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Glass matrices for immobilizing nuclear waste containing molybdenum and phosphorus

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ABSTRACT

Vitrification has been selected in France as the process for immobilizing high-level waste arising from spent fuel reprocessing. Some high-level solutions generated by reprocessing legacy fuel contain high molybdenum concentrations. Molybdenum is known to be sparingly soluble in conventional borosilicate glass, and work is in progress to find suitable glass formulations for such waste. The results of a basic study to identify borosilicate glasses composition zones of potential interest are discussed. A vast composition range was investigated by defining a fine mesh. The limits considered to delimit the range of the study were intentionally extended to identify formulations such as SiO_2–B_2O_3–Al_2O_3–Na_2O–P_2O_5 that are of interest for vitrifying molybdenum-rich waste. Observation of more than 50 tested mixtures revealed two composition zones of potential interest. One forms a homogeneous glass after melting at 1300 °C and rapid cooling; the other vitreous material comprises unconnected microbeads uniformly dispersed in a borosilicate glass.

1. Introduction

Nuclear waste containment in glass has several advantages: it guarantees the stability of the waste package over very long time periods and reduces the waste volume. Vitrification has been used for several decades in France and other countries to immobilize high-level nuclear waste. The first difficulty in fabricating a package is to find glass formulations capable of chemically incorporating the minerals contained in the waste. The glass formulations must be compatible with synthesis by vitrification processes suitable for industrial production in a radioactive environment, and must also produce a matrix that meets long-term behavior requirements. Borosilicate glass compositions are particularly suited to these requirements.

Among the chemical elements in reprocessing waste, molybdenum is one of the most difficult to incorporate in borosilicate glass. In fission product solutions generated by reprocessing UMo fuel, which was used in the past in gas-graphite reactors, molybdenum is the major chemical element in the waste, and is accompanied by phosphorus, also at high concentrations. In order to develop a glass formulation for this wasteform, it is therefore of particular interest to investigate the SiO_2–B_2O_3–Na_2O–Al_2O_3–P_2O_5–MoO_3 phase diagram in greater detail. This study focuses on composition ranges with potential for containment of nuclear waste rich in molybdenum and phosphorus.

2. State of the art of molybdenum immobilization in glass

The results obtained to date with borosilicate glass compositions such as those generally formulated for nuclear waste containment show that separate molybdate phases appear if the molybdenum concentration exceeds a few percent. The maximum MoO_3 concentration in a silicate glass appears to be 4 wt%; this limit has been reached in R7/T7 glass samples at laboratory scale [1]. This solubility limit could be slightly increased by fabricating the glass under more reductive conditions than usual. Lutze [2] described an example of glass production under reducing conditions to increase the molybdenum solubility limit from 2.5 to 3.0 wt%. A borosilicophosphate formulation containing 16 wt% MoO_3 was investigated by the CEA; to enhance the chemical durability of this formulation it must be produced under reducing conditions [3]. Very limited data are generally available concerning high molybdenum loading in silicate glass outside the R7/T7 borosilicate glass composition range [4–7]. Phosphate glasses or borate glasses are capable under certain conditions of incorporating larger quantities of molybdenum [3,8]. These glass formulations were developed for non-nuclear applications, however, and have not been demonstrated at a level comparable with borosilicate glasses. Their chemical durability is generally lower [9] and, in the case of phosphate glass, their corrosiveness is a disadvantage for use in industrial processes under active conditions at high temperatures. Even for immobilizing molybdenum-rich waste, borosilicate glass formulations are therefore still preferred.

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A wide range of borosilicate compositions was explored to identify composition zones that could be promising for loading molybdenum-rich waste.

3. Glass composition range investigated

For the purposes of this study, a tradeoff had to be found between the potential number of chemical elements and their concentration ranges and a reasonable number of glass compositions to be fabricated. We considered six elements: SiO_2, P_2O_5, B_2O_3, Al_2O_3, MoO_3, Na_2O.

The weight percentages of MoO_3 and Na_2O were specified as 10 and 12 wt%, respectively, for all the compositions. A mass fraction of 10% MoO_3 in a nuclear containment glass is well within the molybdenum-rich glass range. A fixed Na_2O concentration was adopted because glass viscosity and chemical durability constraints limit the possible Na_2O variation range, which thus does not have a significant effect on the final glass.

