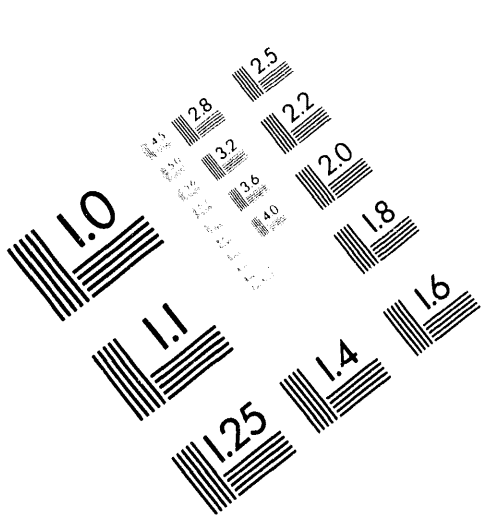

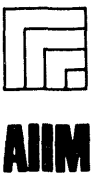

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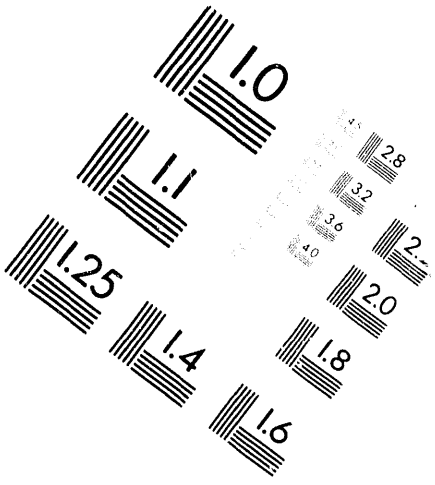

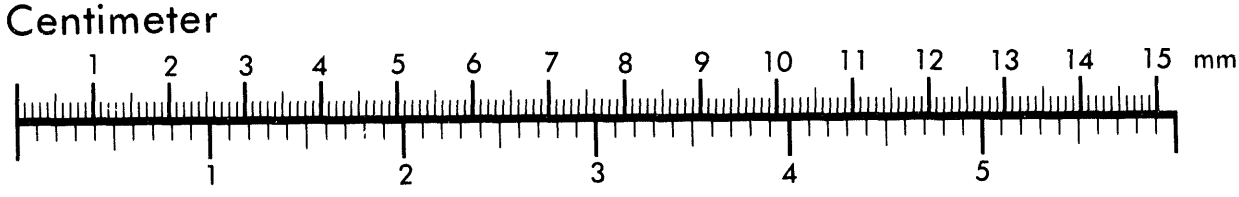

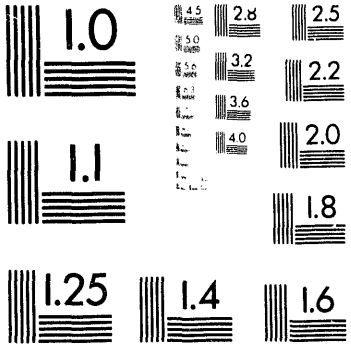

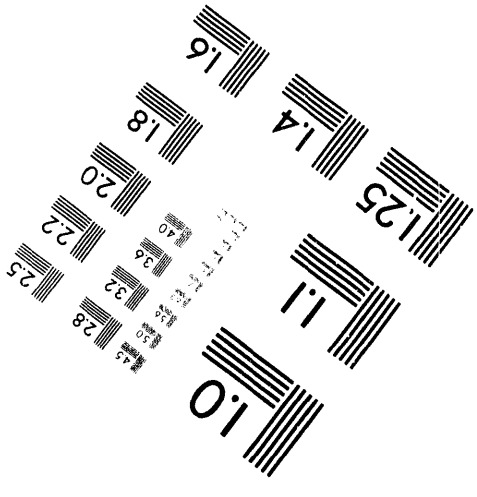

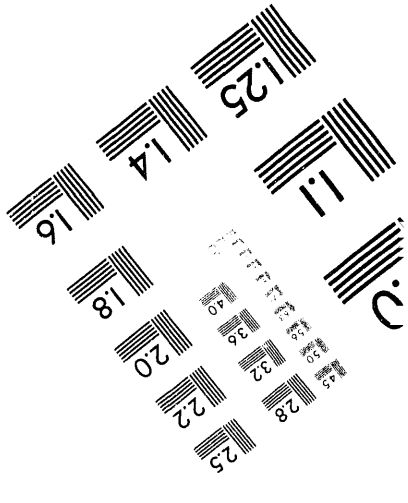

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PREDICTING LIQUID IMMISCIBILITY IN MULTICOMPONENT NUCLEAR WASTE GLASSES

