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Scoping Studies for Low-Temperature Melting ZnO-Bi_2O_3-(B_2O_3, SiO_2) Binder Glass

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ABSTRACT

Low melting point glass systems were explored as candidates for binders of solid oxide nuclear wastes which include volatile elements such as radioactive iodine. The base glass systems considered were ZnO-Bi_2O_3-B_2O_3 and ZnO-Bi_2O_3-SiO_2, with specific compositions selected for synthesis trials based on available phase diagrams and a desire to explore the whole glass-forming region. Ten compositions were synthesized by melt quenching. Promising candidate glass binders were selected based on absence of crystallization and favorable thermal properties, including low glass transition temperature (T_g) combined with a high crystallization onset temperature. These thermal properties indicate stable glass forming which would lead to sintering behavior needed for glass binding. Compositional effects include: higher Bi_2O_3 content lead to lower T_g values, high ZnO content generally led to crystallization on quench, and high SiO_2 content resulted in requirements for excessively high melting temperature. 25ZnO-15Bi_2O_3-60B_2O_3 was down-selected for some detailed crystallization versus time and temperature studies.

INTRODUCTION

The proposed aqueous reprocessing of used nuclear fuels aims to facilitate the capture of I-129 gas which is hazardous both in environmental and biological systems [1]. One possible scenario for the fate of iodine is that it is captured in a combined caustic scrubber solution and downstream packed bed with iodine sorbents [2]. One concept is to produce aluminosilicates with the liquid waste (caustic scrubber solution or eluted sorbent bed) and consolidate them by sintering with a low-temperature glass binder. The optimization of the immobilization of a powder containing volatile iodine requires ensuring that thermal and chemical behavior support low temperature consolidation without releasing iodine during the process [3]. The use of a low-temperature glass binder for iodine waste forms has been considered before, notably glass compositions containing high amounts of ZnO and Bi_2O_3 [4-6]. The thermal integrity and non-toxic nature of ZnO-Bi_2O_3-B_2O_3 and ZnO-Bi_2O_3-SiO_2 glasses are factors which have driven the study of such low-temperature systems for use in nuclear waste immobilization [7-9].

Dyamant et al [10] showed the inverse relationship between increasing Bi_2O_3 fractions and T_g values, where bismuth oxide was found to be a modifier in the SiO_2–B_2O_3–Bi_2O_3–ZnO quaternary glass system. A similar study in a 3-component ZnO-Bi_2O_3-B_2O_3 system reported by Komatsu et al [11] observed lowest T_g values for peak Bi_2O_3 concentrations and the reverse for borate-rich glasses. The structural integrity of select compositions of ZnO-Bi_2O_3-SiO_2 glasses were reported to be influenced by higher SiO_2 content in the system driving the formation of Si-O-Si cross linkages [12]. These glasses were also considered for their electric and dielectric properties, revealing temperature independence of certain conductivity mechanisms. Outside of binder and conductivity studies, such glass systems have been considered for applications requiring good wettability, such as electronics soldering, governed by its viscosity and low-melting temperature [13]. High and low B_2O_3 content in such low-temperature glass has been reportedly linked to improved structural stability and crystallization initiation, respectively [14]. If tendency towards crystallization were a concern, which depends on the specific applications, bulk glass formability and associated thermal correlations were considered, and 20-60 mol% was the recommended B_2O_3 content range for avoiding crystallization [15].

This study aims to investigate factors that drive bulk glass formability in ZnO-Bi_2O_3-B_2O_3 and analogue ZnO-Bi_2O_3-SiO_2 glasses, where SiO_2 is substituted for B_2O_3 on a molar basis. Low temperature melting, degree of crystallization, glass transition temperature, and sintering temperature windows of these studied glasses are considered, in order to down-select candidate glasses for consolidation with iodine-containing powdered waste.

EXPERIMENTS

All starting chemicals used were reagent-grade: zinc oxide (Fisher Scientific 99.9%), bismuth(iii) oxide (Fisher Scientific 99.9%), boric acid (Alfa Aesar 99.99%) and, silicon dioxide (US Silica). Using conventional glass melt-quench techniques, precursor materials were batched and mixed homogeneously via a vortex mix before being placed in a Pt10%Rh crucible, melted in a resistance furnace (DelTech) for 1 h at temperatures between 1000°C and 1400°C. Thereafter, molten glasses were rapidly removed from the furnace, poured out, and thus air-quenched on an Inconel plate; in some cases, expedited quenching was achieved by dipping the outside of the crucible midway into water. Obtained bulk pieces were crushed for 6 seconds in a tungsten carbide mill dish, resulting in powders with an average particle size of ~40 μm. Crushed glass was further investigated with an X-ray diffractometer (XRD, PANalytical X'pert Pro) using Cu Kα radiation ($\lambda = 1.5406$ Å) at 45 kV and 40 mA, and scans performed from 5-90° 2θ with step size of