The variation ranges for the remaining elements were sufficiently broad to avoid excluding portions of the SiO_2–P_2O_5–B_2O_3–Al_2O_3–Na_2O phase diagram that could be of interest for immobilizing molybdenum-rich waste. The maximum and minimum weight percentage limits on oxides in the range were the following:

$$32\% < SiO_2 < 44\%$$
$$4\% < P_2O_5$$
$$5\% < Al_2O_3$$
$$13\% < B_2O_3 < 22\%$$

These limits were dictated by the requirements for the final glass chemical durability [3,10], for synthesis by a vitrification process at temperatures below 1300 °C, and by our existing knowledge of molybdenum loading in borosilicate glass. The minimum phosphorus concentration in the glass was set at 4% to take into account the phosphorus flow accompanying molybdenum in the waste.

4. Experimental procedure

As the vitrification behavior of these mixtures was difficult to predict in the absence of prior studies covering this composition range, we decided to synthesize 52 compositions uniformly distributed over the range. After heating the constituents, the resulting mixtures were visually examined to identify zones within the range that could be promising for vitrifying molybdenum-rich waste.

Table 1 shows the mixture compositions (in oxide wt%). The precursors used were powder samples of oxides (SiO_2, Al_2O_3, MoO_3) carbonates (Na_2CO_3), phosphates ($AlPO_4$, $Na_3PO_4 \cdot 12H_2O$), and boric acid (H_3BO_3). The powders were mixed to obtain a final molten oxide mass of 100 g. As the objective of this study was to identify zones within the composition range potentially interesting for immobilizing waste rich in molybdenum and phosphorus, the process temperature was set at a reasonably high value of 1300 °C to allow favorable assessment of even the most refractory compositions with high liquidus temperatures. The glass specimens with alumina concentrations exceeding 8 wt% were synthesized in alumina crucibles; the other compositions were synthesized in zirconia crucibles to avoid any composition changes by diffusion of alumina into the oxide mixture.

After heating the mixtures to 1300 °C for 3 h in air, the crucibles were removed from the furnace at high temperature. After cooling they were visually examined. These observations were supplemented by scanning electron microscope observations (JEOL 840A equipped with a PGT IMIX EDS analysis system) of several characteristic samples.

Table 1
Compositions (wt%) of the mixtures tested

	L32a	L32b	L32c	L32d	L32e	L32f	L32g	L32h	L32i	L32k	L32l	L32m	L32n	L32o	L32p	L32q
SiO_2	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32	32
Na_2O	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12
B_2O_3	22	22	22	18.5	18.5	18.5	15	15	15	13	13	15	22	18.5	18.5	15
Al_2O_3	16.5	10.75	5	16.5	10.75	5	16.5	10.75	5	10.75	16.5	27	20	23.5	20	21.75
P_2O_5	7.5	13.25	19	11	16.75	22.5	14.5	20.25	26	22.25	16.5	4	4	4	7.5	9.25
MoO_3	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10

	L36a	L36b	L36c	L36d	L36e	L36f	L36g	L36h	L36i	L36k	L36l	L36m	L36n	L36q
SiO_2	36	36	36	36	36	36	36	36	36	36	36	36	36	36
Na_2O	12	12	12	12	12	12	12	12	12	12	12	12	12	12
B_2O_3	22	22	22	18.5	18.5	18.5	15	15	15	13	13	15	18.5	15
Al_2O_3	16	10.5	5	16.5	10.75	5	16.5	10.75	5	10.75	16.5	23	19.5	19.75
P_2O_5	4	9.5	15	7	12.75	18.5	10.5	16.25	22	18.25	12.5	4	4	7.25
MoO_3	10	10	10	10	10	10	10	10	10	10	10	10	10	10