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PREDICTING LIQUID IMMISCIBILITY IN MULTICOMPONENT NUCLEAR WASTE GLASSES

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ABSTRACT

Taylor's model for predicting amorphous phase separation in complex, multicomponent systems has been applied to high-level (simulated) radioactive waste glasses at the U.S. Department of Energy's Hanford site. Taylor's model is primarily based on additions of modifying cations to a Na_2O-B_2O_3-SiO_2 (NBS) submixture of the multicomponent glass. The position of the submixture relative to the miscibility dome defines the development probability of amorphous phase separation. Although prediction of amorphous phase separation in Hanford glasses (via experimental SEM/TEM analysis) is the primary thrust of this work; reported durability data is also provides limited insight into the composition/durability relationship. Using a modified model similar to Taylor's, the results indicate that immiscibility may be predicted for multicomponent waste glasses by the addition of Li_2O to the "alkali" corner of the NBS submixture.

INTRODUCTION

Amorphous phase separation commonly occurs in borosilicate glass systems. Depending on the developing microstructure, phase separation can profoundly affect glass properties, in particular, durability toward aqueous dissolution.[1,2,3] Equally important as the effect on durability is the predictability of amorphous phase separation development within multicomponent systems. Experimental determination of the miscibility dome(s), e.g., using the opalescence method,[4,5] has been well documented in binary silicate glasses, as well as in several alkali and alkaline earth borosilicate systems. As the systems become more complex, so does detailed mapping of miscibility domes. To empirically or theoretically predict miscibility domes, Tomozawa and Kawamoto[6] presented a method based on the similarity in shape of observed immiscibility boundaries of binary silicate systems and on a pseudobinary regular mixing equation. However, this method has not been applied to multicomponent borosilicate systems typical of nuclear waste vitrification. Charles,[7] Levin and Block,[8] Strand and Strand,[9] and Burnett and Douglas[10] developed alternative predictive techniques, which are also limited to binary and a few ternary systems.

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Limited work was performed on mapping immiscibility boundaries in quaternary (X_2O-MO-B_2O_3-SiO_2) systems, where X = Na or K, and M = Mg, Ba, Ca, Mn.[11,12,13] Unlike Chick et al.[14] and Tomozawa[15], who studied phase separation in nuclear waste glasses, yet made no attempt to model the immiscibility, Taylor[1] suggested a simple approach to predict immiscibility in complex borosilicate systems. His approach is based on the observation that the extent of immiscibility is related to the polarization power (or field strength) of the modifier cation.[16,17] Taylor also used the location of the Na_2O-B_2O_3-SiO_2 (NBS) submixture from the multicomponent glass relative to the miscibility dome to predict the development of amorphous phase separation. According to Taylor, some cations more polarizing than Na^+ (Li^+, Mg^{++}, Ca^{++}, Ba^{++}, etc.) further promote phase separation when added to a submixture composition lying within the NBS miscibility dome, but do not tend to induce it when added to a submixture lying outside the dome, assuming problematic components (SO_3, phosphates, and, molydates (VI)) are minimized.

Predicting liquid immiscibility in multicomponent glasses can be a complicated task. This paper applies Taylor's model to Hanford high level (simulated) radioactive waste glasses for the prediction of amorphous phase separation in complex, multicomponent systems.

EXPERIMENTAL PROCEDURES

A series of 24 normalized NBS submixture compositions were chosen [Figure 1(a)] that would allow a direct evaluation of Taylor's immiscibility prediction model. The immiscibility boundary shown is that defined by Haller et al.[18] These glasses were selected from 123 Composition Variation Study (CVS)[19] glasses defining an extensive compositional envelope [Figure 1 (b)]. Glasses were divided into high- and low-durability, based on the initial versions of the Waste Acceptance Preliminary Specifications (WAPS)[20,21] requiring the waste form be capable of limiting normalized elemental release rates for Na, B, Ce-137, and U-238 to less than 1 g/m^2/day averaged over the 28-day Materials Characterization Center-1 (MCC-1) test.[22] Since B is not involved in aqueous reactions, its normalized elemental release accurately measures the glass dissolution process. WAPS[23] now requires that the normalized releases of B, Li, and Na determined by the Product Consistency Test (PCT)[24] are less than the releases of these elements from the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) glass.[25] MCC-1 data have been used as the delineator for durability performance in this study since it minimizes the effect of precipitation reactions that occur in highly concentrated PCT solutions.