0.5° and 10 s per step. XRD patterns were generated from summation of five sequential scans. For thermal characterization, crushed powders were studied by differential thermal analysis (DTA, TA Instruments SDT-Q600) to assess glass transition temperature (T_g), peak crystallization exotherm temperature (T_x), and melting point (T_m). About 30 mg of each glass powder was heated at 10°C /min under 100 mL/min nitrogen from ambient to 1200°C in platinum crucibles. Selected glasses were studied for their crystallization behavior, by heating ~40 µm average particle size powders to various temperatures near and above T_g for 1-4 h, then quenching and measuring any crystallization by XRD.

RESULTS AND DISCUSSION

Selection of glass compositions for study in the ZnO-Bi_2O_3-B_2O_3 and ZnO-Bi_2O_3-SiO_2 systems was informed by the available phase diagrams as follows.

By starting close to the edges of the glass forming region of the ZnO-Bi_2O_3-B_2O_3 system, as determined by Zargarova and Kasumova [16], end-member component-rich glasses were explored to investigate the overall bulk glass formability of the region (Table 1). These included Zn-rich (60 mol% ZnO), Bi-rich (50 mol% Bi_2O_3) and B-rich (60 mol% B_2O_3) glasses (Figure 1). Consistent with previous studies, the Bi-rich glass had the lowest T_g, and was fully XRD amorphous on quench, but had a limited sintering window. The sintering window is here defined as the ΔT temperature gap between T_g and the lowest T crystallization peak or crystallization onset temperature. Crystallization on quench was only observed in the Zn-rich borate sample. By XRD, the crystallized phases were identified as $Zn_3B_2O_6$ and $Bi_4B_2O_9$. From the ternary phase diagram in Figure 1, this behavior could be expected, as this selected composition is located just outside of the glass forming range. Towards the proposed consolidation goal, the high boron glass performed best in terms of sintering window (185°C) with a T_g of ≈513°C.

Analogous compositions to the borates but in the ZnO-Bi_2O_3-SiO_2 ternary phase diagram (Figure 2), based on Skorikov et al [17], were also synthesized. Increasing silica fractions in the silicate system made it impossible to melt at lower temperatures and shorter time intervals, thus glasses were melted for longer or at temperatures ~100-400°C higher than those for the borate series. Ultimately, the Si-rich sample (60 mol% SiO_2) remained unmelted at 1100°C, and no higher temperatures were explored. The high zinc sample (60 mol% ZnO) crystallized out Zn_2SiO_4, ZnO and $Bi_{12}SiO_{20}$ on quenching from 1400°C, as identified by diffraction data (Figure 3). The high Bi composition (50 mol% Bi_2O_3) produced an X-ray amorphous homogeneous glass with no visible signs of phase separation.

To explore changing the melting temperature and reducing the crystallization, several other glasses were formulated and synthesized with lower SiO_2 or lower ZnO. In following a study on similar glass systems for core/shell ^{129}I waste forms [5], a 50 mol% ZnO composition analogous to a commercially available glass (Ferro 2922 [18]) was batched, melted at 1400°C, and rapidly quenched in water to reduce the amount of surface crystallization. Diffraction data (Figure 3) revealed the presence of $Bi_{12}SiO_{20}$ peaks. Note that is difficult for diffraction to differentiate small amounts of $Bi_{12}SiO_{20}$ from similar phases like γ-Bi_2O_3 or Bi_2O_{4-x} [19], but the silicate version sillenite is expected due to the position of the composition in the Alkemade triangle of the phase diagram.

Low zinc glasses (20 mol% ZnO) from the silicate series have a T_g range of 400°C-500°C, with higher Bi_2O_3 fractions producing a T_g lower than 440°C (Table 1). By comparison, high zinc samples (≥25 mol% ZnO) in the silicate series had T_g >485°C, compared to <450°C in the borate series. A 1:1 Bi_2O_3/SiO_2 glass reported the lowest T_g at ≈405°C and a sintering window of ≈39°C.

