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Mechanical properties of nuclear waste glasses

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ABSTRACT

The mechanical properties of nuclear waste glasses are important as they will determine the degree of cracking that may occur either on cooling or following a handling accident. Recent interest in the vitrification of intermediate level radioactive waste (ILW) as well as high level radioactive waste (HLW) has led to the development of new waste glass compositions that have not previously been characterised. Therefore the mechanical properties, including Young's modulus, Poisson's ratio, hardness, indentation fracture toughness and brittleness of a series of glasses designed to safely incorporate wet ILW have been investigated. The results are presented and compared with the equivalent properties of an inactive simulant of the current UK HLW glass and other nuclear waste glasses from the literature. The higher density glasses tend to have slightly lower hardness and indentation fracture toughness values and slightly higher brittleness values, however, it is shown that the variations in mechanical properties between these different glasses are limited, are well within the range of published values for nuclear waste glasses, and that the surveyed data for all radioactive waste glasses fall within relatively narrow range.

1. Introduction and background

Vitrification is widely accepted as a safe process for treating hazardous wastes and converting them into passively-safe, leach-resistant materials. A significant body of work exists on many of the properties of the glasses used for high level waste (HLW) immobilisation (see, for example, Refs. [1–4]). However, there is relatively little published data on the mechanical properties of glasses for the immobilisation of nuclear wastes. This is becoming particularly significant, with recent work into the vitrification of (wet) intermediate level wastes ((W)ILW) [5] which suggests that greater volumes of nuclear waste bearing glasses may be produced in the coming years. The current work addresses the mechanical properties of a selection of glasses developed for the immobilisation of certain WILW arising from the decommissioning of a site in Somerset, England, and compares their properties with those published for existing waste glasses from around the world.

Three (W)ILW base glasses are considered (labelled G1, G2, and G3) which are the result of ongoing research and development work ([5] and Bingham et al. unpublished work) to produce wasteforms with high waste loadings and which give large volume reduction factors. These glasses were designed to immobilise three (W)ILW waste streams, defined here as follows:

- *MP1*: Spent organic ion exchange (IEX) resin, pond water treatment plant (PWTP) sludge (rich in Si and Mg), sand pressure filter (SPF) sand, active effluent treatment plant (AETP) sludge (rich in Si, Fe and Mg);
- *MP2*: PWTP sludge, SPF sand, AETP sludge;
- *MP3*: Spent organic IEX resin;

giving a total of nine waste loaded glasses. The results obtained are compared to the properties of an inactive simulant UK HLW glass and literature data.

Most conventional silicate and borosilicate glasses are brittle materials at room temperature and fracture is an important phenomenon to consider in evaluating the physical integrity of the wasteform. Wasteform fracture increases the glass surface area, which potentially leads to increased chemical corrosion during subsequent storage and ultimately geological disposal; and can create respirable fines ($\leqslant 10^{-5}$ m) that could present an immediate hazard in the environment in the case of container failure.

Fracture of vitrified wasteforms has two likely causes, either thermal shock in the container during cooling [6–9] or impact damage due to accidents during handling [10,11]. Fracture on cooling is inevitable in large-scale glass blocks (typically 0.3–0.6 m in diameter, 1–3 m in length). The only way to prevent fracture on cooling would be to (a) maintain the entire canister and its contents at the pouring temperature during pouring and (b) extend cooling periods from days to months between the glass transformation temperature and ambient temperature [2], so that any thermally induced stresses are minimised and minimal residual stresses are frozen into the glass. Since neither (a) nor (b) are practicable, some degree of cracking is inevitable. The mechanical properties of a glass are affected by its cooling rate and thermal

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history [12,13]. In a radioactive glass block that is subject to radiogenic heating, stresses are maintained due to a temperature gradient between the centreline and the surface. This gradient decreases with time, but persists over hundreds of years until ^{137}Cs and ^{90}Sr have decayed. Self-heating is an issue for vitrified HLW; however, ILW is not heat generating and hence thermally induced cracking of vitrified (W)ILW will be entirely due to the initial cooling of the glass wasteform.