Although both high- and low-durability glasses were selected from within the immiscibility boundary, of primary interest was an evaluation of select high-durability glasses that lie within the dome of the NBS submixture but shift outside with the addition of other oxides to the normalized submixture. Analysis of these glasses should demonstrate whether the high durability is a result of amorphous phase separation (due to the developing microstructural type) or whether the addition of other oxides "pulls" the high durability glasses outside the immiscibility boundary. The remaining glasses were chosen to represent a cross section of compositional positions lying outside the dome.

The simulated waste glasses have a thermal history corresponding to the predicted canister

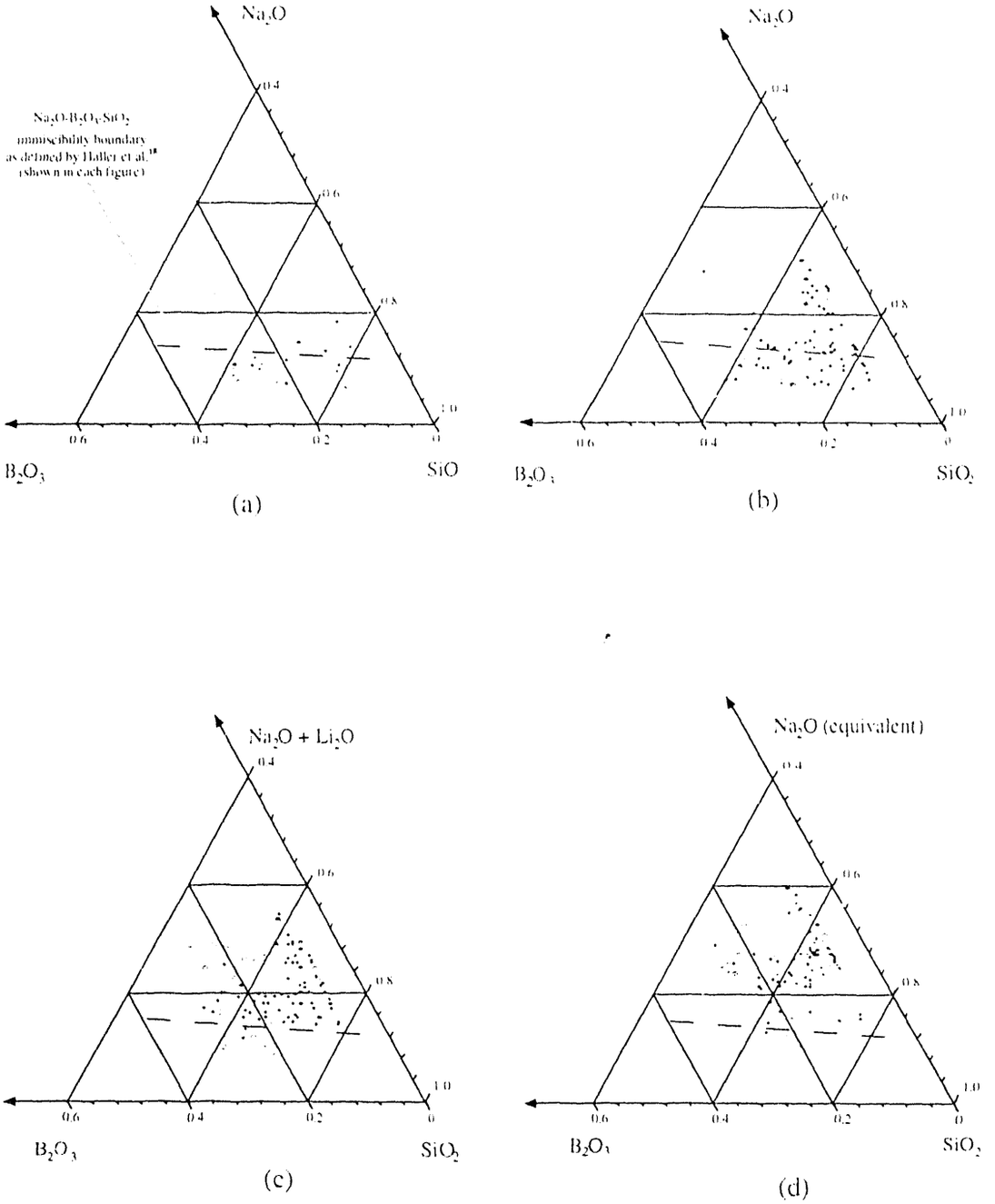

Figure 1. Various Normalized Submixtures Used for Model Evaluation and Selection. The different normalized submixtures include (a) NBS (selection), (b) NBS, (c) NLBS, and (d) NBS (equivalent). Solid points (•) and open circles (○) represent high-($B<28$ g/m^2) and low-($B>28$ g/m^2) durability glasses, respectively.

centerline cooling schedule as defined by the DWPF at the Savannah River Technology Center.[b] Amorphous phase separation was evaluated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. For the SEM analyses, a freshly fractured glass surface was etched with a 5% HF solution at room temperature. Enhanced etching will occur in "low durability" areas (SiO_2-deficient) providing surface relief if amorphous phase separation exists. Due to detectability limits of the SEM, TEM was used as a secondary analytical tool to confirm the presence or absence of amorphous phase separation in select glasses. TEM sample preparation involved thin sectioning, dimple grinding, and ion milling to produce sufficiently thin edges for direct electron transmission.

RESULTS AND DISCUSSION

Table I shows the SEM results for the 24 selected CVS glasses in terms of amorphous phase separation for three normalized submixtures. The glasses are initially classified based on MCC-1 durability data (i.e., low and high durability). The descriptive microstructural characteristics are based on the SEM analyses and are classified into three categories defined as homogeneous or non-phase separated (-), phase separated (Y), and highly crystalline (C). The position of each glass with respect to the immiscibility boundary is also given for each submixture. "Y" corresponds to a glass composition lying within the immiscibility boundary, while "-" defines a composition outside the boundary.