TABLE 1. Compositions in the silicate (1-7) and borate (8-10) systems. Listed also are melting conditions, XRD-observed phases after quenching (AQ) if any, glass transition temperatures (T_g) and sintering window ($\Delta T = T_{x,onset} - T_g$)

No.	ZnO (mol%)	Bi_2O_3 (mol%)	SiO_2 (mol%)	B_2O_3 (mol%)	Synthesis conditions	AQ Phases by XRD	T_g (°C)	ΔT (°C)	Down-selected
1	25	50	25	-	1400°C-1 h	Glass	376	62	X
2	60	15	25	-	1400°C-1 h	Zn_2SiO_4, ZnO, $Bi_{12}SiO_{20}$	578	40	
3	25	15	60	-	1100°C-2h	No melt	-	-	
4	20	40	40	-	1000°C-1 h	Glass	405	39	
5	20	30	50	-	1000°C-1.5 h	Glass	500	33	
6	30	20	50	-	1000°C-1.5 h+ 1100°C-2 h	Glass	533	43	
7	50	20	30	-	1400°C-1 h	$Bi_{12}SiO_{20}$	488	71	X
8	25	50	-	25	1000°C-1 h	Glass	363	24	X
9	60	15	-	25	1000°C-1 h	$Zn_3B_2O_6$, $Bi_4B_2O_9$	447	36	
10	25	15	-	60	1000°C-1 h	Glass	513	186	X

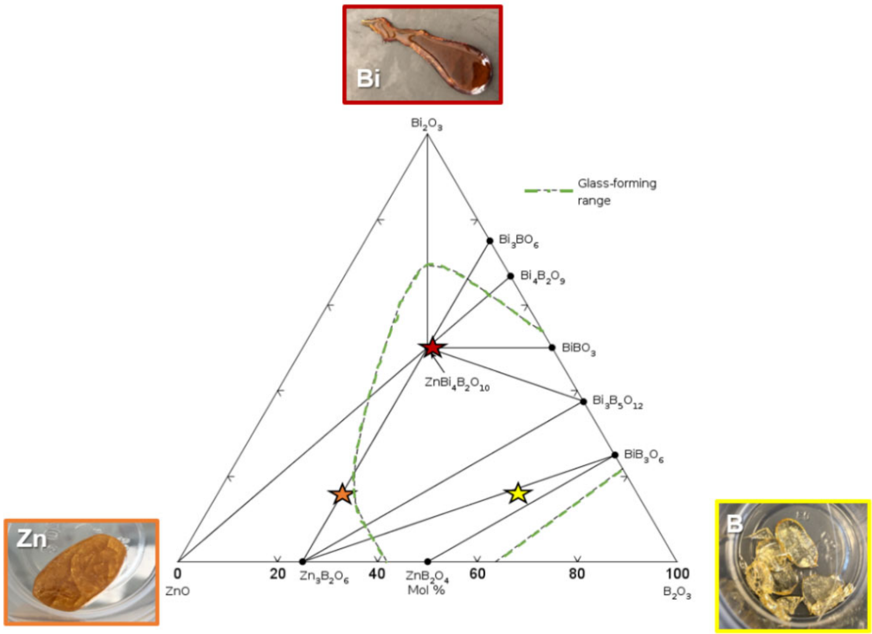

Fig. 1 Ternary phase diagram of ZnO-Bi_2O_3-B_2O_3 system showing compositional location of studied samples in or near the borate glass-forming region. Insert photo borders have colors matched to symbols, and the numbers shown correspond to Table 1. Top: As quenched Bi-rich glass (red, #8); Left: As-quenched Zn-rich sample (orange, #9), Right: As-quenched B-rich glass (yellow, #10).