The temperature dependences of certain mechanical properties of vitrified radioactive wasteforms have been investigated by Okafor and Martin [14] and Matzke et al. [13]. The fracture toughness (and fracture surface energy) of the samples was found to decrease with increasing temperature. Matzke et al. [13] concluded that fracture toughness (K_{Ic}) has a large inherent temperature dependence, far exceeding those of the Vickers hardness and Young's modulus; in general Young's modulus is not a strong function of temperature (see, for example, Rouxel [15]). As fracture mechanics shows that

$$K_{Ic} = \sqrt{2E\gamma} \quad (1)$$

where E is Young's modulus and γ is surface energy, this implies that surface energy is a more strongly decreasing function of temperature than E. A decrease in K_{Ic} with increasing temperature would make the glass more susceptible to fracture at higher temperatures (below T_g). At temperatures approaching the glass transition temperature, T_g, deformation under load will become easier and thus hardness can be expected to decrease.

The possibility of impact damage to canisters during handling must be carefully considered as failure of the canister and significant fracture of the glass can result in the generation of respirable fines [16]. The result of a canister impact can be tested by dropping the canister or smaller scale model glass samples [10] from a significant height and observing the result. However, the drop test technique is expensive and not realistic for all glass compositions. Thus, ideally, the mechanical properties of the vitrified waste could be measured to give an indication of its reaction under impact conditions. Such measurements have also been used to assess the impact performance of radiation damaged glasses that would be difficult to assess by drop test methods [17–20].

The UK does not currently specify requirements for the mechanical properties of nuclear waste forms other than that they are mechanically stable and impact resistant [21]. Thus, it is important to study the properties of vitrified wasteforms used throughout the world as an indication of the appropriate properties required of a waste glass. However, there is no simple mechanical property that can be directly related to the likelihood of production of respirable fines under impact conditions. The most useful property in this regard may be fracture toughness since this is related to the energy required to form a new surface (see Eq. (1)) and the smaller the particle size the greater the total impact energy required [22]. However, Eq. (1) indicates that fracture toughness also depends on Young's modulus and indeed it is implied in the literature that increasing Young's modulus will increase the strength of glass [23], although the relationship between strength and modulus is definitely more complicated than this [24]. There is also an additional, difficult to quantify, energy term reflecting either irreversible processes such as the release of heat, light or sound on fracture, or plastic processes at the crack tip [25]. In metals the latter term dominates the measured fracture toughness. Thus, the actual size of the fines produced will reflect the balance between these various energy terms. Jardine et al. [22] showed that borosilicate glass and SYNROC specimens yielded the same mass fraction of respirable fines whereas FUETAP concrete, high silica and alkoxide glass specimens yielded ca. 2–3 times more and a spinel ceramic yielded ca. 2.5 times less.

No published studies were found in the literature specifically discussing hardness or fracture toughness measurements for vitrified (W)ILW wastes. However, data are available for other waste glasses (primarily vitrified HLW) and vitrified commercial wastes such as incinerator ashes. In general, the Young's moduli of borosilicate nuclear waste glasses vary between 81 and 90 GPa. Although a little higher than the moduli of many silicate glasses (e.g. 72 GPa for float glass) these values are consistent with values reported for a variety of glass compositions (see, for example, [15]). The fracture toughness of such glasses varies between 0.5 and 1 MPa $m^{1/2}$, values which are typical for a wide range of silicate glasses (see, for example, [24,26]). Toughness is also affected by irradiation, which shows variable effects [27–29] and by crystallisation, although Vernaz et al. [30] showed that the effect was significant only at high levels of crystallisation (ca. 54 vol.%) where an increase in K_{Ic} was observed.

