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Borosilicate and lead silicate glass matrix composites containing pyrochlore phases for nuclear waste encapsulation

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Abstract

Glass matrix composites intended for the immobilisation of plutonium bearing nuclear legacy waste have been manufactured. Two different matrices, a soda borosilicate glass and a lead silicate glass, are proposed for encapsulating lanthanum and gadolinium zirconates having pyrochlore crystalline structure. The fabrication of the composites involves powder mixing followed by cold pressing and pressureless sintering or hot-pressing at relatively low temperatures (<620 °C). The hot-pressing route is found to be the most convenient, since it leads to relatively high densification even with substantial loading of pyrochlore phase (40 vol.%). The absence of microcracks, due to the close matching of thermal expansion coefficients of the composite constituents, together with the strong pyrochlore particle/glass matrix interfacial bonding, suggests that the composites have good mechanical properties. The innovative introduction of gadolinium zirconate in a lead silicate matrix represents an attractive approach, since the composites reach reasonably high densities both by pressureless sintering and hot-pressing.

1. Introduction

Extensive research activity has been conducted in the field of the safe immobilisation of the different streams of nuclear wastes, leading to the development of waste forms based on polycrystalline ceramics [1,2] or on amorphous glasses and glass–ceramics [2–5]. Due to the ability of glasses to act like a solvent for high-level wastes (HLW), the fairly low processing temperatures involved, as well as their good chemical durability and radiation resistance, silicate glass based waste forms have been the most widely considered. However, crystalline materials with fluorite and fluorite related structures such as pyrochlore are of increasing interest as possible host phases for fission products and actinides, in particular Pu [6–13]. Pyrochlore phases may be found for example within the multitude of crystalline phases in a Synroc waste [1]. In addition, Pu is known to substitute in other Zr containing ceramics such as zircon [14].

Pyrochlore phases are specially interesting because they are remarkably stable against heavy ion induced amorphization [8,13]. The amorphization phenomenon is particularly detrimental for the waste glass forms, in which a partial devitrification occurs over time: the heavy ion induced amorphization of the newly formed crystalline phase may lead to swelling and microcracking [15].

With the aim of exploiting both the advantages of glass waste forms and the radiation resistance of certain crystalline phases, waste forms based on composite materials containing ceramic and glass phases, or on specifically designed glass–ceramics, have been proposed

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for the immobilization of different types of radioactive waste [14–19], with some early concepts summarised in Refs. [20,21]. Following this approach, a crystalline phase containing the radionuclides is encapsulated in an inert glass or ceramic matrix containing no radionuclides. Several examples of this composite type of nuclear waste form exist. For example, it has been proposed that Synroc could be combined with a glassy phase to form a composite waste form [1]. Other ceramic–glass composite waste forms have been developed at Argonne National Laboratory, where aluminosilicate zeolite crystalline phases are combined with glass frit and hot isostatically pressed [14]. In similar developments, mixtures of glass and crystal forming components have been hot isostatically pressed at Idaho National Laboratory [15] obtaining a glass–ceramic in which most radioactive waste (95 wt%) resides in the crystalline phase encapsulated in the residual glassy phase. A similar glass–ceramic based concept [16] considers the crystallisation of zirconolite ($CaZrTi_2O_7$) in an aluminosilicate glass matrix, with the radioactive components (e.g. lanthanides and actinides) becoming incorporated in the zirconolite phase. French researchers [17] have recently proposed a sol–gel derived high silica glass as a host matrix for actinides. The incorporation of wastes in a silica matrix was used also at the Catholic University in the USA [18], by capillary infiltration of liquid waste through a highly porous host structure. More recently, reaction-sintered glasses have been developed as durable matrices for spinel-forming nuclear waste compositions [19], following previous experiences in Germany [22] and Argentina [23] on sintered glass matrices. In fact, there are several earlier developments regarding the encapsulation of waste containing crystalline phases in silicate glass and glass–ceramic matrices [24–29]. Borosilicate glass, sand, fused silica, lead borosilicate glass, quartz and aluminosilicates have all been proposed as the inert matrix for the encapsulation of calcined PW-4, a typical light-water reactor fuel reprocessed waste. Hot-pressing was used in those early efforts to densify the composite mixtures. In most cases, relatively high temperatures (about 1000 °C) were required and the volume fraction of waste added was relatively low (e.g. 14 vol.% [28]). Addition of a lead borosilicate glass to α-quartz was attempted in order to enhance consolidation of the mixture during hot pressing [28].

