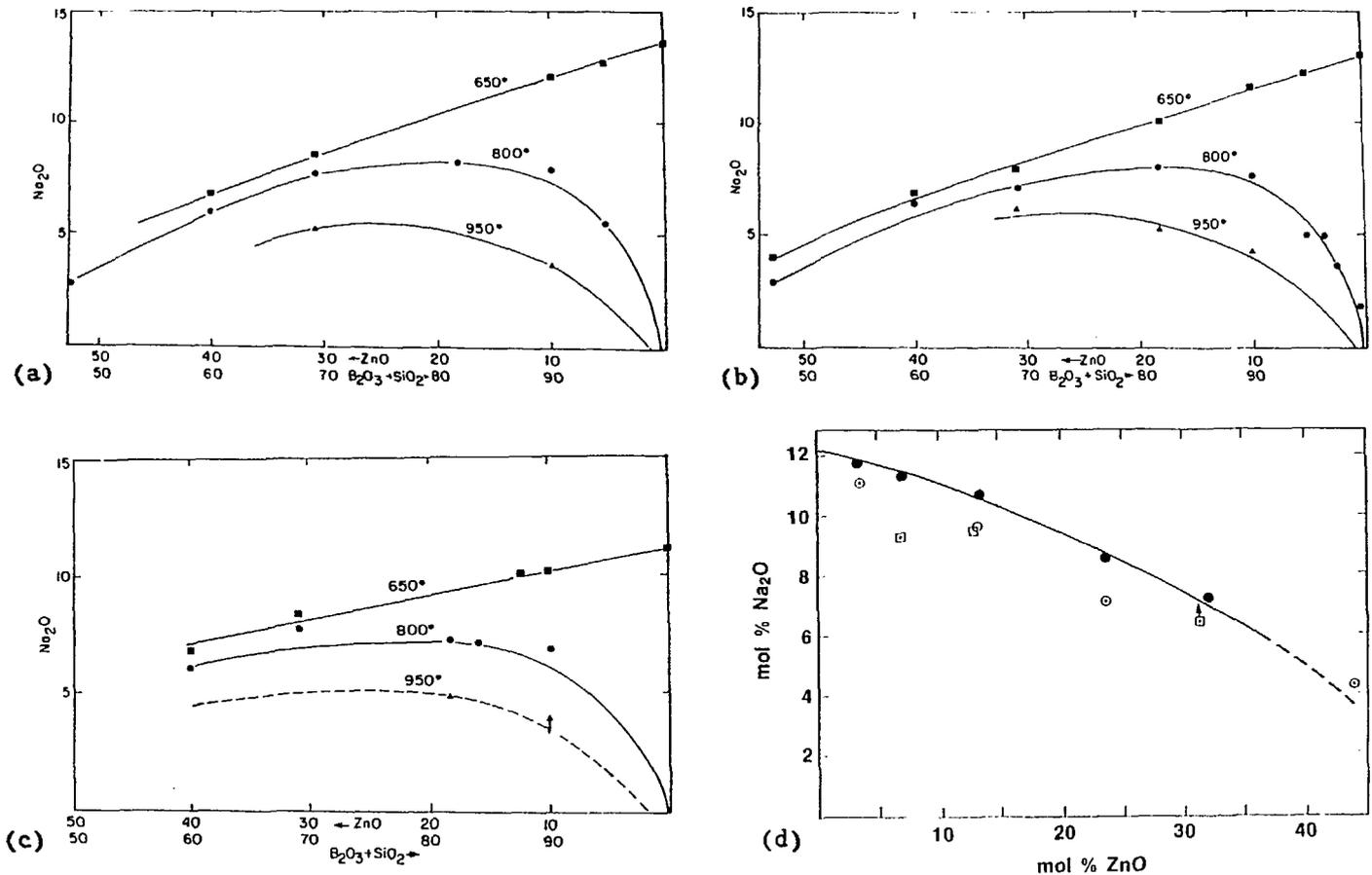
FIGURE 11: Miscibility Limits in the System $Na_2O-ZnO-B_2O_3-SiO_2$ at 650, 800 and 950°C. Weight percent scale; (a) $SiO_2:B_2O_3 = 1:1$; (b) $SiO_2:B_2O_3 = 1:2$, (c) $SiO_2:B_2O_3 = 1:5$, (d) 650°C limits converted to molar scale. Filled circles, open circles and squares correspond to (a), (b), and (c), respectively. The boundary line for $SiO_2:B_2O_3 = 1:1$ (weight; 1:1.16 molar) can be compared with the systems $Na_2O-MO-B_2O_3-SiO_2$ in Figure 15. Note that the direction of the horizontal scale is reversed in (d) from (a) to (c), to facilitiate comparison with Figures 15, 19 and 20.

for the sodium borosilicate miscibility gap (see Section 6). The locus of this intersection is the miscibility boundary in the sodium borosilicate system at a given temperature (e.g., 650°C in Figure 11). The form of the miscibility gap in the three sections shown in Figure 11 thus resembles a typical ternary silicate miscibility gap of the type shown in Figure 3. There is no indication of three-liquid immiscibility. There is also no indication of any inflection or discontinuity in the immiscibility surface, except perhaps in the high-silica region (> 80% SiO_2; see Figure 10B of Taylor and Owen 1981b).

To help visualize the miscibility gap in this system, it is useful to consider the effects of additions and substitutions of sodium and zinc in various zinc borosilicate and sodium borosilicate ternary compositions, respectively, as depicted in Figure 12. The following conclusions can be drawn:

i) Addition of Na_2O to any composition within the $ZnO-B_2O_3-SiO_2$ miscibility gap (lines a to c in Figure 12) tends to suppress phase separation, i.e., it depresses T_b. The degree of depression, $d(T_b)/d[Na_2O]$ varies substantially with zinc content, but is rather insensitive to the SiO_2/B_2O_3 ratio at a given zinc concentration. Thus, glasses containing about 40 wt.% ZnO require about 6 mol% Na_2O to reduce T_b to 650°C, whereas those with 10% ZnO require about 11% Na_2O.

ii) Addition of ZnO to a sodium borosilicate composition (lines d and e in Figure 12) will promote phase separation, i.e., increase T_b, in a glass composition lying well within the sodium borosilicate miscibility gap, but will have little or no effect (perhaps even marginally suppressing phase separation) in a composition near the edge of the miscibility gap.

iii) Substitution of zinc for sodium generally enhances phase separation, and the converse substitution suppresses it, but the degree of the effect depends on the composition (lines f to h in Figure 12). Thus, a substantial amount of ZnO may be substituted for Na_2O in a high-sodium (say, 20%) composition before the miscibility boundary is encountered. A typical example of the effect of substituting zinc for sodium in a low-sodium glass is shown in Figure 13, and a perspective of the effect of such substitution in the whole system is given in Figure 14.