As predicted by Taylor, all glasses lying outside the miscibility dome in the normalized NBS submixture were morphologically homogeneous with respect to amorphous phase separation. Contrary to Taylor's predictions, the high-durability glasses lying within the immiscibility boundary showed no sign of amorphous phase separation. Amorphous phase separation or a high degree of crystallinity was detected by SEM in six of the eight low-durability glasses lying inside the dome. Of the 24 glasses studied, one-half conflicted with Taylor's rules for immiscibility prediction within multicomponent systems.

Thus far, only SiO_2, B_2O_3, and Na_2O have been considered for the submixture's ability to predict amorphous phase separation. Due to the compositional complexity of the CVS glasses, consideration of other oxides may improve the predictability. The high polarization power and ability to extend the immiscibility region in terms of both temperature and composition in the B_2O_3-SiO_2 system make Li_2O a primary oxide for consideration.

Figure 1 (c) shows the durability data of the CVS glasses in terms of a normalized Na_2O-Li_2O-B_2O_3-SiO_2 (NLBS) submixture. Upon the addition of Li_2O to the "alkali" corner of the ternary (on a mass fraction basis), the majority of the high-durability, nonphase separated glasses moved outside the immiscibility boundary that initially were located within the boundary as defined by the NBS submixture [compare Figures 1 (b) and (c)]. This effect is also reflected in Table I. Note the two low-durability, nonphase separated CVS glasses, CVS2-90 and CVS2-26, also shifted outside the boundary in the NLBS submixture.

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[b] M.L. Elmore, "Evaluation of Turntable Design Concepts for the HWVP," HWVP-86-V1132A, Pacific Northwest Laboratory, Richland, Washington (1986).

TABLE I. Predicted Phase Separation for Various Submixtures and the Microstructural Analysis of the 24 CVS Glasses as Defined by the SEM.[c]

	CVS Glass	Microstructure	Submixture Prediction NBS	NLBS	NBS (equiv)
High Durability	CVS2-30	-	Y	Y	Y
	CVS1-11	-	Y	Y	-
	CVS2-52	-	Y	-	-
	CVS2-6	-	Y	-	-
	CVS2-43	-	Y	-	-
	CVS2-74	-	Y	-	-
	CVS2-24	-	Y	-	-
	CVS1-10	-	Y	-	-
	CVS2-12	-	Y	-	-
	CVS2-73	-	Y	-	-
	CVS1-7	-	-	-	-
	CVS2-47	-	-	-	-
	CVS2-38	-	-	-	-
Low Durability	CVS1-4	Y	Y	Y	Y
	CVS2-29	Y	Y	Y	Y
	CVS2-31	Y	Y	Y	Y
	CVS1-9	C	Y	Y	Y
	CVS2-80	C	Y	Y	Y
	CVS2-78	C	Y	Y	Y
	CVS2-90	-	Y	-	-
	CVS2-26	-	Y	-	-
	CVS1-14	-	-	-	-
	CVS2-25	-	-	-	-
	CVS2-81	-	-	-	-

