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The influence of glass composition on crystalline phase stability in glass-ceramic wasteforms

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HIGHLIGHTS

- Crystalline phase formation shown to depend on glass matrix composition.
- Zirconolite forms as the sole crystalline phase only for most aluminous glasses.
- Thermodynamics indicate that low silica activity glasses stabilise zirconolite.

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ABSTRACT

Zirconolite glass-ceramic wasteforms were prepared using a suite of Na_2O–Al_2O_3–B_2O_3–SiO_2 glass matrices with variable Al:B ratios. Zirconolite was the dominant crystalline phase only for the most alumina rich glass compositions. As the Al:B ratio decreased zirconolite was replaced by sphene, zircon and rutile. Thermodynamic data were used to calculate a silica activity in the glass melt below which zirconolite is the favoured crystalline phase. The concept of the crystalline reference state of glass melts is then utilised to provide a physical basis for why silica activity varies with the Al:B ratio.

1. Introduction

Glass-ceramic wasteforms are being developed for the immobilisation of a diverse range of plutonium containing residues on the Sellafield site [1,2]. The target crystalline phase is zirconolite ($CaZrTi_2O_7$), which acts as the host for plutonium, whilst the glass matrix is intended to digest the remainder of the residue. The wasteforms are to be produced by size reduction of the residue streams, blending with an appropriate precursor and consolidation by hot isostatic pressing (HIP). It is emphasised that the term glass-ceramic as used here differs from the established Materials Science concept of a glass-ceramic in that the zirconolite phase forms at the maximum HIP temperature, rather than by separate nucleation and growth heat treatments of a glass.

The current glass-ceramic precursor composition for immobilisation of the residues was derived empirically and is given in Table 1, and a typical glass-ceramic wasteform microstructure is shown in Fig. 1. The formulation in Table 1 arose because early inventories for the residues that would require immobilisation included a large quantity of calcium fluoride slags resulting from production of plutonium metal. To achieve the desired high waste loadings of this slag would lead to a low durability glass matrix with conventional glass formulations, so high alumina contents were used to improve the glass matrix leach resistance. Subsequently, the slags were removed from the residues inventory, greatly lowering the fluoride content of the glass matrix, but the high alumina level was retained. Consequently, calcium fluoride was required in the precursor to facilitate digestion of the residues and enhance growth of the zirconolite grains.

During process development work, a 100 kg batch of this precursor was prepared. An error in the batching was made such that the quantities of alumina and titania were interchanged. When this composition of precursor was HIPped, characterisation studies revealed that zirconolite had been destabilised, despite the fact that none of the zirconolite forming oxides had been reduced; this indicated that the glass composition plays an important role in determining the crystalline phase assemblage. Our initial hypothesis was that the lower alumina content of the misformulated precursor allowed the calcium oxide that is required to form zirconolite to remain dissolved in the glass.

The formulation in Table 1 was derived by an empirical approach and led to a non-classical glass matrix. Carter et al. [3] and Zhang et al. [4] took a more systematic approach to such glass-ceramic wasteforms. These wasteforms were targeted at

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Hanford K-basin sludges and the immobilisation of the primary waste stream from production of molybdenum-99 at the Australian Nuclear Science and Technology Organisation site in Sydney respectively. In the work of Carter et al. and Zhang et al. the intended crystalline phase was the closely related titanate pyrochlore, $CaUTi_2O_7$. The glass matrix was formulated such that the trivalent species in the glass network, boron and aluminium, were charge compensated on a molar basis by sodium. The stoichiometric composition of the glass in this wasteform was $Na_2AlBSi_6O_{16}$. This glass provides a method by which the glass composition can be varied systematically. Given that the initial observations inferred an important role played by alumina, it was decided to prepare a suite of zirconolite glass-ceramics in which the glass matrix was defined by $Na_2Al_{1+x}B_{1-x}Si_6O_{16}$ to investigate the role played by glass composition in controlling crystalline phase stability. The $x = 1$ end member gives the mineral albite, $NaAlSi_3O_8$. The melting point of albite is 1120 °C [5] and the composition cools to a glass at the cooling rates that occur during a HIP cycle. From the available phase diagrams, [6] no boron analogue for albite was shown, and the liquidus estimated from the relevant phase diagram is 1100–1200 °C. No phase diagrams for the quaternary system $Na_2O–Al_2O_3–B_2O_3–SiO_2$ could be found.

Table 1
Composition of baseline glass-ceramic precursor.