	L40a	L40b	L40c	L40d	L40e	L40f	L40g	L40h	L40i	L40l	L40k
SiO_2	40	40	40	40	40	40	40	40	40	40	40
Na_2O	12	12	12	12	12	12	12	12	12	12	12
B_2O_3	22	22	22	18.5	18.5	18.5	15	15	15	13	13
Al_2O_3	12	8.5	5	15.5	10.25	5	16.5	10.75	5	16.5	10.75
P_2O_5	4	7.5	11	4	9.25	14.5	6.5	12.25	18	8.5	14.25
MoO_3	10	10	10	10	10	10	10	10	10	10	10

	L44a	L44b	L44c	L44d	L44e	L44f	L44g	L44h	L44i	L44k
SiO_2	44	44	44	44	44	44	44	44	44	44
Na_2O	12	12	12	12	12	12	12	12	12	12
B_2O_3	22	22	22	18.5	18.5	18.5	15	15	15	13
Al_2O_3	8	6.5	5	11.5	8.25	5	15	10	5	10.75
P_2O_5	4	5.5	7	4	7.25	10.5	4	9	14	10.25
MoO_3	10	10	10	10	10	10	10	10	10	10

Table 2
Observations on samples after cooling

Homogeneous glass	Translucent homogeneous glass with beige inclusions	Opaque beige glass matrices	Two superimposed vitreous phases
L32a, *L32m*, L32n, *L32o*, L32p, *L36m*, L36n	L32b, L32d, L32g, L32l, *L32q*, L36a, L36b, L36d, L36e, L36g, *L36q*, L40a, L40d, *L40g*, *L40m*, *L44g*	L32e, L32h, L32k, L36c, L36h, L36k, L36l, L40b, L40e, L40h, L40k, *L40l*, L44a, L44b, L44c, L44d, L44e, L44h, *L44k*	L32c, L32f, L32i, L36i, L36f, L40c, L40i, L40f, L44f, L44i

Samples in italics and underlined are those exhibiting a lack of reactivity.

5. Results

After cooling, all the samples formed a massive vitreous material. The cooled samples were classified by visual observation into four categories:

- homogeneous transparent samples,
- homogeneous transparent samples with a few beige inclusions,
- opaque beige samples,
- samples comprising two superimposed layers.

All the mixtures were observed to be melted on removal from the furnace. In the samples consisting of two layers after cooling, the phase separation was observed in the molten state on removal from the furnace. Fully-cooled samples of the most refractory compositions showed a few signs of insufficient reactivity: inclusion of

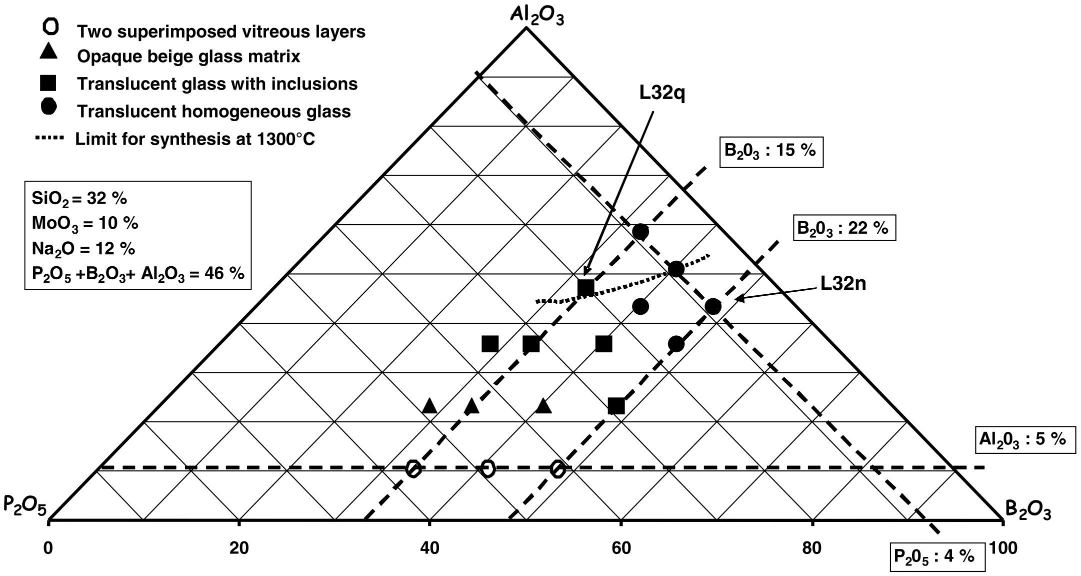

Fig. 1. Projection of visual observations for SiO_2 = 32% onto the Al_2O_3–P_2O_5–B_2O_3 ternary diagram.