8.2   OTHER $X_2O-MO-B_2O_3-SiO_2$ SYSTEMS

After the miscibility gap had thus been elucidated in detail in one quaternary borosilicate system, comparative studies were performed on a variety of related systems. Most work was done with X = K or Na and M = Mg, Ca, Ba or Mn (Ménassa et al. 1985a, 1985b, Taylor et al. 1983a), with more limited investigation of systems containing Li_2O, Cs_2O or SrO (Taylor and Owen 1980).
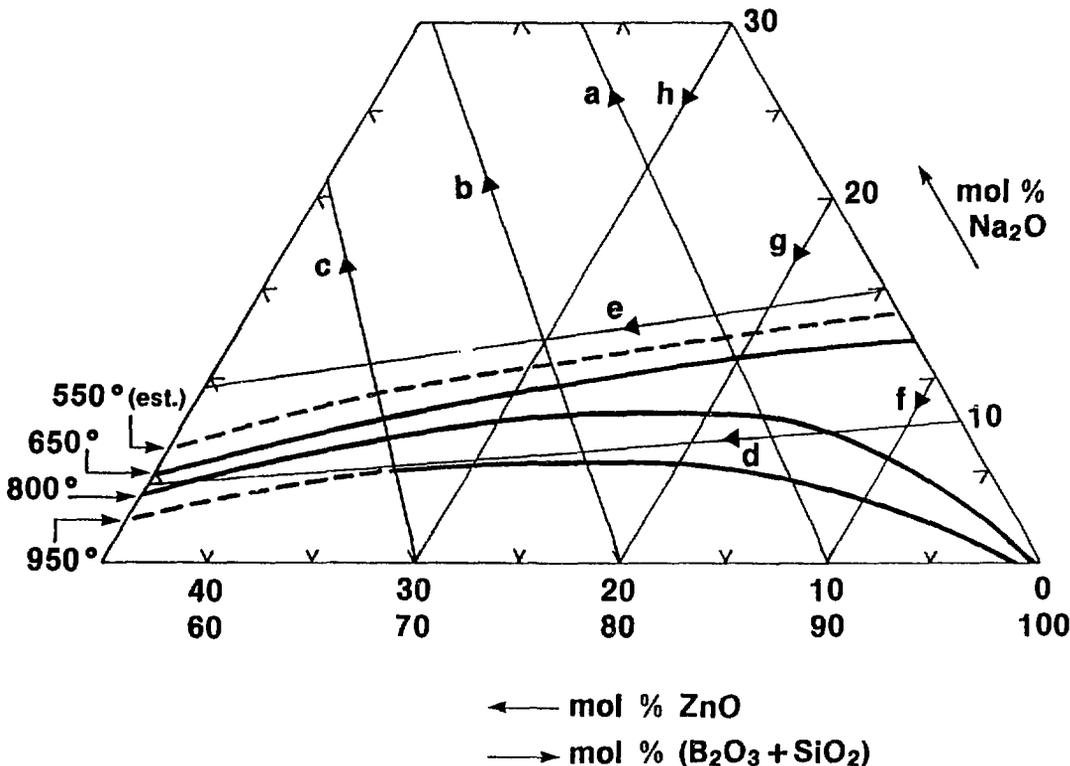
FIGURE 12: Miscibility Limits in the System $Na_2O-ZnO-B_2O_3-SiO_2$ at an $SiO_2:B_2O_3$ Mole Ratio of 1.16:1 (from Figure 11(a), altered to molar scale and triangular coordinates). Arrowed lines illustrate the following systematic changes in composition:
(a) addition of Na_2O to $10ZnO\cdot90(B_2O_3 + SiO_2)$
(b) addition of Na_2O to $20ZnO\cdot80(B_2O_3 + SiO_2)$
(c) addition of Na_2O to $30ZnO\cdot70(B_2O_3 + SiO_2)$
(d) addition of ZnO to $7.5Na_2O\cdot92.5(B_2O_3 + SiO_2)$
(e) addition of ZnO to $15Na_2O\cdot85(B_2O_3 + SiO_2)$
(f) substitution of ZnO for Na_2O in $10Na_2O\cdot90(B_2O_3 + SiO_2)$
(g) substitution of ZnO for Na_2O in $20Na_2O\cdot80(B_2O_3 + SiO_2)$
(h) substitution of ZnO for Na_2O in $30Na_2O\cdot70(B_2O_3 + SiO_2)$.

In order to reduce the number of samples, and investigate as many systems as possible, several systems were investigated at only one temperature and one SiO_2/B_2O_3 ratio. Some experiments were run to confirm that miscibility limits are relatively insensitive to this ratio, over the range from 1 to 5, as was found in the more comprehensive study of the sodium zinc boro-silicate system discussed above.

Six systems, $X_2O-MO-B_2O_3-SiO_2$ (X = Na, K; M = Mg, Ca, Ba) were examined at an $SiO_2:B_2O_3$ molar ratio of 1.07:1; a ratio near one was desirable for ease of preparation (low melting temperatures and less tendency to devitrify than for higher ratios). In these systems, only the 650°C boundary of the miscibility gap was determined. Results are summarized in Figure 15.
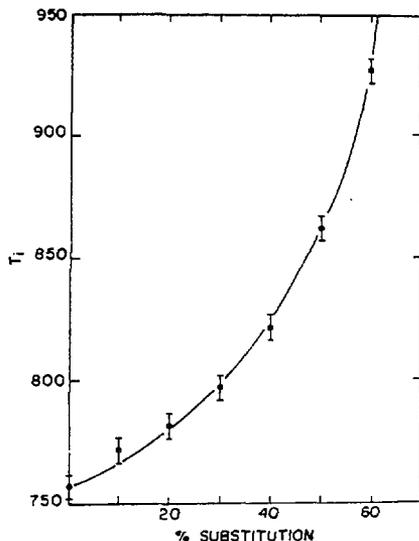
FIGURE 13: Critical Miscibility Limits of a Series of Glasses in which ZnO is Substituted for Na_2O (Mole for Mole) in a Base Composition (Mole %) $5Na_2O \cdot 23B_2O_3 \cdot 72SiO_2$ (from Taylor and Owen 1981b)
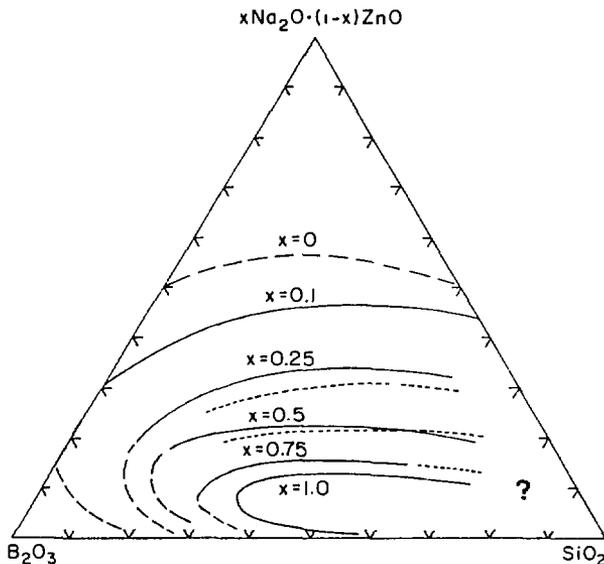

