JOURNAL OF MATERIALS SCIENCE 21 (1986) 1413–1416

Sol–gel production of titanosilicate glass–ceramics for nuclear waste immobilization*

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Titanosilicate glass–ceramics designed for radioactive waste immobilization have been fabricated by a sol–gel route. Calcination and wet-milling, followed by drying, cold-pressing and sintering, produced material having very nearly the theoretical density. A maximum sintering temperature of 900° C was used, which is considerably less than the temperature of $\geqslant 1300°$ C required for production by melting. The materials were characterized by differential thermal analysis, X-ray diffraction, infrared spectroscopy and scanning electron microscopy.

1. Introduction

Na_2O–Al_2O_3–CaO–TiO_2–SiO_2 glass–ceramics containing micrometre-sized sphene ($CaTiSiO_5$, also known as titanite) crystals in an aluminosilicate glass matrix are being studied [1, 2] as alternatives to glasses for the immobilization of waste that would arise from possible future recycling of used nuclear fuel in Canada. The sphene crystals would be thermodynamically stable in the granitic groundwaters [3, 4] which occur deep in the Canadian Shield (the reference location for permanent waste disposal in Canada), and sphene can incorporate, in solid solution, many of the waste fission products and actinides [5, 6]. The aluminosilicate glass phase is also very durable in granitic groundwater [1, 2].

Ignoring waste, the basic composition in mol % is as follows: Na_2O, 6.6; Al_2O_3, 5.1; CaO, 16.5; TiO_2, 14.8; SiO_2, 57.0. These glass–ceramics have to date been fabricated by melting at ~ 1400° C and crystallizing at 1050° C [1, 2]. The present work addresses an alternative means of production of the chemically equivalent glass–ceramics by a sol–gel route in which the maximum temperature is 900° C, with the attendant reduction of fission product volatility and elimination of refractory corrosion. In principle, the sol–gel method allows the formation of a very reactive powder in which the components are mixed on a molecular scale, and which can then be compacted and crystallized at a temperature well below the melting point. Formation of the glass–ceramics by sintering powdered glass frit is also under investigation but will be described elsewhere (paper in preparation with other other authors).

2. Experimental details

The materials were prepared as follows. Nitrate solutions of sodium, calcium and aluminium were first mixed and acidified to pH ~ 1 with nitric acid, and this was followed by the addition of a colloidal suspension of silica (practical grade; EM Industries, Gibbstown, New Jersey, USA). Tetraethyl orthotitanate (purum; Fluka Corp, Hauppange, New York, USA) dissolved in 2-propanol was added slowly, with continuous stirring, to prevent initial formation of a lumpy (titanium-rich) gel. The nitrates were all of Analar grade. Some experiments were conducted using the practical grade of tetraethyl orthotitanate and no differences in the results were apparent. Batches of material (see Table I) were made up to weigh 30 to 100 g after processing. The mixture was evaporated to dryness at ~ 70° C over a period of 1 to 2 days, with gelation taking place as the liquid volume was reduced. The dried gel was then calcined in air at ~ 600° C for several hours to decompose the nitrates and organic material. Subsequent wet-milling in an alumina container was performed for 1 to 2 days, with alumina balls and 2-propanol as the liquid. The 2-propanol was then evaporated away and the powders were sintered (see below). The process flowsheet is shown in Fig. 1.

Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the powders were carried out on a Stanton–Redcroft instrument (STA-781), using a sample weight of 30 to 100 mg, a heating rate of $10° C\,min^{-1}$ and α-Al_2O_3 as the inert reference material. X-ray diffraction (XRD) measurements were made using Cu$K\alpha$ radiation and a diffractometer fitted with a graphite monochromator. Scanning electron microscopy (SEM) was performed with an ISI DS130 instrument, and some of the samples were etched in 1% solution for 20 sec before they were coated with a sputtered gold film. The etching was performed to differentiate between glass and crystalline material. Powder infrared spectra were recorded on a Nicolet MX–1 instrument over the 4000 to $400\,cm^{-1}$ range, using 1.27 cm diameter KBr pellets containing 1 wt % of sample and weighing ~ 300 mg.