Low-durability glasses characterized by either amorphous phase separation or by a high degree of crystallinity remained within the immiscibility boundary of the NLBS submixture. In this particular submixture, only two glasses (CVS1-11 and CVS2-30) did not follow the "modified" rules for predicting immiscibility in Hanford's complex, multicomponent systems. Amorphous phase separation was not detected in either glass, but both are high-durability glasses that lie within the immiscibility dome.

SEM and TEM micrographs of CVS2-30 are shown in Figures 2 (a) and (b), respectively. An unusual pitting within and immediately surrounding the crystalline phase (hematite) is shown in

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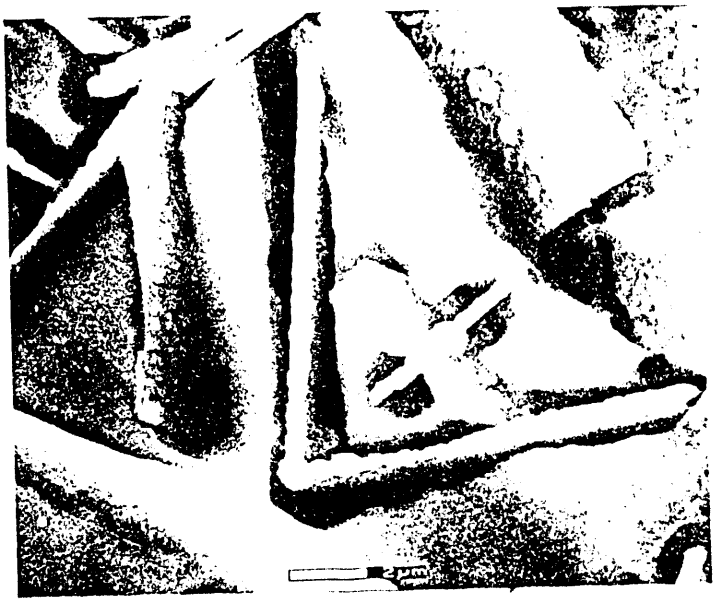
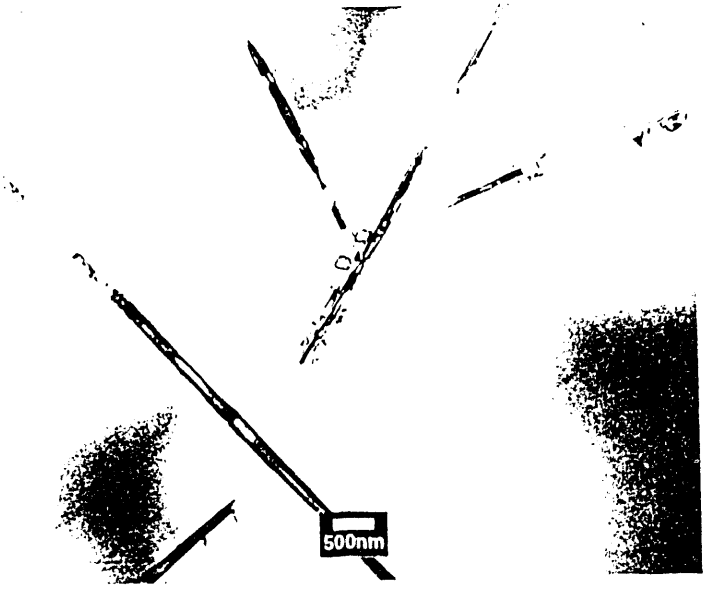
[c] Microstructural characteristics as defined by the SEM analyses are classified into three categories. Symbols representing each class are (-) homogeneous or nonphase separated, (Y) phase separated, and (C) highly crystalline. To define each compositional position with respect to the immiscibility boundary for each submixture, "Y" corresponds to a glass composition lying within the immiscibility boundary, while "-" defines a composition outside the boundary.