2. Experimental procedures

Four sets of glasses were studied. Three sets involved the three WILW glasses G1, G2, G3 and the associated wastes MP1, MP2 and MP3 giving a total of nine waste loaded glasses. In addition some measurements were made on the base glasses G1, G2 and G3, although a complete set of data was not obtained on these glasses. The waste loaded glasses were either formed from the simulant waste plus glass-forming additives, some of which were present in the waste (MP1 and MP2 wastes), or using simulant waste plus a glass frit produced in-house (MP3 wastes). The fourth sample set consisted of a simulated HLW glass which was produced from MW base glass frit (10.5 mol% Na_2O, 10.5 mol% Li_2O, 18.5 mol% B_2O_3, 60.5 mol% SiO_2 glass provided by the National Nuclear Laboratory) melted with inactive simulant HLW calcine at 25 (oxide) wt.% loading at 1050 °C for 5 h, poured, and annealed at 500 °C. This glass is referred to in the following as MW-HLW.

Three "base" glasses, labelled "B" in Table 1, were melted in Pt crucibles using reagent grade (>99% purity) raw materials. Melting of these glasses was carried out in an electric furnace at 1200 °C. Batches to produce 300 g of glass were heated in the crucibles; after 1 h a Pt stirrer was lowered into the melt and the melt was stirred for 2 h at 30 rpm. The stirrer was then removed and the melt was quenched and fritted by pouring into clean, cold water, removed, and dried.

The WILW melts were carried out in recrystallised alumina crucibles. Batch mixtures were placed in each crucible. Each crucible was heated at 2 °C min^{-1} to 1150 °C or 1200 °C and the temperature held for 6 h. The glasses were then poured into steel moulds to form either long thin bars (155 × 15 × 15 mm) or small round 'puck' specimens (diameter ca. 5 cm, depth ca. 0.7 cm) to be used for hardness measurements. These samples were annealed at 500 °C for 1 h and then slow cooled at 1 °C min^{-1}. This common annealing temperature was selected based on the published T_g for HLW glass and Fe-doped HLW glass of ~515 °C [31]. Therefore annealing just below T_g at 500 °C was ideally suited for glasses HLW, G1 and G3 owing to their compositional similarities with one another. Glass G2 is (broadly) similar in composition to barium borosilicate glasses reported in [32] which exhibit T_g's of approximately 500 °C hence an annealing temperature of 500 °C was also suitable for glass G2.

The composition of each glass specimen was analysed using X-ray fluorescence (XRF) and inductively coupled plasma optical emission spectroscopy (ICP-OES) for B and Li. For XRF measurement accuracies for the major components (>10 wt.%) are ±1 wt.%; for the intermediate components (1–10 wt.%) ±0.5 wt.% and for minor components (<1 wt.%) ±0.2 wt.%. For ICP-OES the measurement accuracies are ±10% of the measured value for both Li_2O and B_2O_3. To simplify interpretation of compositional trends

Table 1
Analysed simulated waste glass compositions converted to mol% values where "–" indicates below detection limit in the original analysis. Original analysis normalised to 100% for ease of comparison.

	MW HLW	G1				G2				G3			
		B	MP1	MP2	MP3	B	MP1	MP2	MP3	B	MP1	MP2	MP3
SiO_2	51.4	60.5	54.9	51.4	54.4	56.5	47.5	49.1	48.4	58.9	54	52.7	53
B_2O_3	19.2	10.2	10.9	12.2	11.2	2.5	2.9	2.9	2.6	19.5	18.9	20.3	18.9
Al_2O_3	2.5	2.5	5.8	4.7	5.3	0.4	3.4	1.4	4.1	–	5.8	3.6	5.2
P_2O_5	0.07	–	0.04	0.09	–	–	0.06	0.05	–	–	0.03	0.04	–
Fe_2O_3	0.93	4.83	4.84	5.61	4.61	2.72	3.35	3.36	2.75	3.88	3.65	4.03	3.49
CaO	0.07	–	0.41	0.39	0.31	10.18	11.36	11.29	10.65	–	0.35	0.3	0.29
MgO	6.5	–	0.35	1.43	–	0.15	0.54	0.49	0.16	–	0.33	0.38	–
SrO	0.14	–	–	–	–	0.35	–	–	0.34	–	–	–	–
BaO	0.42	–	–	–	–	16.9	18.5	18.5	16.9	–	–	–	–
Li_2O	8.7	8.3	8.3	8.5	7.9	7	6.3	7	6.2	9.4	8.2	9	8.4
Na_2O	9.4	13.7	14.1	15.6	16.1	3.4	5.8	5.8	7.7	8.3	8.6	9.5	10.5
K_2O	–	–	0.08	0.04	0.07	–	0.09	0.04	0.08	–	0.07	0.03	0.07
ZnO	–	–	0.06	0.04	–	–	0.05	0.05	–	–	0.05	0.05	–
Cr_2O_3	0.18	–	–	–	–	0.05	–	–	–	–	–	–	–
ZrO_2	0.57	–	0.08	–	0.07	–	0.06	–	0.08	–	0.12	0.08	0.12
Total	100.08	100.03	99.86	100	99.96	100.15	99.91	99.98	99.96	99.98	100.1	100.01	99.97