In our own previous work [30,31], the feasibility of producing highly dense glass matrix composites from lead silicate glass and pyrochlore phase consisting of lanthanum zirconate has been demonstrated. The use of lead silicate glass matrix, coming from the dismantling of cathode ray tubes, which is itself a problematic surplus material [32,33], is attractive since this glass provides sinterability at relatively low temperatures, good resistance towards devitrification [34] and potential further shielding from radiation.

The use of sintered glass for the matrix allows, in general, relatively low processing temperatures, much lower than the sintering temperature required for densification of crystalline pyrochlore ceramics, which is approximately 1200 °C [35,36], thus introducing notable production economics. Moreover, the processing temperature for a glass powder based approach will also be lower than the temperatures required for crystallisation of host phases in specifically designed glass–ceramics, which are usually well above 1000 °C [2,16]. In addition, densification by sintering and hot-pressing of selected matrices brings the significant advantage of avoiding devitrification and phase separation phenomena which may occur in glass melting processes [2,3].

In this work we discuss the manufacturing of glass matrix composites containing lanthanum zirconate $La_2Zr_2O_7$ or gadolinium zirconate $Gd_2Zr_2O_7$ inclusions as alternative nuclear waste forms. As previously mentioned, pyrochlore phases are particularly effective as host phases for actinides. Consequently, the waste forms proposed could find applications in the treatment of certain weapons based legacy waste. Lanthanum zirconate is proposed as inclusion phase in a lead silicate glass matrix in a much higher concentration than that achieved in previous work (40 vol.%) [30]. Moreover, $La_2Zr_2O_7$ is also incorporated in a soda borosilicate glass. Since $La_2Zr_2O_7$ may not be the most radiation resistant pyrochlore [6,9,37], $Gd_2Zr_2O_7$ is proposed in this investigation, for the first time, as its substitute in a lead silicate glass matrix. $Gd_2Zr_2O_7$ exhibits physical properties similar to those of $La_2Zr_2O_7$ [38], the most significant being the thermal expansion coefficient, which is well matched to the thermal expansion coefficient of the selected glass used as matrix. The microstructure of the composites produced is characterised and their fracture behaviour investigated.

2. Experimental procedure

2.1. Starting materials

Lanthanum zirconate and gadolinium zirconate powders were received from Los Alamos National Laboratory (LANL, USA). The synthesis of the lanthanum zirconate powder from commercial powders of La_2O_3 (Alpha Aesar 99.99% purity) and ZrO_2 (Alpha Aesar 99.978% purity) has been described elsewhere [30]. The morphology of the lanthanum zirconate powder used to fabricate the composites is shown in Fig. 1(a). Agglomerates of different sizes have formed during the powder synthesis and primary particles have coalesced during the high-temperature fabrication, leading to the formation of large agglomerates. The microstructure of these agglomerates is that of sintered primary particles of sizes in the range 1–10 μm with considerable residual