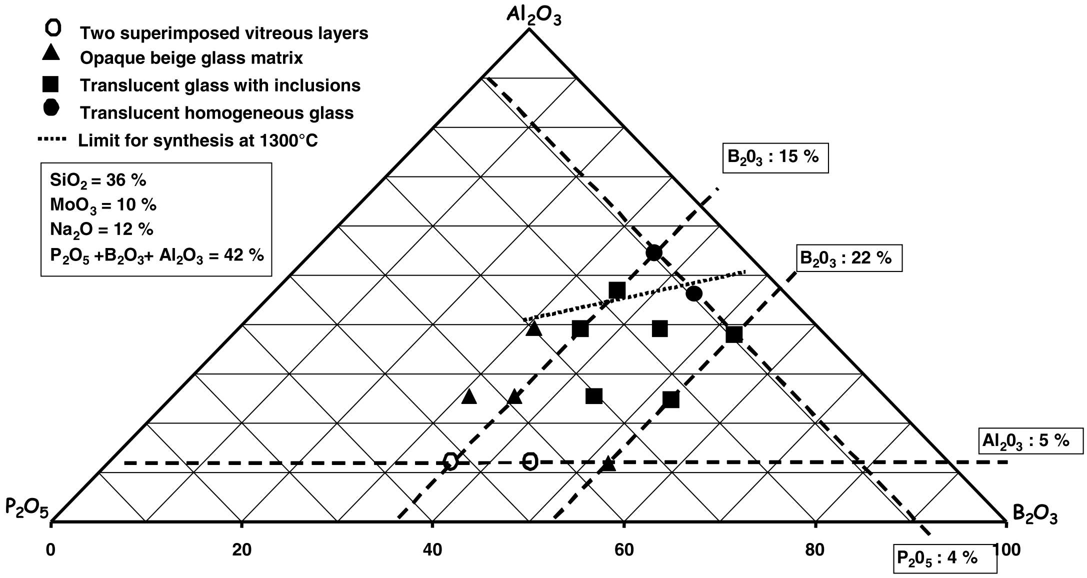

Fig. 2. Projection of visual observations for SiO_2 = 36% onto the Al_2O_3–P_2O_5–B_2O_3 ternary diagram.

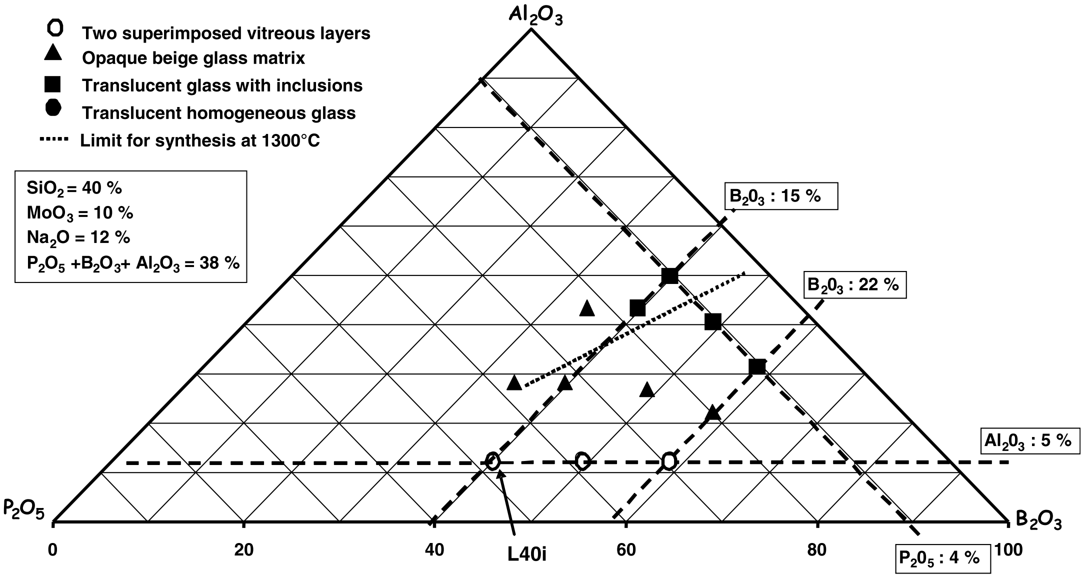

Fig. 3. Projection of visual observations for $SiO_2 = 40\%$ onto the Al_2O_3–P_2O_5–B_2O_3 ternary diagram.