the analysed weight percent data have been normalised to 100 and converted to mole percentage values in Table 1. The observed increase in Al_2O_3 content between the base glasses and the waste loaded glasses are consistent with a combination of crucible dissolution (which is unavoidable since melting in Pt was not possible for the waste loaded glasses because of the reducing nature of some of the components) and low levels of Al_2O_3 in the waste simulants, and does not give evidence of excessive crucible corrosion.

Density measurements were carried out on cut and ground hardness samples, prior to polishing, using the Archimedes method. The results shown in Table 2 are averages of five separate measurements on each sample. The standard deviation of these measurements was always $\leqslant$0.001 Mg m^{-3}.

For indentation testing samples were ground to give two parallel sides one of which was then progressively polished using SiC grits and then diamond polished to 0.25 μm. Each sample was then re-annealed at 500 °C to remove any residual stresses introduced by the polishing process.

Vickers indentation was used to measure both hardness and indentation fracture toughness. For each sample the test-piece surface was loaded by indenter with loads of 1.96 N, 4.91 N and 9.81 N using a Mitutoyu HM Micro-Hardness tester and at 9.81 N, 24.53 N, and 49.05 N using a conventional Vickers-Armstrong Engineering hardness tester. In both cases the load was held for 20 s duration and removed. Testing was carried out according to the protocols described in British Standard BS EN 843-4:2005 Advanced Technical Ceramics – Mechanical Properties of Monolithic Ceramics at Room Temperature, and ASTM E384 Standard Test Method for Micro-hardness of Materials.

Vickers hardness in GPa was calculated using

$$H_V = \frac{1.854P}{(2a)^2} \tag{2}$$

where P is the load in Newtons and $2a$ is the average diagonal length of the impression. The Vickers hardness values were obtained by from averaging the $2a$ values from each indent obtained at load of 9.81 N.

Median/radial cracks that form during a Vickers indentation can be used to assess the fracture toughness of brittle materials [33,34]. This approach assumes that measurements based on crack arrest give the same result as measurements based on crack initiation. Indentation is convenient in that multiple measurements may be made on the same sample whereas in crack initiation measurements such as the single edge notch bend test only one result can be obtained per sample. A number of models of have been proposed for evaluating fracture toughness from indentation cracks. These models have been thoroughly reviewed by Ponton and Rawlings [35] who showed that the indentation fracture toughness, K_c, given by

$$K_c = \frac{0.0824P}{c^{3/2}} \tag{3}$$

Table 2
Measured mechanical properties.