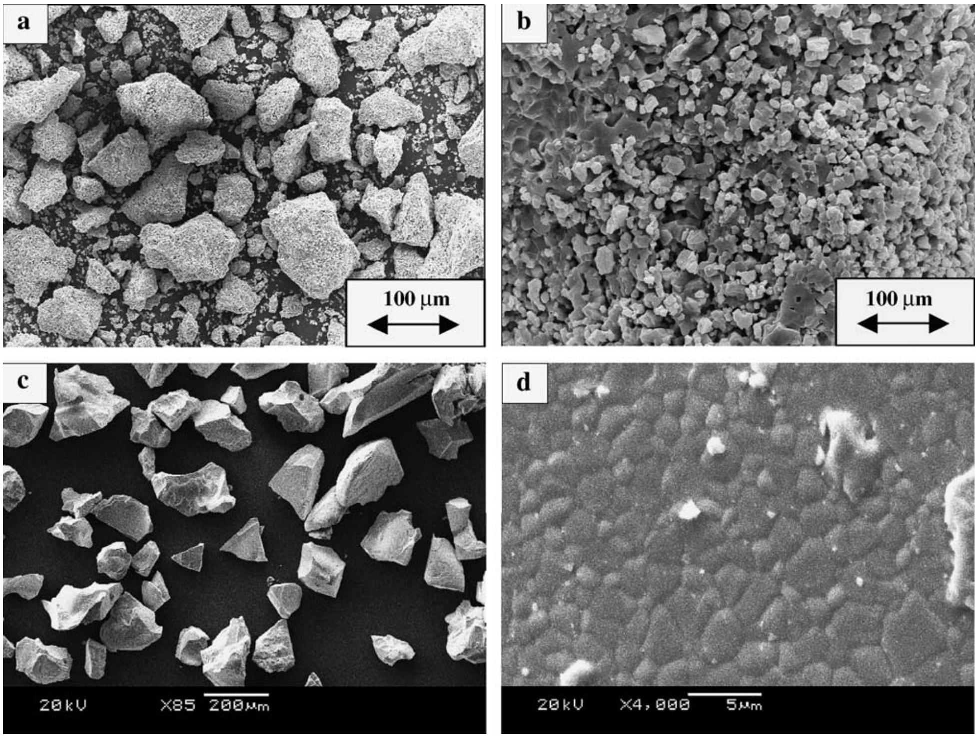

Fig. 1. SEM images of the as-received zirconate powders showing large agglomerates and their microstructure: $La_2Zr_2O_7$ at (a) low and (b) high magnification, $Gd_2Zr_2O_7$ at (c) low and (d) high magnification.

intergranular porosity, as shown in Fig. 1(b). Previous analyses [30] have shown that the lanthanum zirconate powder has stoichiometric pyrochlore structure, which was retained after calcination treatments at 800 °C in air or argon.

Gadolinium zirconate powder was prepared at LANL by co-precipitation synthesis. The starting materials were gadolinium chloride ($GdCl_3 \cdot 6H_2O$) and zirconium dichloride oxide ($ZrOCl_2 \cdot 8H_2O$). The description of the preparation method followed at LANL is given elsewhere [39]. The morphology of the gadolinium zirconate powder is shown in Fig. 1(c) and (d). The relatively large particle size and angular morphology of the powder is evident in Fig. 1(c), while Fig. 1(d) shows the dense microstructure of the particles, which have a fine and uniform grain size (<5 μm). Relevant physical and mechanical properties of lanthanum and gadolinium zirconate are given in Table 1 [35,36,38,40,41]. X-ray diffraction (XRD) and DTA/TG (differential thermal analysis and thermogravimetry) analysis were conducted on the as-received gadolinium zirconate powder in order to assess the crystallinity of the pyrochlore phase and to investigate its thermal stability. The heating rate for the DTA/TG analysis was 10 °C/min.

The lead-containing glass powder was obtained from discarded TV sets. More particularly, it consists of the glass employed for the manufacture of the cone, i.e. the part hidden inside the TV sets. This glass was chosen because of its thermal expansion coefficient, which matches almost exactly that of the lanthanum zirconate and is close to that of gadolinium zirconate (see Table 1). Moreover, it has a relatively low softening point, which causes the glass to exhibit viscous flow sintering at relatively low temperatures (<700 °C) [33]. Despite recent advances in strategies to remelt these glasses for new TV cone glass production [32], difficulties in recycling Pb-containing glasses remain with an anticipated environmental impact due to their heavy metal content: it is well known, for example, that there is a risk of

Table 1
Physical properties of $La_2Zr_2O_7$ [35,36,40] and $Gd_2Zr_2O_7$ [38,41]

	$La_2Zr_2O_7$	$Gd_2Zr_2O_7$
Density (g/cm^3)	6.05	6.99
Melting/softening point (°C)	2300	2250
Linear thermal expansion coefficient (10^{-6} K^{-1})	9.1	11.6
Thermal conductivity (W/m K)	1.5	1.6
Elastic modulus (GPa)	175	205
Hardness (GPa)	9.9	10
Fracture toughness (MPa $m^{1/2}$)	1.1	Not available

Table 2
Properties of the lead silicate glass [33] and the VG98 borosilicate glass [47] employed in this investigation

Glass	Lead silicate glass	VG98 borosilicate glass
Chemical composition (wt%)		
SiO_2	65.19	56.70
B_2O_3	–	12.40
Al_2O_3	4.24	26.00
Na_2O	11.62	17.50
K_2O	5.68	–
CaO	0.91	4.10
MgO	1.36	2.10
BaO	1.20	–
PbO	9.80	–
TiO_2	–	4.60
Average particle size (μm)	2	5.5
Density ($g\,cm^{-3}$)	2.89	2.57
Linear thermal expansion coefficient (10^{-6} K^{-1})	9.1–9.3	10.6
Softening point (°C)	580	537

extensive PbO volatilisation during remelting of lead containing glasses at temperatures >1000 °C. There is therefore strong motivation to develop alternative technologies for their reuse, exploiting sintering routes at moderate temperatures [33,42–44].