FIGURE 14: Limits of Miscibility in the System $Na_2O-ZnO-B_2O_3-SiO_2$ at 650°C, with Compositions Expressed in the Form $a[xNa_2O \cdot (1-x)ZnO] \cdot bB_2O_3 \cdot (100-a-b)SiO_2$. This shows progressive contraction of the miscibility gap as Na_2O is substituted for ZnO. The $x = 0$ and $x = 1.0$ contours represent the ternary systems, $ZnO-B_2O_3-SiO_2$ and $Na_2O-B_2O_3-SiO_2$, respectively. The dotted contours represent 800°C (upper line) and 950°C (lower) miscibility limits for $x = 0.25$.
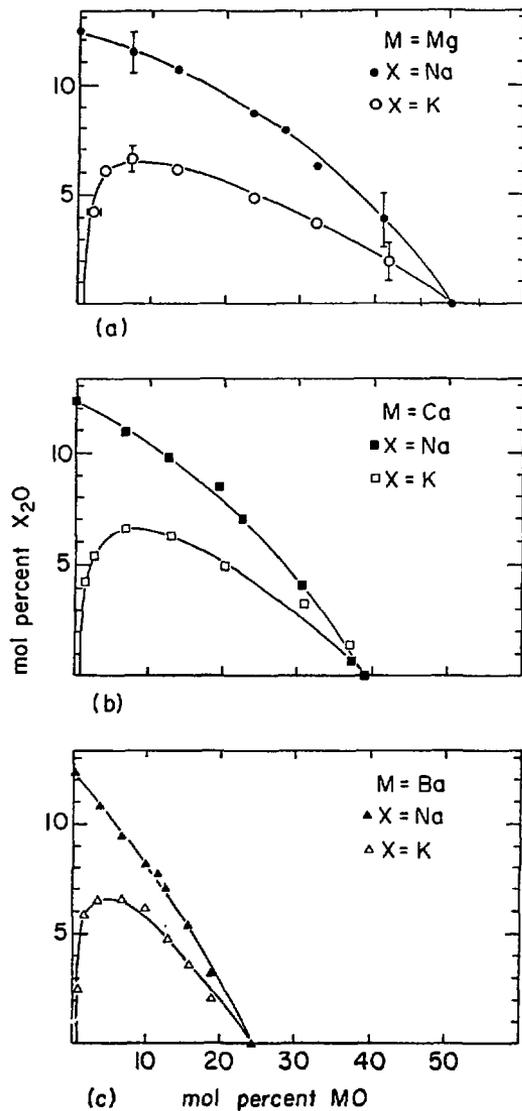
FIGURE 15: Limits of Miscibility at 650°C in the Systems $X_2O-MO-B_2O_3-SiO_2$, at an $SiO_2:B_2O_3$ Mole Ratio of 1.07:1. In each case the two-phase field lies below the boundary shown. For the sodium systems, additional minute one-phase fields exist at the lower left corner of each diagram. (From Taylor et al. 1983a).

The shape of the miscibility gaps in these systems closely resembles that in the sodium zinc borosilicate system. The extent of the gaps, in terms of MO content, increases with cation polarizing power (the inverse order of the ionic radii of M^{2+}), as expected: Ba (< Sr) < Ca < Mg $\simeq$ Zn. The miscibility gap is less extensive in the X_2O direction for $X = K$ than Na for each given divalent cation M, which is again expected from the respective radii of the alkali cations: Na < K. Because the consolute temperature of the $K_2O-B_2O_3-SiO_2$ system lies a little below 650°C (Voldan 1977, Galakhov et al. 1981, Taylor and Owen 1981a), the 650°C miscibility boundaries in the $K_2O-MO-B_2O_3-SiO_2$ systems do not quite extend to the $K_2O-B_2O_3-SiO_2$ face of the phase diagrams. A schematic perspective drawing of the miscibility gaps in these systems, again at a fixed SiO_2/B_2O_3 ratio, is shown in Figure 16.
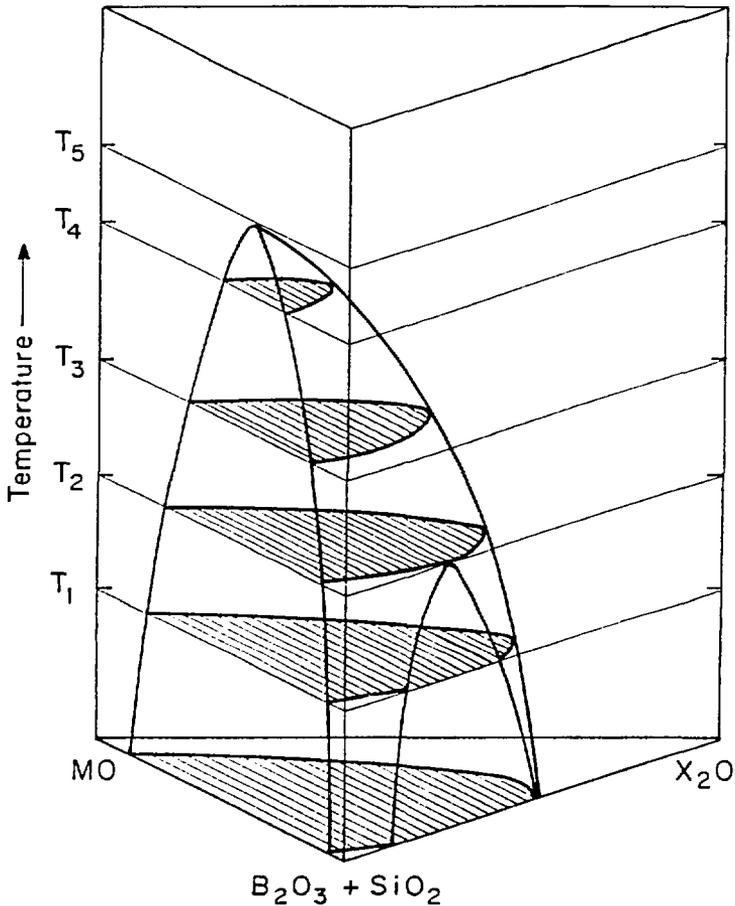

FIGURE 16: Schematic Perspective Drawing of Miscibility Gap in a System $X_2O-MO-B_2O_3-SiO_2$ at a Fixed $SiO_2:B_2O_3$ Ratio Between 1 and 5. (From Taylor et al. 1983a).