(a)



(b)

Figure 2. SEM (a) and TEM (b) Micrographs of CVS2-30

the SEM micrograph. TEM analysis [Figure 2 (b)] shows a homogeneous glassy matrix in which the crystalline phase is embedded. The Hanford CVS glasses lying outside the dome in the NLBS submixture showed no sign of amorphous phase separation based on the SEM analysis. The results of the normalized NLBS submixture indicate that immiscibility within multicomponent systems may be more accurately predicted by the addition of Li_2O to the "alkali" corner of the ternary.

The final system listed in Table I categorizes the CVS glasses based on a normalized NLBS submixture, but instead of adding Li_2O on a mass fraction basis and normalizing, the Li_2O is added as an equivalent Na_2O content. The equivalent Na_2O content is defined as:

$$\kappa * Li_2O \text{ (Mass \%)} + Na_2O \text{ (Mass \%)} = Na_2O \text{ (equivalent)}$$

where $\kappa = 61.98 / 29.88$, the ratio of the molecular masses of Na_2O and Li_2O, respectively. This submixture is identified as NBS (equivalent) throughout this report.

Figure 1 (d) shows the results of the NBS (equivalent) submixture. The most noticeable effect is a shift of the majority of glasses toward the "alkali" corner of the ternary leaving a select number of glasses below the constant normalized 20% Na_2O (equivalent) line. The low-durability glasses remained relatively stable with respect to their compositional positioning in this particular submixture. Only eight glasses remained within the immiscibility boundary seven of which were evaluated by SEM. Of those seven, six were characterized by amorphous phase separation or a high crystalline volume percent.

The high-durability, nonphase separated CVS1-11 glass shifted outside the immiscibility boundary, leaving CVS2-30 as the only glass that cannot be accounted for by the current submixture. As expected, all glasses outside the dome show no sign of amorphous phase separation in the NBS (equivalent) submixture.

Figure 3 shows a collage of various CVS glasses within the NBS (equivalent) submixture. The observed SEM microstructures as well as their positions relative to the miscibility dome are shown. The four glasses lying outside the dome (CVS2-24, 26, 52, and 74) showed no sign of amorphous phase separation. Similar microstructures were characterized by limited crystallization isolated in a "homogeneous" glassy matrix. Of those glasses within the dome, the high degree of crystallinity associated with CVS1-9 and CVS2-78 (Figure 3) may be in part the result of prior amorphous phase separation serving as a precursor to nucleation/crystallization mechanisms.[26] Amorphous phase separation and less extensive crystallization was observed in a quenched sample of CVS1-9. The CVS2-29 and CVS2-31 glasses were characterized by amorphous phase separation. The scale of separation appears to be more extensive in CVS2-29 relative to that detected in CVS2-31 (shown in Figure 3).

Crystallization may affect the formation probability of amorphous phase separation in the glass matrix. A crystal develops by extracting particular element(s) from the surrounding matrix. Depending on the type and degree of crystallization, the composition of the adjacent glassy matrix may be more or less favorable to the formation of amorphous phase separation, than if no crystallization occurred. For example, if a particular normalized submixture crystallizes a Li_2O-