The soda borosilicate glass, named VG98, was originally developed in Germany [45]. It has been already employed in the past in studies on the immobilization of nuclear waste [22,45]. It has also been used for production of metal reinforced glass matrix composites [46,47] and porous glasses with controlled porosity [48]. Moreover, the sintering behaviour of VG98 glass has been studied [49]. Due to the soda content (being higher than that of common borosilicate glasses [34]) glass VG98 has a low softening point and consequently low sintering temperature and relatively high thermal expansion coefficient (10.65×10^{-6} K^{-1}), which closely matches the thermal expansion coefficient of the zirconates. Table 2 presents a summary of relevant physical and mechanical properties of the glasses used.

2.2. Composites manufacturing

Three glass/pyrochlore systems were investigated in this work, as summarized in Table 3. The first system consisted of a lead silicate glass matrix incorporating 40 vol.% $La_2Zr_2O_7$. The previous work [30,31] demonstrated the feasibility of composites with lower concentration of pyrochlore addition: the aim of this investigation was thus to infer the upper limit for the concentration of pyrochlore in the same lead silicate glass matrix with the obtainment of the highest possible density. The second system consisted of VG98 borosilicate glass incorporating 5 or 30 vol.% $La_2Zr_2O_7$. The proportions were the same investigated in previous work [30,31] using a lead silicate glass matrix. Finally, the third system consisted of a lead silicate glass composite containing 10 vol.% $Gd_2Zr_2O_7$, which has not been previously studied.

Table 3
Summary of the three glass/pyrochlore systems investigated

System	Glass matrix	Pyrochlore inclusions	vol.% pyrochlore
1	Lead silicate glass	$La_2Zr_2O_7$	40%
2	Borosilicate glass	$La_2Zr_2O_7$	5%
			30%
3	Lead silicate glass	$Gd_2Zr_2O_7$	10%

The glass and pyrochlore powders were weighted in the suitable proportions and placed into plastic bottles. The mixtures were added with a small amount of ethanol and mixed for 30 min in a tubular mixer. The content of the bottle was then emptied into a glass petri dish. The powder was dried using a hot plate at about 40 °C and then crushed with pestle and mortar to destroy any remaining agglomerates. Cylindrical samples were then uniaxially cold pressed using a pressure of 100 MPa in a stainless steel die of 8 mm diameter. Samples height varied from 1.7 to 4 mm. The pressing time, 4 min, was optimised to avoid the delamination of the samples after ejection from the die. Zinc stearate was applied to the die plunger to enable an easy extraction of the green compacts.

In order to determine the optimum sintering conditions for the borosilicate glass matrix composites, a preliminary study was conducted on the 5 and 30 vol.% $La_2Zr_2O_7$ containing pellets by means of heating microscopy (Leica Systems, Wetzlar, Germany). The optimum sintering temperatures were found to be 620–630 and 650 °C, for the 5 and 30 vol.% composites, respectively. For the lead silicate glass with low inclusion content (10 vol.% $Gd_2Zr_2O_7$) the sintering temperature was chosen at 600 °C, consistently with previous studies [30]. For samples with a high inclusion content (40 vol.% $La_2Zr_2O_7$) the retardation in sintering caused by the crystalline inclusions [50–52] was thought to be counterbalanced by enhancing the sintering temperature to 750 °C. The heating rate was maintained constant at 3 °C/min and the holding time varied between 2 and 6 h. The sintering conditions for all composites fabricated are summarized in Table 4.