Sample	Density (Mg m^{-3})	H_V at 1 kg/GPa	K_c (M Nm$^{-3/2}$)	B (μm^{-1})	E (GPa)	G (GPa)	v
MW-HLW	2.68	6.6 ± 0.3	0.84 ± 0.09	7.9 ± 0.9	87.0 ± 2.1	34.6 ± 0.3	0.258 ± 0.007
G1-B	2.61	6.7 ± 0.4	0.81 ± 0.13	8.3 ± 1.4			
G1-MP1	2.61	6.9 ± 0.4	0.86 ± 0.07	8.0 ± 0.8	81.7 ± 0.3	32.8	0.25
G1-MP2	2.65	6.5 ± 0.5	*	*	82.8 ± 0.4	32.7 ± 0.7	0.266 ± 0.006
G1-MP3	2.62	6.5 ± 0.3	1.06 ± 0.10	6.1 ± 0.6	81.8 ± 0.3	32.9 ± 0.3	0.243 ± 0.002
G2-B	3.39						
G2-MP1	3.39	6.0 ± 0.2	0.65 ± 0.02	9.2 ± 0.4	85.9 ± 0.7	34.2 ± 0.7	0.256 ± 0.006
G2-MP2	3.44	6.0 ± 0.2	0.65 ± 0.03	9.2 ± 0.5	87.8 ± 0.1	34.5 ± 0.1	0.274 ± 0.001
G2-MP3	3.33	5.9 ± 0.2	0.65 ± 0.03	9.1 ± 0.5	85.0 ± 1.0	32.9 ± 1.3	0.246 ± 0.010
G3-B	2.52	6.4 ± 0.3	0.89 ± 0.13	7.2 ± 1.1			
G3-MP1	2.52	6.7 ± 0.2	1.04 ± 0.14	6.4 ± 0.9	80.7 ± 0.9	32.4 ± 0.1	0.244 ± 0.003
G3-MP2	2.52	6.8 ± 0.6	*	*	80.3 ± 0.8	32.2 ± 0.1	0.246 ± 0.003
G3-MP3	2.54	7.1 ± 0.5	0.87 ± 0.07	8.2 ± 0.9	82.7 ± 0.7	33.0 ± 0.2	0.253 ± 0.003

* No results reported due to anomalously large scatter in the data.

where c is the half the surface crack length in m, gives good agreement, both in terms of ranking and absolute values, with conventional fracture toughness measurements based on crack initiation. However, the use of indentation for fracture toughness means that whilst the results obtained reliably rank different glasses they may not be directly comparable with results from other more destructive techniques; this lack of direct comparability has led Quinn and Bradt [36] to conclude that indentation should not be used for fracture toughness measurement. That said the results of Ponton and Rawlings [35] shows that comparative toughness data can be meaningfully extracted from indentation data and thus it is reasonable to use the technique here as the intention is to compare the toughnesses of similar materials. All indentation dimensions and crack length were measured 24 h after indentation. A graph of $c^{3/2}$ against load was plotted. The gradient of this line was then used to calculate indentation fracture toughness using Eq. (3).

Although less widely reported, brittleness provides a measure of the relative susceptibility of a material to the competing mechanical responses of deformation and fracture. In the calculation of brittleness, hardness may be taken as the deformation parameter. In ideally plastic solids hardness relates directly to the yield stress: for silicate glasses this correspondence is not perfect but can be utilised. Meanwhile indentation fracture toughness may be taken as a fracture parameter and thus brittleness is defined as

$$B = \frac{H_V}{K_c} \tag{4}$$

Young's modulus and shear modulus were measured using resonant frequency techniques. These measurements were conducted by an external testing house using an Erudite Resonant Frequency Tester. For a rod shaped sample

$$E = 4\rho v_f^2 L^2 \tag{5}$$

where E is Young's modulus, ρ is the sample density, v_f is the fundamental longitudinal resonant frequency and L is the length of the rod. Meanwhile shear modulus, G, is given by

$$G = 4\rho v_j^2 L^2 F \tag{6}$$

where F is a form factor related to the geometry of the sample. Poisson's ratio, v, can then be calculated using

$$v = \frac{E}{2G} - 1 \tag{7}$$

3. Results

The measured values of density, hardness, indentation fracture toughness, brittleness, Young's modulus and shear modulus are summarised in Table 2 along with the calculated values of Poisson's ratio. All of the data fall into a relatively narrow range of values indicating that the differences in mechanical properties between the various glasses are limited. However, there are some differences in detail and these are considered.