When miscibility-limit data for these six systems were normalized with respect to their extent in the MO direction, the data for the three sodium and three potassium systems fell on "master curves" (Figure 17), which proved to have some predictive value for determining miscibility limits in multicomponent systems (specifically Na_2O-MgO-BaO-B_2O_3-SiO_2, Taylor et al. 1983a). To determine the quantities m' and n' in Figure 17, compositions from Figure 15 were first expressed in molar units in the form $nX_2O \cdot mMO \cdot B_2O_3 \cdot 1.07SiO_2$. The values of m for $n = 0$, i.e., the intercepts of the respective miscibility gaps on the MO-$(B_2O_3 + SiO_2)$ axes in Figure 15, were defined as m_0. Values of m were then expressed as percentages of m_0:

$$m' = 100m/m_0$$

The X_2O content for each composition was then expressed as a mole percentage of the base composition, $mMO \cdot B_2O_3 \cdot 1.07SiO_2$:

$$n' = 100 \ n/(m + 2.07)$$

This empirical treatment was found to give close correspondence between the three data sets (M = Mg, Ca, Ba), as shown in Figure 17.
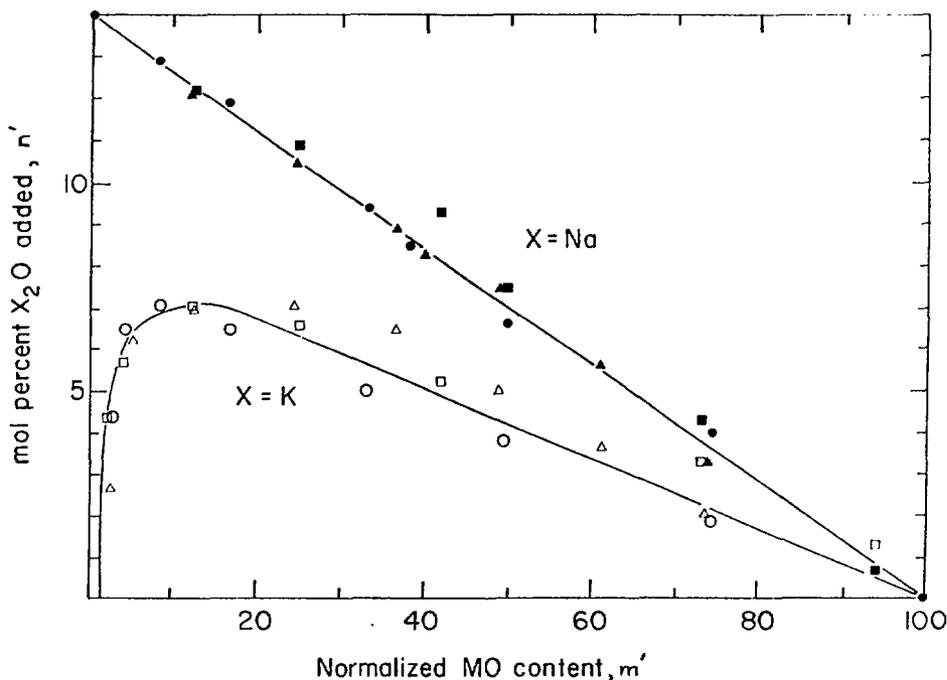

FIGURE 17: Miscibility-Limit Data for the Systems X_2O-MO-B_2O_3-SiO_2 (X = Na, K; M = Mg, Ca, Ba) from Figure 15, Normalized with Respect to the Extent of each MO-B_2O_3-SiO_2 Miscibility Gap, and Expressed in Terms of Moles of X_2O Added to Given MO-B_2O_3-SiO_2 Compositions (SiO_2/B_2O_3 Mole Ratio = 1.07:1). For details, see Taylor et al. (1983a).

The most important practical conclusion by Taylor et al. (1983a) was that, as in the sodium/zinc system, addition of MO to glasses near the observable miscibility limit in the sodium borosilicate system tends not to markedly promote phase separation, and at high concentrations tends to suppress it. The situation in the K_2O systems is complicated somewhat by the lower T_c of the K_2O-B_2O_3-SiO_2 system, but in all cases the miscibility gap is less extensive in K_2O than Na_2O systems, and probably does not extend beyond about 10 mol% K_2O.

The approach to investigating the Na_2O-MnO-B_2O_3-SiO_2 system was different from other systems of this type. The main aim of this work was to investigate the luminescence spectrum of Mn^{2+} as a means of detecting the onset of phase separation (Ménassa et al. 1985b, 1986). For this purpose a series of manganese-doped sodium borosilicate glasses (up to 2 wt.% MnO) was prepared, with compositions lying along a tie line in the Na_2O-B_2O_3-SiO_2 system. This work included detailed determination of miscibility limits and microstructures within this small portion of the quaternary system (Ménassa et al. 1985a). The microstructural aspects closely parallel those reported by Ehrt et al. (1977) for CoO-doped sodium borosilicate glasses. The results were fully consistent with a miscibility gap of the type already described for other X_2O-MO-B_2O_3-SiO_2 systems, as discussed above (Taylor and Owen 1980, 1981b; Taylor et al. 1983a).

The luminescence spectra were interpreted in terms of two distinct Mn^{2+} species, tetrahedrally coordinated in the Si-rich phase and octahedrally coordinated in the (Na + B)-rich phase (Ménassa et al. 1986). The spectra also indicated that molecular-scale segregation occurred during quenching, and truly homogeneous glasses were not obtained (Ménassa et al. 1985b). This was consistent with similar conclusions drawn by White (1982) and McMillan (1984a, 1984b) from Raman spectroscopic studies of other glass-forming systems. It is not clear whether this should be regarded as extremely fine-scale phase separation or a submicrononuniformity of the type discussed by Golubkov et al. (1977) and Vasilevskaya et al. (1980) for some binary borate systems. It is unlikely that segregation on such a fine scale has much impact on glass dissolution properties. Usually, a strong effect on dissolution is observed only in glasses where phase separation is readily apparent by visual and/or microscopic examination (Taylor et al. 1987).

9. SYSTEMS CONTAINING TRIVALENT METAL OXIDES, E_2O_3, IN ADDITION TO B_2O_3

With the exception of Al_2O_3, the influence of trivalent metal oxides on phase separation in glasses has received comparatively little attention. There is a large subliquidus miscibility gap in the Al_2O_3-SiO_2 binary system. There is much confusion in the literature as to its exact extent (Mazurin and Porai-Koshits 1984, Galakhov et al. 1982a); the determination by Galakhov et al. (1976a) appears to be the most reliable. They observed phase separation in compositions between 7 and 35 mol% Al_2O_3 and estimated a consolute point at 23 mol% Al_2O_3, with T_c = 1300°C. Important ternary

aluminosilicate systems in which liquid immiscibility has been studied in some detail include $Li_2O-Al_2O_3-SiO_2$, $MgO-Al_2O_3-SiO_2$, and $CaO-Al_2O_3-SiO_2$ (Nakagawa and Izumitani 1972b, Galakhov et al. 1976b, 1982b, Kawamoto 1985). The lead aluminoborate system, $PbO-Al_2O_3-B_2O_3$, has also been investigated at some length (Zarzycki and Naudin 1971). A number of quaternary or more complex systems have been studied less comprehensively. An exception is the $K_2O-FeO-Al_2O_3-SiO_2$ system, and related systems of geological importance, which have received detailed attention. Phase separation in these systems is a distinct area of geochemical research. Since the principal components differ from those of most radioactive waste glasses, this topic lies beyond the scope of this review. For current information, see Barron (1981), Carstens (1979), Freestone and Powell (1983), Henry et al. (1983), Naslund (1983), Visser and van Groos (1979a, 1979b), and references therein.