A second series of samples was uniaxially hot-pressed in vacuum. Discs of 38 mm diameter and 4 mm thickness were fabricated by using a custom-made facility, which has been described previously [53]. The graphite dies used were covered with a thin layer of boron nitride powder in order to facilitate removal of the samples after hot-pressing. Approximately 15–20 g of powder mixture were placed in the die for each hot-pressed

Table 4
Summary of the sintering and hot-pressing treatments for the manufacturing of pyrochlore containing glass matrix composites

System	Composition	Temperature (°C)	Holding time (h)
Pressureless sintering (3 °C/min heating rate)			
1	40% $La_2Zr_2O_7$/lead silicate	750	3
1	40% $La_2Zr_2O_7$/lead silicate	750	6
2	5% $La_2Zr_2O_7$/borosilicate	620	2
	30% $La_2Zr_2O_7$/borosilicate	650	2
3	10% $Gd_2Zr_2O_7$/lead silicate	600	2
Hot pressing (10 °C/min heating rate, 5 MPa compaction pressure)			
1	40% $La_2Zr_2O_7$/lead silicate	610	0.5
2	30% $La_2Zr_2O_7$/borosilicate	620	1
3	10% $Gd_2Zr_2O_7$/lead silicate	600	0.5

sample. A pressure of 5 MPa was applied when the sample had reached the processing temperature, which varied from 600 to 620 °C. The holding time varied between 30 min, for the samples with a lead silicate glass matrix, and 1 h, for samples with borosilicate glass matrix, in agreement with previous work [31,47]. The heating rate was held constant at 10 °C/min. The samples were left to cool down in the hot-press. The hot-pressing conditions are also summarized in Table 4.

2.3. Characterization of the samples

The density of the samples was determined geometrically and by the Archimedes method, and then compared with the theoretical density. The theoretical density was calculated by applying the 'rule of mixtures'. The porosity of the samples was estimated from the measured and theoretical densities.

Both sintered and hot pressed samples were broken to obtain fracture surfaces to be analysed by SEM (T200 JEOL). Some fragments were mounted in a resin matrix and polished to investigate the microstructure by SEM. Tiny fragments of the samples were crushed into powder for X-ray diffraction (XRD) analysis.

3. Results and discussion

3.1. Crystalline structure of the pyrochlore phases

Fig. 2 shows the XRD pattern of the La zirconate and Gd zirconate powders used. In the same plot, the spectrum of the as-received $Gd_2Zr_2O_7$ powder is compared with the spectrum of the same powder after it had been heated to 800 °C. All strongest peaks coincide with each other, thus indicating that the pyrochlore phase is stable up to 800 °C. Such result was confirmed by the DTA/TG analyses, which showed the thermogravimetric plot (the graph of weight versus temperature) being constant and the DTA plot not revealing any exo- or

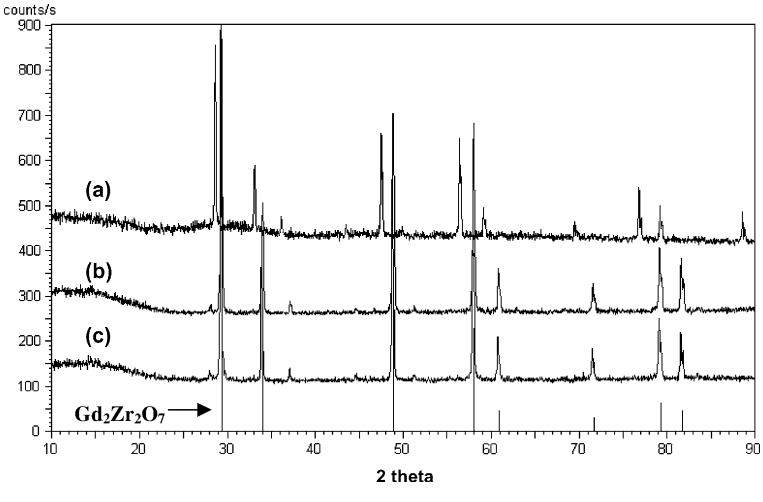

Fig. 2. XRD patterns of (a) original $La_2Zr_2O_7$ powder, (b) original $Gd_2Zr_2O_7$ powder, (c) 800 °C calcined $Gd_2Zr_2O_7$ powder. The pattern for stoichiometric $Gd_2Zr_2O_7$ structure (code number 80-0471) is also shown. Non-identified minor peaks correspond to the compound $3Gd_2O_3 \cdot 6ZrO_2$.