1.27 or 2.54 cm diameter pellets of powders were

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*Issued as AECL–8695

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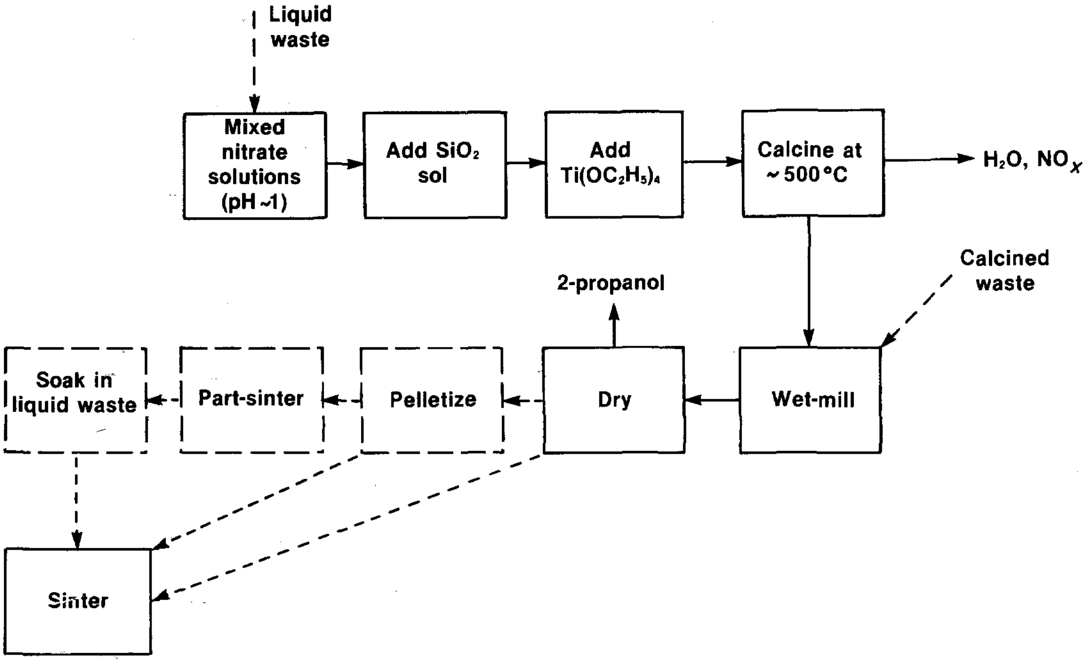

Figure 1 Process flowsheet for glass–ceramic preparation by sol–gel route. Dashed lines indicate possible alternative routes.

pressed in steel dies, with an applied pressure of ~ 50 MPa, prior to sintering. Densities and open porosities were measured by Archimedes' method on samples weighing 2 to 6 g, using water as the immersion liquid. All these samples were boiled in deionized water for at least 1 h to allow water to fill any open pores. Autoradiographs were registered by placing a sample in contact with X-ray film (Kodak; DER-392).

3. Results and discussion

3.1. Waste-free material

The calcined powder was amorphous to X-rays, although some very diffuse peaks were observed in the vicinity of angles corresponding to the Bragg reflections of anatase (Fig. 2a). Infrared spectra (Fig. 2b) were similar to those obtained [1] for the equivalent glasses prepared by melting. The broad absorption bands centred near 1000 and 500 $\mathrm{cm^{-1}}$ were due to silicate vibrations and the spectrum was quite similar to that of vitreous silica [7]. SEM of the milled powders showed that a variety of apparent grain sizes were present, ranging from several micrometres to less than a micrometre. EDX spectra taken with a micrometre-sized beam (E = 15 keV) on several grains did not reveal any compositional deviation from the average value, indicating chemical homogeneity on the micrometre scale. The specific surface area of one milled powder was determined as 20 $\mathrm{m^2\,g^{-1}}$ by the Brunauer–Emmett–Teller (BET) method, using the adsorption of nitrogen gas.