It can be seen that glasses G1-B and G1-MP1 exhibit similar hardness, indentation fracture toughness and brittleness values to MW-HLW. Although glass G1-MP3 has a similar hardness to the other G1 glasses it has a notably (~20%) higher indentation fracture toughness and therefore a lower brittleness value than the other G1 glasses and MW-HLW. The Young's and shear moduli of glasses G1-MP1, G1-MP2 and G1-MP3 are ~7% lower than the equivalent MW-HLW moduli. A similar pattern is observed with the G3 glasses. In this case the hardness, indentation fracture toughness and brittleness values of glasses G3-B and G3-MP3 are similar to those of MW-HLW. However, although glass G3-MP1 has a similar hardness to the other G3 glasses it has a notably (~17%) higher indentation fracture toughness and thus correspondingly lower brittleness value than MW-HLW. Unfortunately the indentation toughness data collected for glasses G1-MP2 and G2-MP2 were subject to large scatter and thus it was not possible to obtain meaningful indentation fracture toughness and brittleness data for these glasses.

The G2 glasses exhibit a different pattern. For all waste types glass G2 glass exhibits lower hardness (~10% lower) and indentation toughness (~20% lower) values than MW-HLW and higher brittleness values than MW-HLW or any of the other glasses tested. The moduli of the G2 glasses are, however, similar to the modulus of MW-HLW.

4. Discussion

As shown in Table 1, considerable compositional differences arise between the G2 glasses and the G1, G3 and MW-HLW glasses. The G2 glasses contain significantly lower total glass network formers ($SiO_2 + B_2O_3$) than the other glasses considered here. The G2 glasses also contain large amounts of alkaline earth oxides, particularly CaO and BaO, whereas none of the other candidate glasses contain significant levels of alkaline earths. As barium is a relatively large ion with a low ionic field strength, lower hardness values for the G2 glasses, by comparison with the others, are not surprising and lower hardness results have previously been reported by one of the present authors (RJH) for a series of K_2O–BaO–MgO–SiO_2 (KBMS) glasses [24]. Nevertheless, the hardness

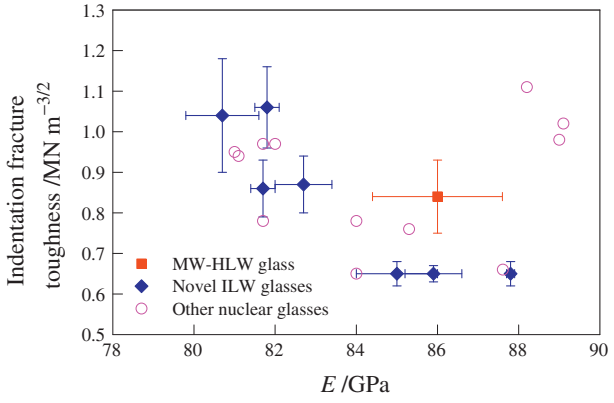

Fig. 1. Indentation fracture toughness versus Young's modulus for the glasses considered in this study and for other nuclear glasses (data taken from Donald et al. [1], Weber et al. [37] and O'Holleran et al. [38]).

Table 3
Literature data.

Glass type (and data source)	Density (Mg m^{-3})	H_V	K_c (MNm$^{-3/2}$)	E (GPa)	v
Borosilicate [1]	2.60	7.2	0.97	82	0.22
PNL 76–78 [1]		6.2	0.65	84	
SON68 [1]		9.1	0.95	81	
SM513 [1]		7.2	0.98	89	
MCC 76–68 [37]	2.953	6.16	0.94	81.1	0.241
VG 98/12 [37]	2.564	6.30	0.78	81.7	0.231
VG 98/12 + Mo [37]	2.577	6.39	0.78	84.0	0.230
GP 98/12 [37]	2.772	6.12	0.97	81.7	0.238
SM 58 LW 11 [37]	2.606	7.09	1.11	88.2	0.229
SM 513 LW 11 [37]		7.17	1.02	89.1	
DWPF S00194 [38]		5.89	0.76	85.30	
DWPF S00412 [38]		5.93	0.66	87.61	