It has been known since Greig's pioneering work that small additions of Al_2O_3 tend to suppress phase separation in silicate melts (Greig 1927, Mazurin and Porai-Koshits 1984, Bondarev et al. 1977, 1979). Topping and Murthy (1973) studied this effect in some detail in the Na_2O-SiO_2 system, and observed the same effect to a somewhat lesser degree for Ga_2O_3. Similar effects on sodium borosilicate glasses have been reported by Aver'yanov and Danilova (1974), and confirmed by Taylor et al. (1986). Balskaya et al. (1969) have shown, however, that higher concentrations of Al_2O_3 may reverse the trend and actually promote phase separation. Also, Kingery et al. (1983) showed that a combination of Na_2O or K_2O and Al_2O_3 is much less effective than either additive alone in suppressing immiscibility of $CaO-SiO_2$ melts, and similar results were reported by Wu et al. (1986a, 1986b) for calcium and zinc borosilicates. These observations illustrate the dangers of generalizing about the effects of additives, and the importance of mapping regions of immiscibility in as much detail as the complexity of a system and available resources permit. In particular, caution is needed in predicting phase separation of glasses containing substantial quantities of Al_2O_3.

Comparatively little is known about the effects on phase separation of rare-earth oxides and other sesquioxides of large metal cations. Levin (1966) reported stable miscibility limits at the liquidus, and monotectic liquidus temperatures[*], for a large number of $E_2O_3-B_2O_3$ systems (E = Sc, Y, and 11 lanthanides). Aver'yanov and Danilova (1974) found that La_2O_3, unlike Al_2O_3 and Ga_2O_3, promoted phase separation when substituted (up to 2 mol%) for SiO_2 in a glass with composition 5 $Na_2O \cdot 23B_2O_3 \cdot 72SiO_2$. Taylor et al. (1986) observed similar behaviour when these oxides were added to a slightly different glass, $9Na_2O \cdot 31B_2O_3 \cdot 60SiO_2$. Furthermore, the latter authors investigated the effects of other trivalent oxide additives, E_2O_3 (E = Sc, In, Yb, La), and found a smooth progression from suppression of phase separation by the smallest cations (Al, Ga) to promotion by the largest. Thus, addition of 1 mol% Al_2O_3 lowered the critical miscibility temperature of the glass in question by 38°C, whereas 1% of La_2O_3 increased it by 35°C. This progression is illustrated in Figure 18. Again, it must

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[*]   Invariant temperatures (at given pressure) for solid-liquid-liquid equilibrium.
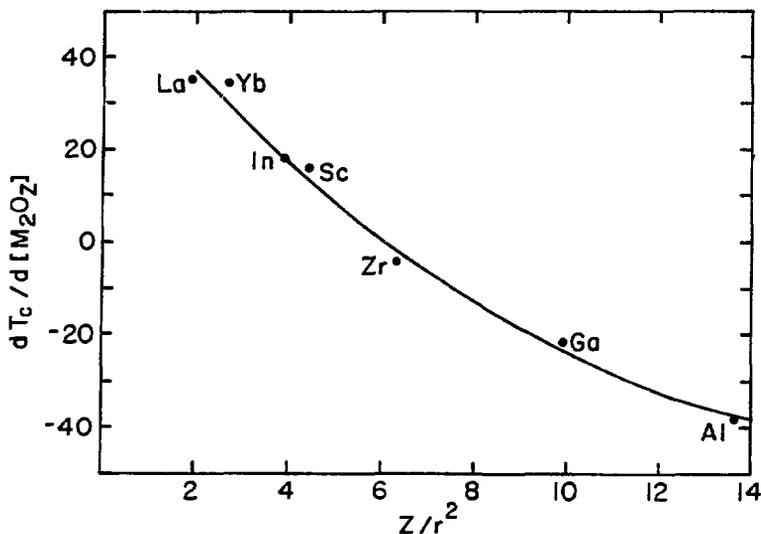
FIGURE 18: Effects of ZrO_2 ("Zr_2O_4") and Various Trivalent Metal Oxides, E_2O_3 on the Critical Miscibility Temperature, T_b, of a Sodium Borosilicate Glass, Composition (mol%) $9Na_2O-31B_2O_3-60SiO_2$. The effect is expressed as the change in T_b per mole of added E_2O_3 or Zr_2O_4, plotted against cation polarizing power, Z/r^2, with appropriate choice of coordination number (see Taylor et al. 1986).

be emphasized that these are observations on small additions of oxides to one glass composition, and extrapolation beyond closely comparable compositions, or to high additive concentrations, is not advised. Rare-earth oxides comprise up to 30 wt.% of high-level wastes, and so could amount to several weight percent of a waste glass. Further research on the effects of rare earths on phase separation would therefore be warranted if high waste loadings are envisaged in waste immobilization programs.

Taylor and Owen (1981b) and Taylor et al. (1983a, 1984, 1986) found that detection of phase separation of glasses containing E_2O_3 oxides, and, to a lesser extent, MO, was hindered at higher oxide concentrations by limited solubility of the oxide. In some cases, crystallization of either the oxide itself or a borate or silicate (e.g., $LaBO_3$, Zn_2SiO_4) occurred during the heat treatment intended to induce phase separation (600-800°C), and in some cases the oxide did not dissolve completely in the melt (1200-1400°C) in the first place.

On the basis of these observations, we may expect crystalline phase segregation to be more likely to be induced than liquid immiscibility in heavily loaded waste glasses, so long as the base-glass composition is appropriate as discussed below. This could be deleterious, if the residual glass phase is less durable than a homogeneous composition, or if some radionuclides are concentrated and readily leached at crystal/glass interfaces. On the

other hand, crystallization of some radionuclides in refractory, insoluble phases can improve the overall durability of glassy waste forms. This has been exploited in the development of glass-ceramic waste forms, recently reviewed by Hayward (1988). Here, many of the longer-lived radionuclides are partitioned into a durable crystalline phase (e.g., sphene, nominally $CaTiSiO_5$) by controlled partial crystallization of a glass precursor. Glass ceramics also have superior mechanical properties to glasses in many cases. The role of amorphous phase separation as an initial step in the formation of a glass ceramic is discussed by Cahn (1968), Scherer and Uhlmann (1976), McMillan (1979) and Hayward et al. (1989), among others.