DTA of the calcined powder yielded a single exothermic peak at ~ 830° C with a half-width of ~ 20° C, due to the crystallization of sphene; the exothermic peak obtained with milled material had a half-width of 10 to 15° C. These results are very similar to those observed [2] in finely powdered glass of the same composition made by melting. Weight losses from TGA on heating the milled powders to 600° C were ~ 2%, but further losses on heating in the DTA apparatus to 1000° C were < 0.2%. The weight losses on heating to 600° C are attributed to removal of volatiles, such as adsorbed atmospheric water and traces of organic material.

Sintering of the calcined materials was studied. Pellets inserted directly into a furnace preset at 800 to 1100° C exhibited swelling, presumably from evolution of the aforementioned residual water and organic

TABLE I Starting materials for preparation of 32 g (0.5 mole) of sphene glass–ceramic by sol–gel method

Chemical	Weight (g)	
$NaNO_3$	5.6	
$Al(NO_3)_3 \cdot 9H_2O$	19.1	in 400 ml water
$Ca(NO_3)_2$	13.5	
Colloidal SiO_2 (30% dry weight)	57.0	
$Ti(OC_2H_5)_4$	16.9	in 200 ml 2-propanol

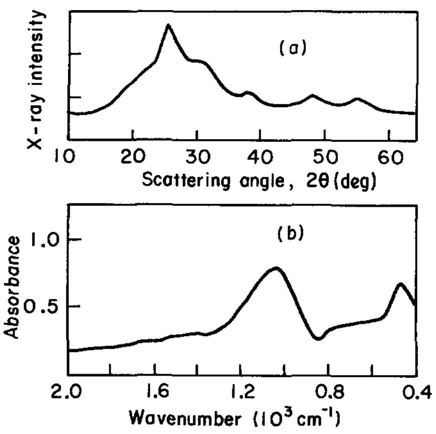

Figure 2 X-ray scattering and infrared absorption from Na_2O–Al_2O_3–CaO–TiO_2–SiO_2 calcined sol–gels. (a) X-ray scattering in arbitrary units as function of scattering angle. Cu$K\alpha$ radiation. (b) Absorbance of KBr pellet containing 1 wt % of sample over 2000 to 400 $\mathrm{cm^{-1}}$ range.

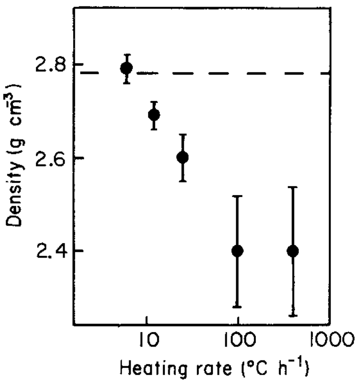

Figure 3 Density of sphene glass–ceramics made by cold-pressing and sintering calcined, milled precursor powders from 700 to 900° C at variable rates. Values represent averages obtained from at least two pellets. The horizontal dashed line gives the density of the glass–ceramic prepared by melting and reheating.

material at temperatures above ~700° C. Densification of the pressed pellets to near-theoretical values could only be brought about by the use of milled powders, together with slow heating rates at temperatures above 700° C. Better than 97% of the theoretical density (2.78 g cm^{-3}, known from work with materials made by melting) and open porosities of < 1% were achieved with wet-milled calcines that were pelletized and heated rapidly to 700° C (≈ 1000° C h^{-1}) and then from 700 to 900° C at < 12° C h^{-1}. XRD showed that sphene was the only crystalline phase present. Some results obtained with different heating rates over the temperature interval 700 to 900° C are shown in Fig. 3.

Samples heated at 6° C h^{-1} over the 700 to 900° C temperature range had the theoretical density and had zero open porosity within experimental error. The essential coincidence of the densities of these pellets and that of the fully crystallized glass–ceramic made by melting and reheating (Fig. 3) showed that crystallization of sphene in the pellets was complete. As further evidence of this, no density change was observed when these sintered pellets were heated to 1100° C. No grain structure could be detected by SEM at a magnification of 30 × 10^3. Some closed porosity was present however (Fig. 4).