Component	Wt.%
SiO_2	26.9
Al_2O_3	24.3
B_2O_3	5.3
Na_2O	6.1
CaO	6.6
Gd_2O_3	4.9
TiO_2	10.0
ZrO_2	10.9
CaF_2	5.0

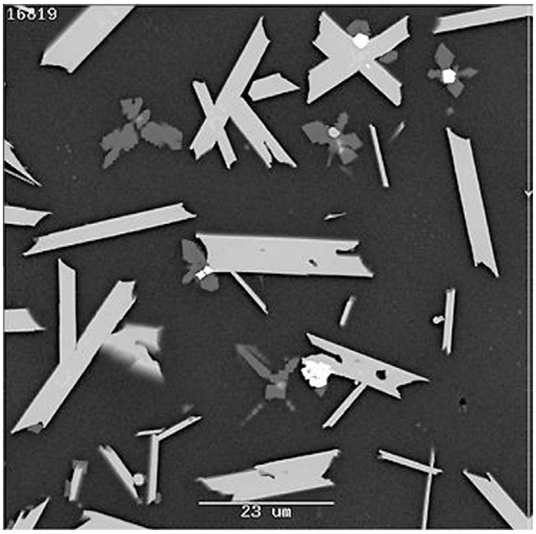

Fig. 1. Microstructure of baseline glass-ceramic wasteform. Light grey laths are zirconolite; mid grey dendrites are CaF_2; dark matrix is glass; bright inclusions are undigested actinide oxide.

Table 2
Composition of model glass-ceramics (g).

	$x = 0$	$x = 0.2$	$x = 0.4$	$x = 0.6$	$x = 0.8$	$x = 1.0$
HIP can	NS274	NS275	NS276	NS277	NS278	NS279
Glass frit	15.22	12.10	9.02	5.98	2.97	0.00
Na_2SiO_3	6.90	7.87	8.83	9.78	10.71	11.64
SiO_2	22.41	23.69	24.95	26.20	27.43	28.64
Al_2O_3	5.01	5.98	6.93	7.87	8.80	9.72
$CaTiO_3$	33.99	33.99	33.99	33.99	33.99	33.99
ZrO_2	30.81	30.81	30.81	30.81	30.81	30.81
TiO_2	19.97	19.97	19.97	19.97	19.97	19.97

2. Experimental

A suite of six samples was prepared based on the glass composition $Na_2Al_{1+x}B_{1-x}Si_6O_{16}$ described above, with $x = 0–1$ in increments of 0.2. The standard batch size comprised nominally 50 g of glass together with 0.25 moles of the zirconolite forming oxides. This blend gives an approximately equivolume mixture of glass and crystalline material if zirconolite forms as the crystalline phase.

The glass forming components were supplied by silica, alumina, sodium metasilicate and the glass frit used for high level waste vitrification on the Sellafield site. The latter component was chosen as a stable source of boron oxide. The glass frit is a mixed alkali borosilicate glass containing both sodium and lithium and for the purposes of glass composition calculation lithium was treated as being a molar equivalent for sodium. In all formulations, sodium accounted for at least 85 mol% of the total alkali. The crystalline phase forming oxides were added as perovskite ($CaTiO_3$), titania and zirconia. The compositions of the six glass-ceramic samples are summarised by mass in Table 2, and the glass compositions are presented by mole in Table 3; the absolute molar quantities are then normalised to indicate the composition according to the overarching formula – $Na_2Al_{1+x}B_{1-x}Si_6O_{16}$. Note that because the glass components were calculated to give a constant nominal mass per batch, the molar amount of glass decreases slightly as alumina is substituted in for boron oxide in the glass network.

All samples were prepared from standard laboratory reagents. Powder batches were milled in a Retsch PM 100 planetary mill for 20 min at 300 rpm using a 250 ml hardened steel pot and 10 mm diameter balls. 2-Propanol was used as a carrier fluid and the slurry dried at 80 °C. The dried powders were packed into straight-walled stainless steel HIP cans using a uniaxial pressure of 50 MPa. After welding on the lids, which included evacuation tubes, the HIP cans were baked out and evacuated at 600 °C for a minimum of 4 h and sealed. The samples were then HIPped at 1250 °C and 100 MPa with a 2 h dwell. Heating rates were 10 °C min^{-1}–900 °C,

Table 3
Composition of glass matrices on a molar basis.

	NS274		NS275		NS276		NS277		NS278		NS279	
	Moles	Norm'd	Moles	Norm'd	Moles	Norm'd	Moles	Norm'd	Moles	Norm'd	Moles	Norm'd
SiO_2	0.5902	6.000	0.5865	6.000	0.5828	6.000	0.5792	6.000	0.5756	6.000	0.5720	6.000
$NaO_{0.5}$	0.1688	1.716	0.1733	1.773	0.1777	1.830	0.1821	1.886	0.1864	1.943	0.1907	2.000
$LiO_{0.5}$	0.0279	0.284	0.0222	0.227	0.0165	0.170	0.0110	0.114	0.0054	0.057	0	0.000
$BO_{1.5}$	0.0984	1.000	0.0782	0.800	0.0583	0.600	0.0386	0.400	0.0192	0.200	0	0.000
$AlO_{1.5}$	0.0984	1.000	0.1173	1.200	0.1360	1.400	0.1544	1.600	0.1727	1.800	0.1907	2.000
Sum	0.9837	10	0.9775	10	0.9713	10	0.9653	10	0.9593	10	0.9534	10