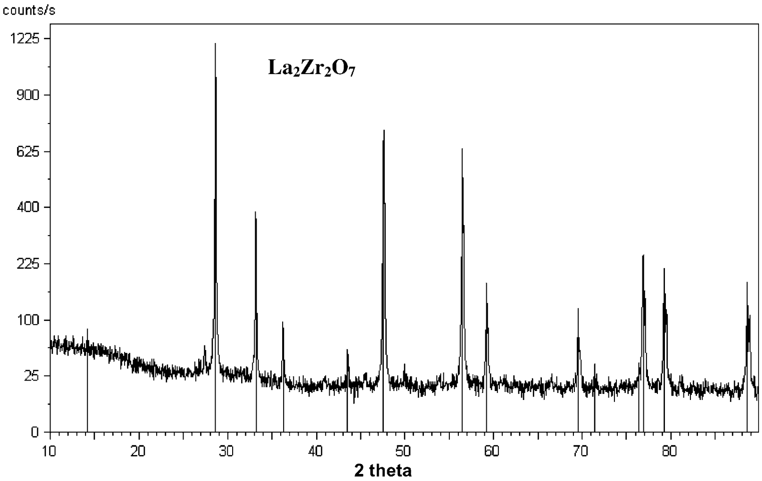

Fig. 3. XRD pattern of a borosilicate glass matrix composite containing 30 vol.% lanthanum zirconate sintered at 650 °C, showing no extra crystalline peak due to possible devitrification of the glass matrix.

endo-thermic peak due to crystalline transitions. As a consequence, the crystal phase of Gd zirconate and La zirconate powders should not transform over the temperature range used in the present investigation ($\leqslant$ 750 °C) [30].

Fig. 3 shows the XRD spectra of the sintered composites containing 30 vol.% lanthanum zirconate in the borosilicate glass, sintered at 650 °C. The pyrochlore phase is found to be the unique crystalline phase in the composite, as no devitrification process occurred in the borosilicate glass matrix. A similar result was found for the 5 vol.% containing composite. The sintering process did not modify the initial crystalline structure of the lanthanum zirconate powder, since the peaks correspond to those reported in Fig. 2. The XRD spectrum of the sintered composite made from 10 vol.% gadolinium zirconate and lead silicate glass is shown in Fig. 4 (sintering temperature: 600 °C). The peaks are all corresponding to the spectra of the gadolinium zirconate phase. Since the hot-pressing treatments were performed at lower temperatures and with shorter holding times than those required by pressureless sintering, the thermal stability of both pyrochlore phases can be inferred from the above described spectra. Similarly, the XRD results indicate the absence of any devitrification phenomenon in the selected glass matrices for all fabrication routes and composites produced in the present investigation.

3.2. *$La_2Zr_2O_7$/lead silicate glass composites*

The results of the density measurements of all composites are shown in Table 5. The sintered lead silicate glass matrix composite containing 40 vol.% $La_2Zr_2O_7$ resulted to be very porous. The relative density (the ratio of measured to theoretical density) was 0.50, even though the sintering temperature (750 °C) was much higher than the softening point of the glass [27] and the holding time was very long (6 h). A lower holding time (3 h) yielded an even more porous sample, very brittle and prone to fracture. This is consistent with the fact that the effective viscosity of the sintering vitreous mass is dramatically enhanced by increasing the content of rigid, non-sintering crystalline inclusions [50]. The increased viscosity, in turn, causes the densification rate to be notably lowered; consequently, as reported in the literature [50–52] composites containing more than 25 vol.% crystalline inclusions in a viscous matrix may hardly reach a high compaction degree when manufactured by pressureless sintering.

As expected, hot-pressed samples exhibited higher densities than pressureless sintered samples of the same composition, the relative density being 81.6%. The lower porosity of the hot-pressed samples should guarantee better mechanical properties, high structural integrity and adequate chemical resistance of the composites, in comparison to those of pressureless sintered samples, which were very fragile and prone to fracture. The porosity of the composite containing 40 vol.% $La_2Zr_2O_7$ in a lead silicate glass was significantly reduced, even for a relative brief holding time of 2 h. With a longer holding time or a slight enhancement of the processing temperature, a further reduction of the porosity is probable. This result demonstrates that a relatively high content of pyrochlore phase, the host phase for actinides, may be encapsulated in the glass matrix, maintaining a reasonably dense and mechanically resistant sample.