Phase separation was studied in more detail in the systems $Na_2O-Yb_2O_3-B_2O_3-SiO_2$, $K_2O-Yb_2O_3-B_2O_3-SiO_2$, and $Na_2O-Sc_2O_3-B_2O_3-SiO_2$ (Taylor al. 1984, 1986). Solubility limitations were somewhat less severe with Yb_2O_3 and Sc_2O_3 than with some of the other trivalent metal oxides, notably In_2O_3 and La_2O_3. Nonetheless, these studies were limited to about 5 mol% of E_2O_3 in each case.

In each of these studies, miscibility limits were again mapped on a join of constant $SiO_2:B_2O_3$ ratio (2:1 in this case), as shown in Figures 19 and 20. The results demonstrate that oxides of large trivalent metal ions (Sc, lanthanides, and probably Y, In, actinides) behave much like alkaline earth oxides with respect to phase separation in sodium borosilicate glasses. Once more, the important point is that glass compositions lying well within the observable miscibility gap are profoundly affected (much higher T_c) by addition of these oxides, but phase separation appears not to be induced when the oxides are added to glasses outside the $Na_2O-B_2O_3-SiO_2$ miscibility gap. This is demonstrated in Figures 19 and 20, where the 650°C contours in the sodium systems lie almost parallel to the Yb_2O_3 or Sc_2O_3 axes, respectively (i.e., the 650°C miscibility limits are insensitive to addition of E_2O_3). From a waste management viewpoint, these data indicate that, so long as the base-glass composition contains sufficient alkali metal oxide(s) to lie outside the miscibility gap, addition of rare-earth oxides (at least up to about 5 mol%) should not in itself induce amorphous phase separation.

The similar behaviour of many E_2O_3 and MO oxides parallels similarities between borate and silicate binary systems of both groups of oxides, as discussed by Taylor et al. (1984, 1986). In all known cases, large stable two-liquid fields exist in the high-SiO_2 or high-B_2O_3 portions of the phase diagrams. Data on many such systems are summarized in Table 1 (pp. 105-107) of Mazurin and Porai-Koshits (1984).

Tomozawa et al. (1982) have described an interesting study of phase separation in glasses containing both divalent and trivalent iron. They measured T_b for a series of glasses, $10Na_2O \cdot 50B_2O_3 \cdot 40SiO_2 \cdot 0.5FeO_x$, with different relative amounts of Fe^{2+} and Fe^{3+}. They observed a minimum in T_b at a ratio Fe^{2+}/Fe (total) $\simeq 0.1$. This coincided with minima in antiferro-magnetic ion pairing, as indicated by magnetic susceptibility measurements and electron-spin-resonance spectroscopic signal strength. It thus appears that, in this system, the influence of cation field-strength on immisci-bility is modified by magnetic interactions between the cations. This may
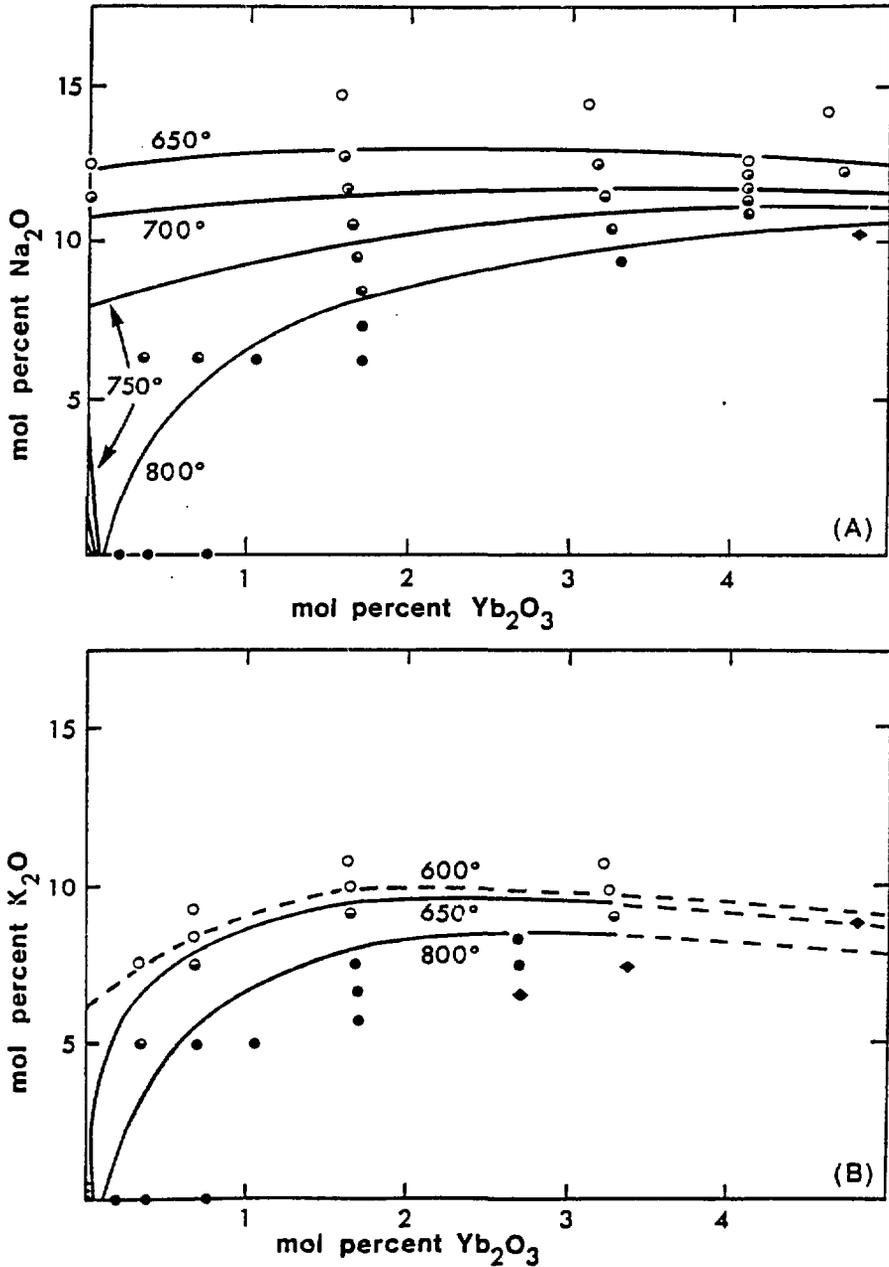
FIGURE 19: Miscibility Limits in the Systems (A) $Na_2O-Yb_2O_3-B_2O_3-SiO_2$ and (B) $K_2O-Yb_2O_3-B_2O_3-SiO_2$, at an $SiO_2:B_2O_3$ Mole Ratio of 2:1. Symbols indicate that T_b for a given composition lies within the range < 650°C (O), 650-700°C (◑), 700-750°C (◑), 750-800°C (◑), or > 800°C (●). A diamond symbol indicates that T_b could not be determined, because of crystallization. From Taylor et al. (1984).