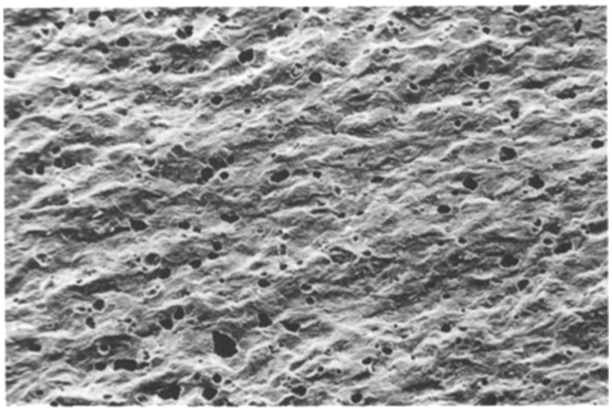

Figure 4 SEM photograph of sphene glass–ceramic made by cold-pressing and sintering calcined, milled powder at 6° C h^{-1} over the 700 to 900° C temperature range.

TABLE II Constituents of simulated Purex waste [10]

Oxide	Content (wt %)	Oxide	Content (wt %)
PdO	11.9	SrO	2.1
UO_2	12.0	BaO	4.1
La_2O_3	6.3	MoO_3	18.1
Pr_2O_3	1.4	ZrO_2	9.0
Nd_2O_3	11.1	SnO_2	0.3
Y_2O_3	1.3	Fe_2O_3	3.4
CeO_2	7.5	Cr_2O_3	0.9
Cs_2O	7.7	NiO	2.8

In an attempt to simplify the process, the possibility of sintering without the pressing of pellets was investigated. Thus, 5 cm^3 alumina crucibles were filled with the milled calcines, the powder being compacted by shaking and tapping only, and the same heating routines were carried out. Considerable three-dimensional shrinkage was observed and the resultant densities were 85 to 98% of theoretical. The variability was probably due to the non-standardized method of initial compaction, but part of the difficulty lay in the tendency of the milled powders to aggregate into loosely bound lumps upon evaporation of the liquid after wet-milling. The use of liquids (2-propanol or water) to try to improve the pre-sintering compaction of the milled powders in containers has not been encouraging insofar as gross cracking resulted after drying, and the pellet-pressing method remains the better option.

The effects of varying the starting conditions for the sol–gel preparation were explored briefly, keeping the heating rate of the pressed pellets from 700 to 900° C constant at 6° C h^{-1}. Adjustments were made as follows:

(a) The atomic substitution of barium for 30% of the calcium lowers the softening temperatures of the equivalent glasses produced by melting [8] and this might be expected to assist densification on sintering. In the present work, however, such substitution had no detectable effect on the results.

(b) A five-fold dilution of the starting solutions (Table I) similarly had no detectable effects on the final products.

(c) Spontaneous gelation was induced by adding ammonia to the mixed solutions such that the final pH was ~9; the subsequent sintering behaviour of the calcined, milled material was poor (~90% of theoretical density), and the rapid gelation presumably produced a chemically inhomogeneous material.

(d) Evaporation of the mixed solutions was allowed to take place over a period of 14 days at 40° C, instead of 1 to 2 days at 70° C; here again the sintering behaviour of the material was poor (~90% of theoretical density), possibly due to chemical inhomogeneity of the gel via an over-ageing process.