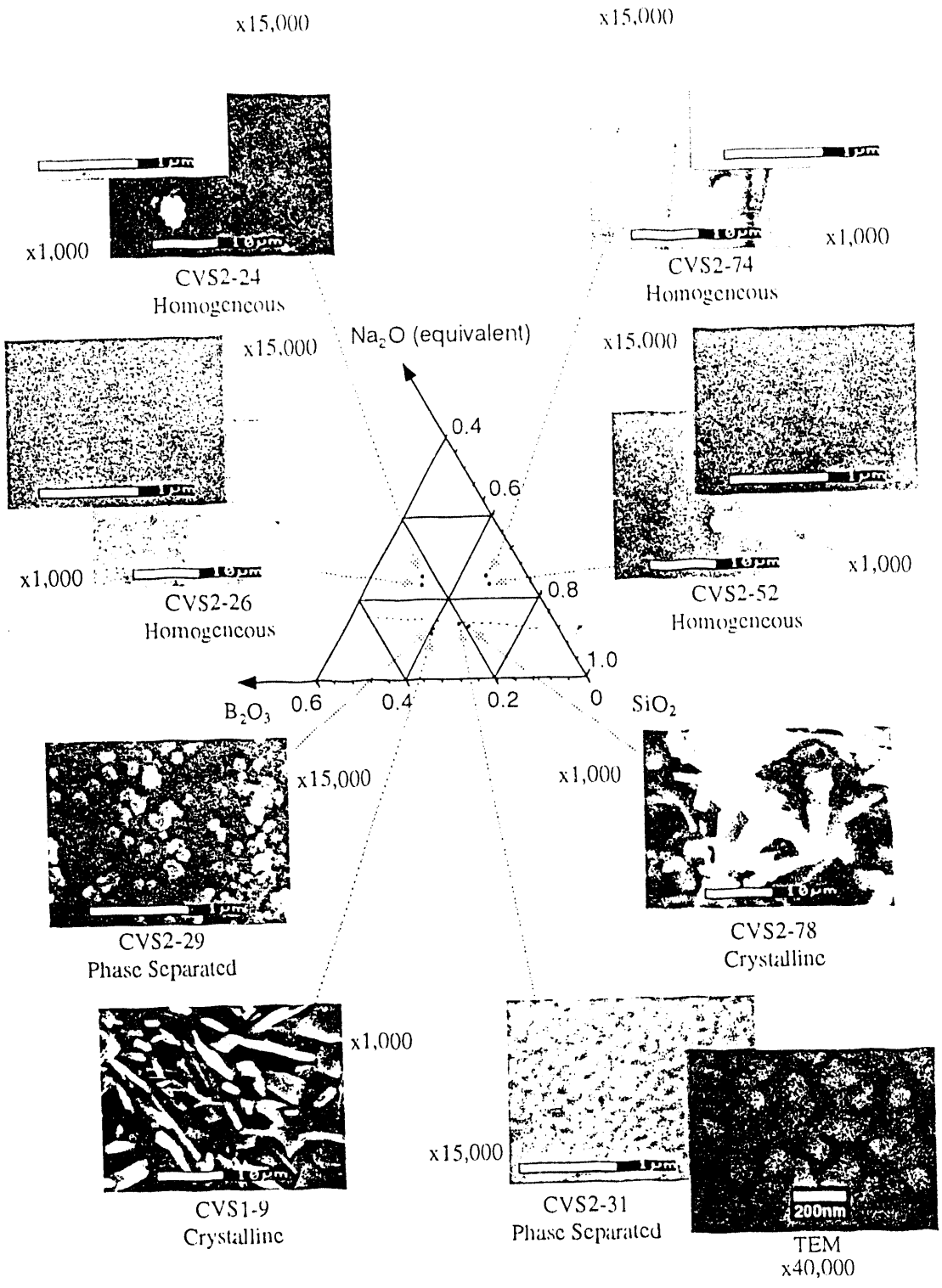


Figure 3. SEM Microstructures of Various CVS Glasses Within the NBS (equivalent) Submixture

based crystal, the glassy matrix would become depleted in lithium. If the degree of crystallization is extensive enough, the composition of the glass matrix may be "pulled" into the miscibility dome causing amorphous phase separation to occur in an otherwise "predicted" homogeneous glass. The converse of this argument is also a possibility.

CONCLUSIONS

Amorphous phase separation has been observed in a limited number of Hanford simulated waste glasses. The use of the normalized NBS submixture may be inadequate in its ability to predict amorphous phase separation for Hanford's compositionally complex glasses. Several high-durability, nonphase separated glasses were studied which lie within the miscibility dome of the NBS submixture.

With the addition of Li_2O to the NBS submixture, either as an equivalent Na_2O content or normalized on a mass fraction basis, the experimental results indicate that amorphous phase separation may be more accurately predicted for multicomponent systems. The increased predictability precision is illustrated by the system's capacity to effectively sort those glasses which were experimentally determined to be phase separated from the "homogeneous" glasses. Although these submixtures [NLBS and NBS (equivalent)] seem to adequately predict amorphous phase separation, neither is 100% accurate based on the SEM analysis. This is not surprising due to the compositional complexity of the glasses involved.

Because of the limited number of glasses evaluated in this research, it is difficult to conclude which of the two Li_2O-based submixtures should be used as an immiscibility predictor. Only two glasses that were evaluated define the difference between these two submixtures. In fact, other submixtures need to be evaluated for their ability to predict immiscibility within these complex glasses. For example, a normalized Na_2O-Li_2O-B_2O_3-SiO_2-Al_2O_3-ZrO_2 submixture may enhance the prediction accuracy since Al_2O_3 and ZrO_2 usually suppress phase separation and may aid in the development of the three-dimensional network.

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