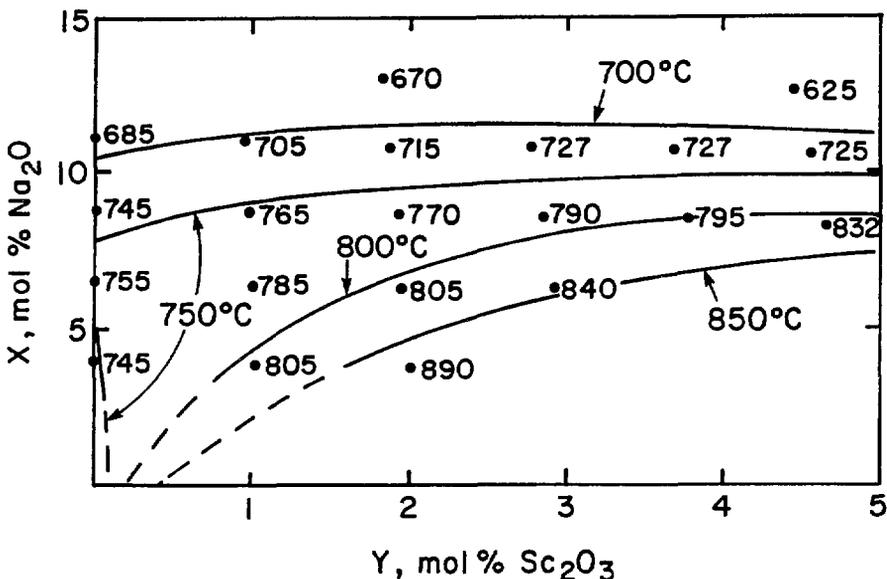FIGURE 20: Miscibility Limits (°C) of Glasses in the System $Na_2O-Sc_2O_3-B_2O_3-SiO_2$ with an $SiO_2:B_2O_3$ Mole Ratio of 1.94:1. From Taylor et al. (1986).

be significant in nuclear waste glasses, since high-level fuel-recycle wastes contain significant quantities of iron from corrosion of structural materials by the highly acidic dissolver solutions. The possibility of similar behaviour by other polyvalent elements (e.g., Mo, see below) should also be considered.

10. SYSTEMS CONTAINING OXIDES OF METALS WITH VALENCY GREATER THAN THREE

Little fundamental work has been reported on phase separation in borosilicate systems of this type. Large stable miscibility gaps have been reported for the binary silicate and borate systems TiO_2-SiO_2, ZrO_2-SiO_2, $Nb_2O_5-SiO_2$, UO_2-SiO_2, $TeO_2-B_2O_3$, $ThO_2-B_2O_3$, and $Nb_2O_5-B_2O_3$, as tabulated in the monograph by Mazurin and Porai-Koshits (1984). Behaviour in multicomponent systems was summarized on p. 142 of that monograph, as follows:

"As to other components, we think the data of their effect on T_b are still deficient for drawing any far-reaching conclusions... P_2O_5 greatly increases the tendency towards phase separation of many oxide melts... a number of publications provide data on the complicated effect of titanium dioxide on phase separation."

The expansion of the miscibility gap in the Na_2O-SiO_2 system upon addition of 1 mol% P_2O_5 (and corresponding contraction with Al_2O_3 addition) was mapped by Tomozawa and Obara (1973). A wider range of phosphosilicate compositions was investigated by Rabinovich et al. (1980). Work by Matusita et al. (1974) on a variety of additives to lithium silicate glasses also showed major promotion of phase separation by P_2O_5, and, to a somewhat lesser extent, V_2O_5; effects of tetravalent oxides were minor in comparison. A recent study by Zhang and Ye (1989) showed that addition of V_2O_5 expands the miscibility gap in the sodium borosilicate system.

Several oxides in this category are used as nucleating agents in the manufacture of glass-ceramics because of their limited compatibility with the bonding network in silicate glasses (McMillan 1979). Amorphous phase separation commonly occurs prior to crystallization in glass-ceramic systems (McMillan 1979), notably in the titanosilicates developed as nuclear waste forms (Hayward 1988, Hayward et al. 1989). Tomozawa (1972) investigated the effects of nucleating agents on phase separation in binary sodium silicate glasses, and found that TiO_2 and ZrO_2, unlike P_2O_5, tend to suppress immiscibility when present at low concentrations. Thus, as discussed by Uhlmann and Kolbeck (1976) and McMillan (1979), the function of nucleating agents is not determined solely by their influence on phase separation, although it may be important in some cases (Cahn 1969).

Taylor et al. (1986) investigated the effect of added ZrO_2 on phase separation in a variety of sodium borosilicate glasses, covering most of the observable miscibility gap in the ternary system $Na_2O-B_2O_3-SiO_2$ (again excluding high-silica compositions > 70 mol% SiO_2). They found that ZrO_2 had little influence on T_b for any composition, usually lowering it slightly. The results indicate behaviour intermediate between the small and large trivalent cations, and this is consistent with relative cation field strengths, as shown in Figure 18. This investigation was limited to low ZrO_2 concentrations ($\leq$ 6 mol%), because of crystallization of ZrO_2 and/or $ZrSiO_4$, or incomplete dissolution of ZrO_2 in the melt, at higher concentrations. This problem was even more severe with TiO_2, and prevented any comparable work on the $Na_2O-TiO_2-B_2O_3-SiO_2$ system. A paper by Kozorog and Gorodetskaya (1980) on the sodium zirconium borosilicate system includes information on microstructures, but not miscibility limits.

Recently, data on phase separation in the system $Li_2O-Al_2O_3-TiO_2-SiO_2$ have been reported by Galakhov and Varshal (1987) and Galakhov et al. (1988). For many compositions in this system, submicroscopic heterogeneity, as opposed to distinct phase separation, was detected.

An item of interest, but little relevance to waste glasses, is the report by Tabata et al. (1983) on miscibility gaps in a number of binary germanate systems. These resemble those in the corresponding silicate systems, but are less extensive. More recent work in this area has been reported by Morinaga and Nakashima (1988).

Kawamoto et al. (1981a) have reported that addition of MoO_3 causes some expansion of the sodium borosilicate miscibility gap (much like V_2O_5, Zhang and Ye 1989). A related study (Kawamoto et al. 1981b) showed that partial

reduction of the molybdenum countered this effect, but extensive reduction to Mo^{4+} promoted crystallization of MoO_2 (cf. the limited solubilities of ZrO_2 and TiO_2, discussed above). The authors suggested that, under optimum redox conditions, both crystallization and phase separation could be minimized, but such precise control will be difficult to achieve in a radioactive waste-glass melting process. Note that this work (Kawamoto et al. 1981a, 1981b) refers to the influence of Mo on borosilicate phase separation, rather than the separation of a distinct Mo-rich phase (a soluble, yellow alkali sulphate-molybdate-chromate) that sometimes occurs in waste-glass processing (Lutze 1988, Morris and Chidley 1976). The latter process is akin to the sodium sulfate/silicate phase separation described by Pearce and Beisler (1965), and similar phase separation also seems to occur in the $Na_2O-WO_3-B_2O_3-SiO_2$ system, based on a recent report by Sarukhanishvili and Razmadze (1988). Tomozawa et al. (1979) have reported evidence that the addition of carbon. primarily to eliminate formation of the yellow, Mo-rich phase during glass melting, may also lower T_b for the resulting melt, as a consequence of reducing Fe^{3+} to Fe^{2+}, concomitant with Mo reduction.