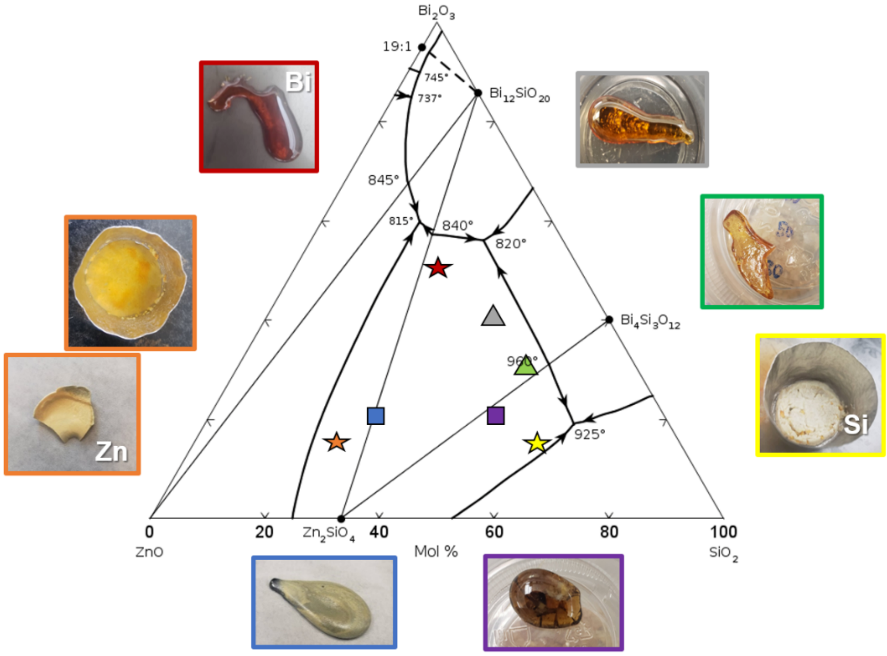

Fig. 2 Ternary phase diagram of ZnO-Bi_2O_3-SiO_2 system, showing compositional locations of studied samples in the silicate glass system. Insert photo borders have colors indicated in parentheses which are matched to symbols, and the numbers shown correspond to Table 1. Element labels indicate samples with maximum concentration of that element. Counterclockwise from upper left: As-quenched Bi-rich glass (red, #1); As-quenched Zn-rich glass: 1200°C melt, unlabeled; 1400°C melt, labeled "Zn" (orange, #2); 50ZnO-20Bi_2O_3-30SiO_2 (blue, #7); 30ZnO-20Bi_2O_3-50SiO_2 (purple, #6); unmelted Si-rich sample (yellow, #3), 20ZnO-30Bi_2O_3-50SiO_2 (green, #5), 20ZnO-40Bi_2O_3-40SiO_2 (grey, #4).

Differential thermal analysis was conducted on all of the compositions producing mostly a glassy phase (see Supplementary material for figures). For the borate system, multiple crystallization peaks were evident in lower temperature regimes or the Zn-, Bi-rich glasses (~503-527°C for the lowest temperature peak) as compared to much higher temperatures for the B-rich glass (720°C for the lowest crystallization) (see Figure S-1). Melting point data varied across the studied glasses in this system with 640-665°C as the range for Zn-, Bi-rich glasses and 840-880°C for the B-rich glass. The silicate system reported multiple crystallization peaks between 470-730°C for low Zn glasses (Figure S-2) and between 570-716°C, exothermic peaks were observed in low Bi glasses (Figure S-3). Studied silicate glasses had higher melting temperatures in the neighborhood of 800-960°C which is attributed to SiO_2 in the system as opposed to B_2O_3.

The ultimate goal of this glass development is to consolidate aluminosilicates, containing waste ions, with binder glass material by sintering at low temperature in order to ensure iodine retention. Pursuant to this goal, the glasses evaluated here were downselected (Table 1) on the basis of factors such as low glass transition temperature (T_g) and large sintering window (ΔT). This rationale should ensure thermal integrity, controlled crystallization and most importantly, iodine retention. As identified in Table 1, 25ZnO-50Bi_2O_3-25SiO_2 was selected for its low T_g (lowest in the silicate series) and reasonably high ΔT; 50ZnO-20Bi_2O_3-30SiO_2 had the highest ΔT in the silicate series, and was similar in composition to a commercially available glass. In the borate series, 25ZnO-50Bi_2O_3-25B_2O_3 had the lowest T_g (of all the studied glasses, attributed to its high bismuth fraction) while 25ZnO-15Bi_2O_3-60B_2O_3 had the highest ΔT in the series and of all the glasses considered in this scoping study.

One candidate glass was selected and studied in detail for its crystallization behavior at various temperatures without any aluminosilicate additions. The choice of 25ZnO-15Bi_2O_3-60B_2O_3 was informed by the size of its sintering window (highest ΔT) which is useful in extending viscous flow of the glass composite prior to crystallization of the glass. According to XRD, heat treatment of this glass for 4 h at 500°C, or 1 h at 550°C, retained its amorphous structure. A 1 h heat treatment at 600°C promoted the growth of a zinc tetraborate phase (α-ZnB_4O_7) whose fraction appeared to increase when heat treating at 1 h at 750°C (Figure 3). Longer heat treatment, 4 h, at 600°C or 650°C resulted in a different phase becoming the major one, Bi3B5O12, with ZnB_4O_7 still being evident. As the T_g of this glass is 513°C, it is promising for viscous sintering at temperatures below crystallization of the glass and iodine release from aluminosilicates like sodalite (<900°C). Further studies are planned to optimize the sintering behavior, accounting for densification, open and closed porosity, dimensional change, and encapsulation of the waste oxides.