3.2. Incorporation of waste

The possibility of process simplification by omitting the step of wet-milling a waste-loaded (radioactive) material was then considered, bearing in mind that the presence of relatively large grains in a matrix of fine particles would inhibit sintering [9]. A simulated nitrate waste mixture (Table II) based on the main

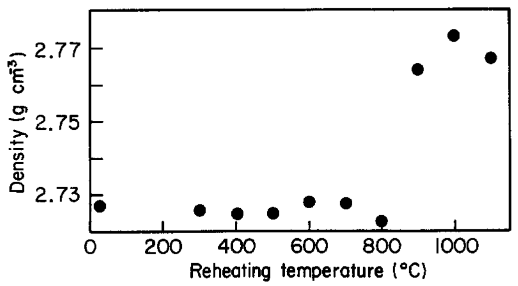

Figure 5 Density of equivalent $Na_2O-Al_2O_3-CaO-TiO_2-SiO_2$ glass made by melting, as a function of reheating temperature. Reheating performed for 1 h, at successively higher temperatures. Crystallization complete after 1 h at 1100° C.

constituents of Purex waste [10] derived from used Candu^{TM} reactor fuel, was calcined and mixed with the standard (Table I) calcined, milled $Na_2O-Al_2O_3-CaO-TiO_2-SiO_2$ powder in a 1:9 ratio by weight. Anticipating sintering problems, the standard heat-treatment of fast heating to 700° C, followed by heating at $6^\circ C h^{-1}$ from 700 to 900° C, was replaced by one in which the heating rate from 700 to 900° C was slightly slower and the rate from 500 to 700° C considerably slower. When pressed pellets were heated from ambient temperature to 500° C at $\sim 300^\circ C h^{-1}$, from 500 to 700° C at $50^\circ C h^{-1}$ and from 700 to 900° C at $5^\circ C h^{-1}$, their densities ($2.5 \pm 0.05\,g\,cm^{-3}$) were considerably less than those of waste-free pellets ($2.80\,g\,cm^{-3}$). XRD showed additional (unidentified) reflections to those characteristic of sphene. It was clear that sintering was far from complete, and compaction may require uniaxial or isostatic hot pressing.

An alternative method of forming a waste-loaded material is to soak a porous pellet of the inactive sol–gel-derived powder in waste solution, and then to sinter it. A Purex waste solution would be strongly acidic. To sufficiently suppress chemical reactions of the pellet with the acid waste, the pellet had to be part-sintered to ~ 720° C for 1 h prior to soaking. The open porosity of the part-sintered pellet was only ~ 30% compared to ~ 60% for the as-pressed pellet. (Reaction with acid tended to preferentially remove calcium from the pellet, so that after subsequent heating, phases such as rutile and cristobalite were observed by XRD in addition to sphene.)

A problem encountered with soaking the porous pellets in near-neutral solutions of (simulated) fission products was that ion exchange between Ca^{2+} and H^+ appeared to produce high pH values in the solution near the surface of the pellet; this caused certain metals (such as uranium) to precipitate as hydroxides, with the result that they apparently prevented further penetration of the liquid and were only incorporated near the surface of the pellet. This was confirmed for uranium by autoradiography. Subsequent heating resulted in cracking of the pellets due to non-uniform densification.

To determine whether the presence of waste elements themselves affected the formation of the pellets, equal parts by weight of caesium, strontium, lanthanum (representative and relatively abundant fission products) and uranium were added as nitrates to the starting solutions (Table I) to give a total elemental waste loading of 5 wt % in the final form. The properties of the loaded glass–ceramic were essentially identical to those of the basic glass–ceramic composition, so there does not seem to be any intrinsic difficulty in preparing the waste-loaded glass–ceramics.

4. Conclusions and final remarks

The sol–gel route, together with sintering at a maximum temperature of 900° C, appears to be a feasible alternative to melting for the production of sphene glass–ceramics. As mentioned in Section 1, the lower processing temperature compared with melting (~ 1400° C) should offer significant advantages with regard to losses of volatile fission products and the absence of a refractory melter. More work is necessary to get quantitative data on process simplification by eliminating milling and/or pelletizing of the waste-containing materials.

Acknowledgements

Helpful discussions with P. J. Hayward, J. C. Tait and A. G. Wikjord are acknowledged. Thanks are due to I. M. George, R. Haines, D. Hodgson and J. Snider for obtaining SEM, IR, BET and XRD data respectively.

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Received 13 May
and accepted 12 June 1985