Makishima et al. (1979) reported that small additions of P_2O_5, V_2O_5, MoO_3 or WO_3 to sodium borosilicate glasses decreased their durability towards aqueous corrosion after phase separation. Tomozawa et al. (1980) interpreted these results in terms of expansion of the miscibility gap, and consequent reduction in the silica content of the borate-rich phase, rather than a direct effect of the additives per se on the dissolution rate.

The influence of uranium on phase separation has not been investigated. Like molybdenum, it has a complex redox chemistry, with oxidation states 4, 5 and 6 all occurring in glass melts (Calas 1979, Schreiber and Balazs 1982, Schreiber et al. 1985). Diffusion studies by Dunn (1987) indicated that uranium (VI) is present in borosilicate melts as the well-known UO_2^{2+} cation, with an effective ionic radius of 0.174 nm. With respect to phase separation, therefore, UO_2^{2+} may be expected to behave like a very large alkaline-earth cation, although the affinity of UO_2^{2+} for anion complexation in the equatorial plane (perpendicular to the O-U-O axis of the cation) may promote phase separation more than might be expected from its effective ionic radius alone. The behaviour of uranium (V) would depend on whether it is present as UO_2^+ or a U^{5+} species with more nearly spherical coordination symmetry. Based on its field strength (Figure 18), uranium (IV) would be expected to be intermediate in behaviour between Zr and the rare earths. At fairly low concentrations (< 2 wt.%), it is unlikely that uranium will dramatically influence phase separation in typical waste-glass compositions. For high concentrations of Th or U, envisaged in certain fuel recycle schemes, some further research would be advisable, but it is likely that crystallization processes would be more important than amorphous phase separation in such cases.

11. CONCLUSIONS

From the foregoing discussions of phase separation in a variety of glass-forming borate, silicate and borosilicate systems, we can draw conclusions about the influence of various classes of oxides on phase separation.

i) The oxides of cations more weakly polarizing than Na (K, Rb, Cs) show very limited regions of immiscibility in their respective borosilicate systems, and tend to suppress immiscibility when substituted for Na_2O in sodium borosilicate glasses. The most important oxides in this group, in the context of nuclear waste management, are K_2O as a glass-modifying additive, and Cs_2O as a major fission-product component; Rb is a less abundant fission product (and is also present in fuel wastes as a decay product of radioactive Kr). For base-glass compositions lying near the edge of the sodium borosilicate miscibility gap, substitution of K for Na might be considered as a means of suppressing phase separation.

ii) A large number of oxides show more extensive regions of immiscibility in borosilicate systems than Na_2O. These are all oxides of cations more polarizing than Na^+, and include a number of fission-product oxides or possible glass additives. Examples include oxides of Li, Mg, Ca, Sr, Ba, Zn, Mn(II) and other divalent transition metals, La and other rare-earth elements including Y and Sc. These oxides tend to promote phase separation when added to glass compositions lying within the sodium borosilicate miscibility gap. They have little influence, however, on the boundaries of the gap. Thus, they do not tend to induce phase separation when <u>added</u> to a sodium borosilicate glass composition lying outside the miscibility gap. When <u>substituted</u> for Na_2O, they may induce phase separation, if the Na_2O content is reduced sufficiently for the composition to enter the miscibility gap. Most of the oxides in this group tend to promote crystallization when present in borosilicate glasses at high concentrations.

iii) Some oxides of very small trivalent cations, e.g., Al_2O_3, Ga_2O_3, tend to suppress phase separation, at least at low concentrations. Additions of small quantities (a few weight percent) of Al_2O_3 may thus be an appropriate method for avoiding phase separation in a waste glass; higher concentrations should be used with caution, since they may induce phase separation. Addition of Al_2O_3 to glass compositions, however, usually increases melt viscosity, necessitating higher process temperatures. This is not desirable because it increases losses of volatile radionuclides (e.g., Cs, Ru, Tc), and shortens the lifetime of structural components of the melter. Also, whereas K_2O and Al_2O_3 separately suppress phase separation, they are likely to be less effective when added together.

iv) A few strongly acidic oxides, all formally containing very small, highly charged cations, but in reality having a substantial co-valent contribution to their bonding, tend to promote phase sepa-ration, and expand the miscibility gap in the sodium borosilicate system. They also tend to separate in their own right as molten salt phases. Examples include SO_3, P_2O_5, V_2O_5, CrO_3, MoO_3 and probably WO_3. The presence of such oxides in a waste glass formulation should be minimized, by avoiding their presence in the waste streams as either process additives or impurities. The presence of Mo (fission product) and Cr (corrosion product) is probably unavoidable; control of redox conditions during glass melting and annealing is therefore needed to avoid conversion of these elements to their hexavalent states. In general, the ef-fect of elements with several oxidation states on phase separa-tion depends on the redox chemistry of the melt.

v) Many oxides, including most M_2O_3 and MO_2 species, have limited solubility in borosilicate melts. For such components, crystallization or incomplete dissolution may be of greater concern than amorphous phase separation. Many of these oxides, however, are refractory and insoluble, so their presence as discrete crystalline phases within a glass may not adversely affect durability.

vi) One oxide, ZrO_2, was found to have very little influence on phase separation in sodium borosilicates, apparently because Zr^{4+} is intermediate in polarizing power between Al^{3+} and Ga^{3+} (which suppress phase separation) and La^{3+} and related cations (which promote it).

In summary, although the influence of various oxides on phase separation of sodium borosilicate glasses is complex, few oxides actually expand the re-gion of immiscibility in the sodium borosilicate system. Phase separation is therefore not expected to be a problem in moderately loaded waste glasses (< 20 wt.% waste oxides), so long as the basic sodium borosilicate composition lies outside the observable miscibility gap and problematic components such as sulfate, phosphate and molybdate (VI) are minimized. These are the most important points to consider in tailoring a glass com-position to avoid phase separation. This is consistent with the findings of Engell and Roed (1982), who investigated the effects of simulated mixtures of fission products and glass-modifying additives on miscibility boundaries. They found a slight net suppression of phase separation by such mixtures. Finally, it is important to reiterate that amorphous phase separation can be a desirable process in some circumstances, and is an integral stage in the preparation of some novel waste forms, such as glass-ceramics (see Section 10) and "stuffed glasses" (see Section 4).

ACKNOWLEDGEMENTS

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