values of the G2 glasses are still ~25% higher than those of the KBMS glasses, probably reflecting the difference in composition between the two sets of glasses and the higher level of large, low ionic field strength alkali (potassium) ions in the KBMS glasses, even though they contained higher levels of SiO_2 than the G2 glasses. Indeed the G2 glasses exhibit higher hardness values than all of the glasses studied by Hand and Tadjiev [24]. The glasses studied by Hand and Tadjiev consisted of various combinations of silica, alkali oxides (Na_2O, K_2O) and alkaline earth oxides (MgO, CaO and BaO) and all contained a minimum of 65 mol% SiO_2; considerably higher than in any of the glasses studied here. This may reflect the fact that the atoms constituting the glasses studied here are more densely packed, and therefore may be more difficult to deform than those studied by Hand and Tadjiev [24]. The atomic packing density can be calculated using

$$C_g = \rho N_A \frac{\sum_i f_i V_i}{\sum_i f_i M_i} \tag{8}$$

where N_A is Avogadro's number, f_i is the atomic fraction of species i, V_i is the ionic volume of species i (calculated using the mean of the crystal radius and the effective ionic radius; the values considered do not differentiate between bridging and non-bridging oxygen bonds as the effective ionic radii in glasses are not usually known to high accuracy [15]) and M_i is the molar mass of species i. The calculated atomic packing densities for the glasses studied here are ~0.54 (except for MW-HLW for which packing density is ~0.58) whereas for the glasses studied by Hand and Tadjiev the calculated atomic packing densities lie between ~0.49–0.51.

Eq. (1) suggests that increasing modulus will increase fracture toughness. Fig. 1 shows that this is not the case for the glasses studied here along with some nuclear waste glasses reported in the literature ([1,37,38]; for details see Table 3). A similar observation was previously made by Hand and Tadjiev [24]. Although Fig. 1 suggests that there may be an inverse correlation between fracture toughness and modulus, it should be noted that the range of moduli values measured here is very limited. Hand and Tadjiev [24] pointed out that in general hardness tends to increase as modulus increases and on this basis one would expect toughness to decrease, since harder materials tend to be less tough. However, as shown in Fig. 2, for the various nuclear waste glasses considered here, as hardness increases toughness also tends to increase. This may simply reflect the fact that the data do not span a wide range of moduli values, reflecting the fact that all of these glasses exhibit similar mechanical properties.

Eq. (1) can be used to calculate a fracture "surface" energy term from the measured indentation fracture toughness and moduli values. This is not a pure surface energy, and would not be even if fracture toughness had been measured by conventional techniques, hence the use of inverted commas. The G2 glasses all exhibit fracture "surface" energy values between 2.4 and 2.5 J m^{-2}; the MW-HLW gives a value of 4.1 J m^{-2}; G1-MP1 and G3-MP3 glasses give values between 4.5 and 4.6 J m^{-2}; whilst the G1-MP3 and G3-MP1 glasses give values between 6.7 and 6.9 J m^{-2}. As shown in Fig. 3 increased brittleness, calculated from toughness and hardness values using Eq. (4), correlates with decreased fracture "surface" energy. Thus there may be some advantage in identifying glasses such as G1-MP3 and G3-MP1 which are less brittle, although it should be noted that the G1-MP1 and G3-MP3 glasses give results that are in line with the MW-HLW glass.

Sehgal and Ito [26] have previously suggested that in general brittleness increases with increasing density for so-called normal glasses which do not densify under indentation (straight line in Fig. 4). For anomalous glasses where densification occurs under indentation then there is a deviation from this general trend (curved line in Fig. 4). Although some of the data obtained here falls around the general trend proposed by Sehgal and Ito it is notable that the densest (G2) glasses fall well away from this line; this is also true of some of the data for other nuclear waste glasses found in the literature. Thus, whilst increased density does seem to imply increased brittleness, the densest glasses reported here are not as brittle as might have been expected if the Sehgal and Ito relationship [26] were of general application. The higher density of these G2 glasses reflects their high BaO content. Hand and Tadjiev [24] have reported that toughness appears to decrease with increased (CaO + BaO) content in silicate glasses and the G2 glasses follow the same trend. These doubly charged species are expected to be relatively tightly bonded into the network (by comparison with, for example, singly-charged alkali cations) and hence immobile, which would mean that they do not readily participate in dissipative effects during crack growth. Dissipative effects are important in increasing fracture "surface" energy and therefore fracture toughness.