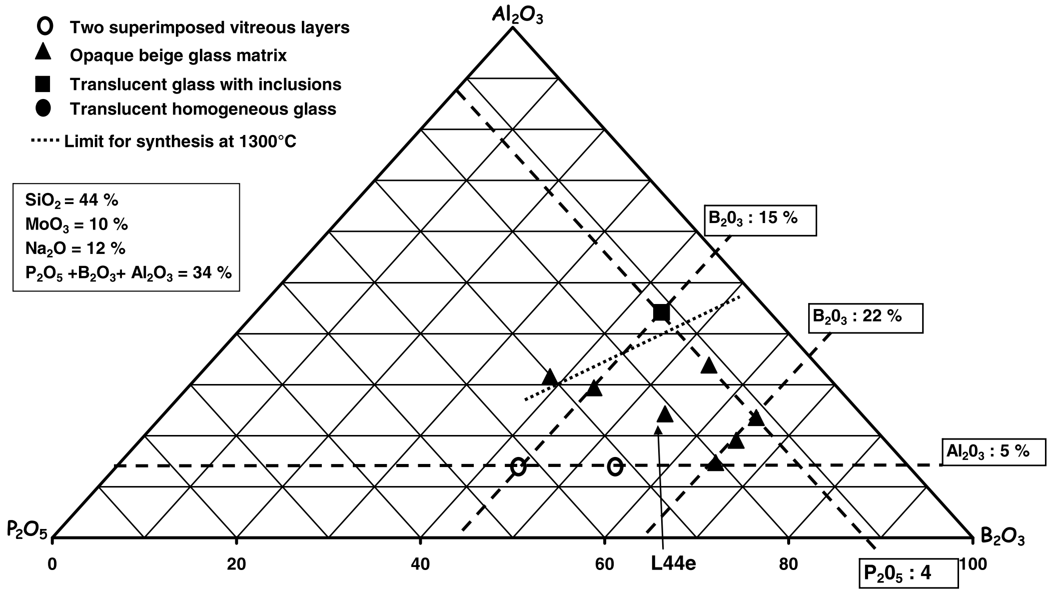

Fig. 4. Projection of visual observations for $SiO_2 = 44\%$ onto the Al_2O_3–P_2O_5–B_2O_3 ternary diagram.

a few millimetric white spots characteristic of poorly reacted powder. This result can be attributed to the lack of stirring and to an insufficient synthesis temperature. The samples to which these observations are applicable are identified in Table 2, which summarizes the observations for each mixture tested.

Figs. 1–4 are projections of the studied compositions and visual observations of cooled samples on the B_2O_3–P_2O_5–Al_2O_3 ternary diagram. The SiO_2 concentrations determined for the mixtures shown in these four figures were 32, 36, 40 and 44 wt%, respectively.

For each of the four sample categories, a standard specimen was characterized by scanning electron microscopy. Specimen L32n was observed for the homogeneous translucent glass samples, and specimen L32q for the translucent glass with beige inclusions. Both specimens were homogeneous at micrometer scale. For the opaque beige glass samples, SEM observation of specimen L44e

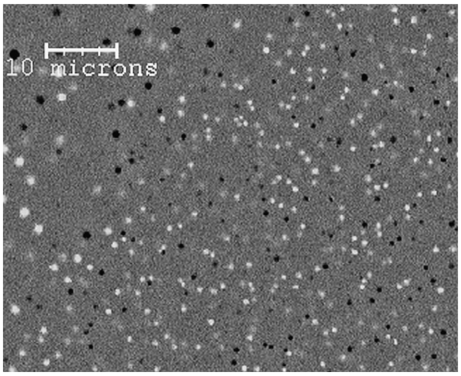

Fig. 5. EDS image of visually opaque beige specimen L44e.