Other glass candidates studied here may also be useful, but at present is not yet known whether the glasses will interact with the waste on sintering, or whether this would necessarily be undesirable, as the ultimate goal is to ensure good chemical durability in the presence of water and retention of the radioactive ions when exposed to environmental conditions relevant to a waste repository. The main reason for targeting single-phase glasses without crystals in this initial study was to simplify the system, since multi-phase (i.e., glass + crystalline phases) can make understanding performance of the final glass-composite waste form more difficult, and thus the design intent was to keep the binder glass distinct from the crystalline waste phases.

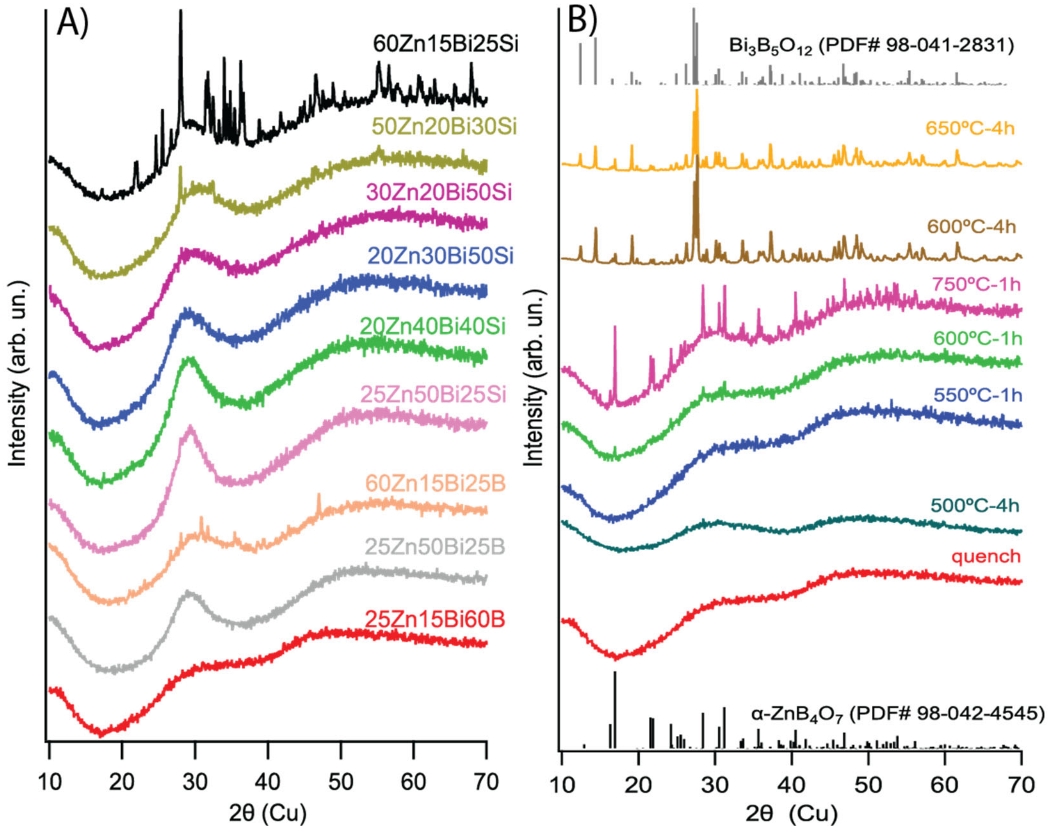

Fig. 3 Diffraction measurements of candidate glasses. **A)** XRD of all as-quenched compositions. **B)** Candidate glass (25ZnO-15Bi_2O_3-60B_2O_3) powder, heat treated at various temperatures and times, showing also the patterns of the observed crystalline phases.

CONCLUSIONS

This investigation reaffirmed, across the two glass systems studied, the driving effect of Bi_2O_3 and B_2O_3 contents on lowering glass transition temperatures and maintaining a fully amorphous phase. The B-rich glass was observed to be a good performer in terms of a sizable sintering window, an advantage for maintaining viscous flow prior to crystallization. In both the silicate and borate series, Bi-rich glasses reported the lowest glass transition temperatures of 376°C and 363°C, respectively. A similar composition to a commercially available binder glass, previously studied, was observed to phase-separate with a slightly higher T_g value than contained in the product literature (488°C-observed, 465°C-Ferro 2922 datasheet). Crystallization occurs in both the SiO_2 and B_2O_3 series of glasses containing at least two of the 3 metals, and the dominant phase depends on heat treatment time. Further experiments will take the downselected glasses from this study and perform consolidation and sintering with the aluminosilicate waste, followed by investigation of any crystallization and reaction products and ultimately chemical durability.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

COMPLIANCE WITH ETHICAL STANDARDS

Conflict of Interest: The authors declare no known conflicts of interest.

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