Putting these trends together may, purely from the perspective of mechanical properties, suggest that there may be a small advantage in selecting glasses with lower moduli and which are less dense. However, it is also necessary to ensure that any nuclear waste glasses exhibit desirable processing behaviour, high waste loading capacity and high chemical durability, and given the relatively limited variation in mechanical properties for all of the glasses observed here, for these glasses at least, the mechanical properties should probably be a secondary selection criteria. Therefore given the narrow range of mechanical properties exhib-

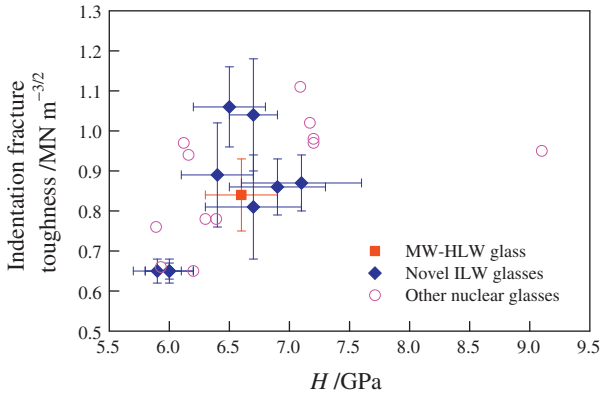

Fig. 2. Indentation fracture toughness versus hardness for the glasses considered in this study and for other nuclear glasses (data taken from Donald et al. [1], Weber et al. [37] and O'Holleran et al. [38]).

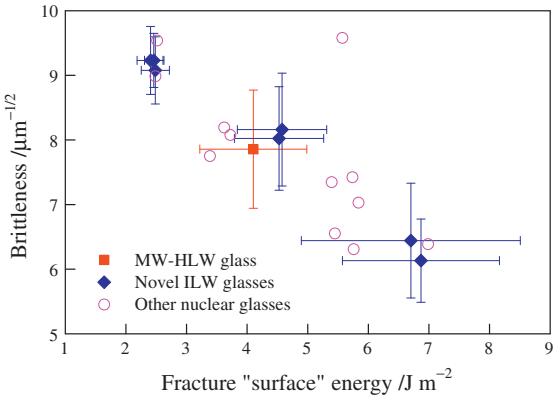

Fig. 3. Brittleness calculated from indentation toughness and hardness values using Eq. (4) versus fracture "surface" energy calculated from measured indentation toughness and moduli values using Eq. (1).

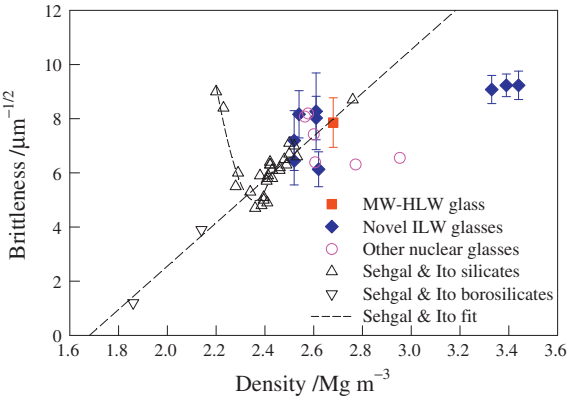

Fig. 4. Brittleness versus density for the glasses considered in this study, other nuclear glasses (data taken from Donald et al. [1] and Weber et al. [37]) and a range of silicate and borosilicate glasses (data from Sehgal and Ito [26]).

ited by the surveyed glasses, it can be confirmed that all of the glasses investigated have similar mechanical properties to the UK MW-HLW glass which has already been accepted as a vitreous wasteform.

5. Conclusions

The mechanical properties of a number of potential ILW glasses have been investigated and compared with an inactive simulant of the UK MW-HLW glass and with some nuclear waste glass data reported in the literature. It has been shown that the properties of all of the glasses considered fall into a relatively limited range of values indicating that the differences in mechanical properties between these various glasses are small. Within the range of values observed it has been found that the indentation fracture toughness tends to decrease with increasing modulus and that brittleness scales with density and the inferred fracture "surface" energy.

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