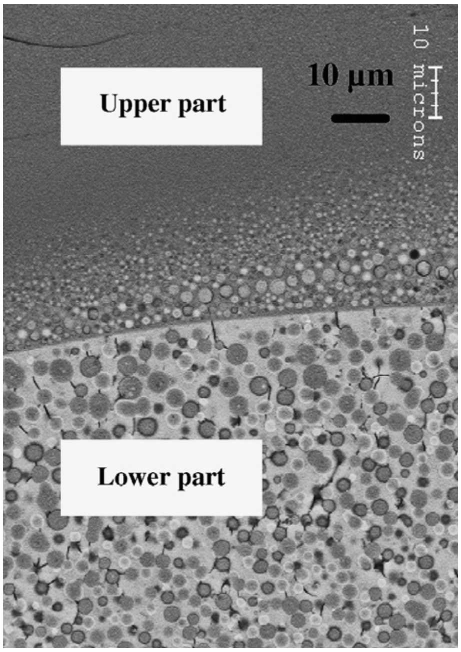

Fig. 6. EDS image of specimen L40i comprising two superimposed layers.

identified micrometric beads enriched in molybdenum and phosphorus dispersed uniformly in a borosilicate glass (Fig. 5). Specimen L40i was observed as an example of two superimposed opaque glass layers (Fig. 6): The upper layer consisted of beads up to 10 µm in diameter, enriched in molybdenum and phosphorus compared with the silicate glass in which they were dispersed. The lower layer consisted of beads up to 10 µm in diameter, enriched in silica compared with the glass in which they were dispersed. The beads were larger near the interface (see Fig. 7).

6. Discussion

All these results confirm the difficulty of loading high molybdenum concentrations in borosilicate glass. The compositions studied exhibited a strong phase separation tendency despite heat treatment at 1300 °C. However, significant differences were observed within the composition range: some compositions yielded stratified samples on removal from the furnace while others were fully homogeneous. The homogeneous glasses are situated in the composition ranges with the highest alumina concentrations and the lowest phosphorus concentrations. The stratified samples were obtained with low alumina concentrations and higher phosphorus concentrations (Figs. 1 and 2). Microstructural analysis revealed that one layer contained mainly phosphate and the other mainly silicate. Projecting all the compositions on the SiO_2–Al_2O_3–P_2O_5 ternary diagram shows the importance of alumina for obtaining homogeneous glass. Between the two extremes, the vitreous materials obtained contained a uniform dispersion of microbeads enriched in phosphorus and molybdenum. This confirms the results already obtained on silicophosphate glass: Toplis et al. showed that tetrahedral $[AlO_4]^-$ groups are distributed between the silicate and phosphate networks and interconnect them. A high alumina concentration results in homogeneous silicophosphate glass [11].

Except for a limited fraction of noble metals and a few tenths of a percent of crystallization, the nuclear waste containment glasses currently produced industrially are homogeneous [12]. Implementing this strategy for glass rich in molybdenum would thus imply using compositions rich in alumina. However, the homogeneous glass range is very limited and consists of highly refractory glass: only four of the 52 samples studied produced homogeneous glass without any signs of insufficient reactivity. Three of these samples contained 32% silica and the fourth contained 36% silica. Given that the synthesis temperature is necessarily below 1300 °C, the option of immobilizing molybdenum-rich solutions in homogeneous glass would imply the use of formulations with lower silica concentrations than generally adopted for nuclear glass. The impact of the lower silica content on the glass durability would have to be evaluated. The test samples here were cooled faster than the glass poured into an industrially produced nuclear glass canister. The microstructure could thus be different, i.e. the glass could be partially crystallized or contain micrometric separated phases.

Another region of the composition range resulted in the production of materials comprising two layers. The observations on the cooled samples reflected a phase separation already visible at 1300 °C. Stratified material is undesirable, as the industrial feasibility and performance of such a package cannot be demonstrated.

An intermediate composition region corresponding to homogeneous melts yields glass samples containing micrometric separated

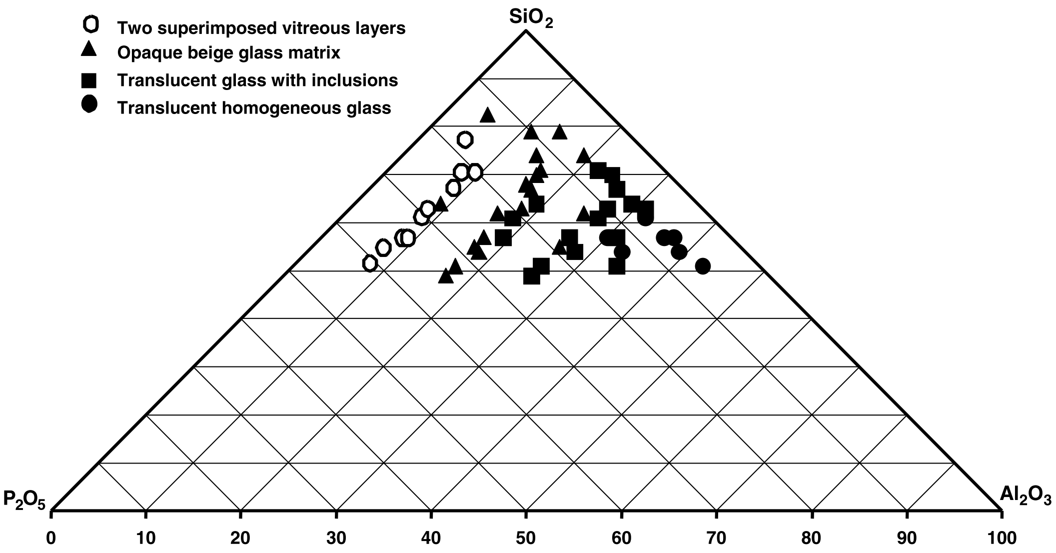

Fig. 7. Projection of visual observations onto the Al_2O_3–P_2O_5–B_2O_3 ternary diagram.

phases after cooling. These opaque beige samples are macroscopically homogeneous, but microscopic observations reveal separate, uniformly distributed microbeads. The micrometric dimensions and uniform distribution of these inclusions in the vitreous material are characteristic of a liquid–liquid phase separation phenomenon occurring during cooling. Cooling was rapid enough compared with the glass viscosity to prevent aggregation. The chemical durability of such materials can be expected to be controlled by the glass encapsulating the microbeads [13]. As long as the encapsulating glass has high silica content, the chemical durability of such samples could be acceptable. The composition zone resulting in such samples covers about a third of the glass composition range investigated.

The samples described as 'homogeneous glass with beige inclusions' are situated at the boundary between the homogeneous glass and the opaque beige glass. These compositions are slightly less rich in alumina than those producing perfectly homogeneous glass, and confirm the major role of alumina for incorporating silica, molybdenum oxide and phosphorus in the same glass network.

7. Conclusion

Composition ranges of interest for the containment of nuclear waste rich in molybdenum and phosphorus were identified. A vast composition range was investigated by defining a fine mesh. The limits considered to delimit the range of the study were intentionally extended to identify formulations such as SiO_2–B_2O_3–Al_2O_3–Na_2O–P_2O_5 that are of interest for vitrifying molybdenum-rich waste. The relevance of these limits was confirmed by the fact that compositions near the limits result in mixtures that are too refractory or immiscible at 1300 °C,

Two remarkable regions were identified within the composition range: one produces homogeneous glass after melting at 1300 °C and rapid cooling; the other produces a vitreous material comprising separate microbeads uniformly dispersed in a borosilicate glass. Each of these composition regions is potentially of interest for waste vitrification applications. The first composition region gives a homogeneous glass that is easier to characterize and qualify. The second composition region is vast, allowing greater composition fluctuations; the compositions in this region have higher silica concentrations capable of producing more durable matrices. In the second region the compositions have low alumina concentrations that would allow synthesis at melting temperatures below the 1300 °C used for this study.

More detailed characterization of these two types of matrices should allow us to select the most relevant formulations for our requirements [1,14].

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