The micrographs in Fig. 5 show the polished and fracture surfaces of the hot-pressed sample containing

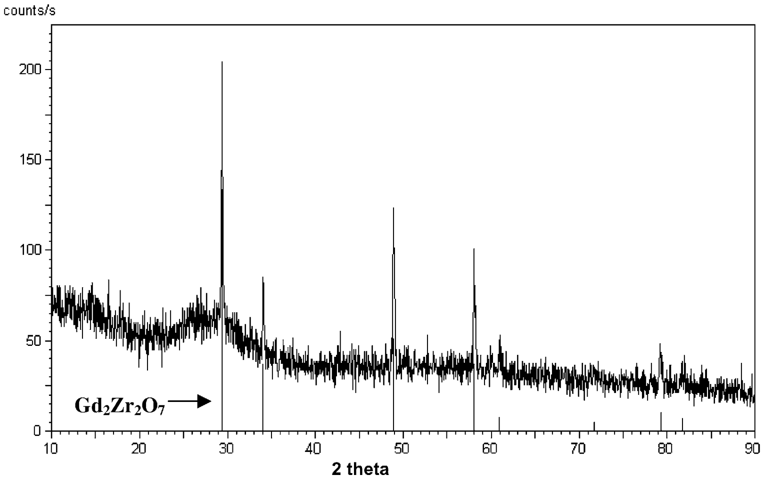

Fig. 4. XRD pattern of a lead silicate glass matrix composite containing 10 vol.% $Gd_2Zr_2O_7$ sintered at 600 °C, showing no extra crystalline peak due to possible devitrification of the glass matrix.

Table 5
Summary of the density measurements of pyrochlore containing glass matrix composites manufactured by different treatments (relative densities in square brackets)

System	Composition	Density ($g\,cm^{-3}$)	
		Pressureless sintering	Hot pressing
1	40% $La_2Zr_2O_7$/lead silicate glass	2.08 [50.1%]	3.39 [81.6%]
2	5% $La_2Zr_2O_7$/borosilicate glass	2.03 [74.0%]	–
	30% $La_2Zr_2O_7$/borosilicate glass	2.59 [71.7%]	3.36 [93.0%]
3	10% $Gd_2Zr_2O_7$/lead silicate glass	2.72 [82.4%]	3.02 [91.5%]

40 vol.% $La_2Zr_2O_7$ inclusions. In Fig. 5(a) (polished surface) it can be seen that, even for the substantial loading of $La_2Zr_2O_7$ inclusions, there is no significant interconnection between the particles, which are almost totally surrounded by the matrix. Such morphology plays a fundamental role regarding the chemical durability of the composite, since the host phases should be protected by the matrix from possible long-term contact with water, which could cause the radioactive loading in the pyrochlore phase to leach out. Moreover, the little amount of porosity is consistent with the measured density. Fig. 5(b) (fracture surface) illustrates that, like in previous work [30,31], no significant pull-out of the inclusions has occurred during fracture indicating that the interfacial pyrochlore particle/glass matrix bonding is particularly strong. The fracture surface is almost planar, thus confirming the absence of crack deflection and secondary cracks. This is expected from the close matching between the thermal expansion coefficients of the two phases, which does not cause significant residual stresses in the composites upon cooling from the processing temperatures. The absence of residual stresses and microcracks is favourable for the long-term maintenance of the mechanical strength of the composites and minimization of stress corrosion, i.e. ‘static fatigue’.

3.3. $La_2Zr_2O_7$/borosilicate glass composites

The pressureless sintered borosilicate glass matrix composites containing $La_2Zr_2O_7$ reached a significant densification (>70%) (see Table 5), in agreement with the data for composites made from lead silicate glass matrix with the same concentration of inclusions investigated earlier [30]. The assessed sintering behaviour is coherent with heating microscopy plots shown in Fig. 6. It is seen that the percentage of height contraction during sintering reaches a maximum for the 5 and 30 vol.% $La_2Zr_2O_7$ containing composites at 630 and 650 °C, respectively, for the holding time of 2 h employed in the sintering treatment.

Hot-pressing of the borosilicate glass sample with 30 vol.% $La_2Zr_2O_7$ resulted in a high compaction degree (93.0%), quite close to that achieved with a lead silicate glass as reported previously [31]. This fact is promising as soda borosilicate glass can be offered as an alternative matrix to the previously investigated lead silicate glass

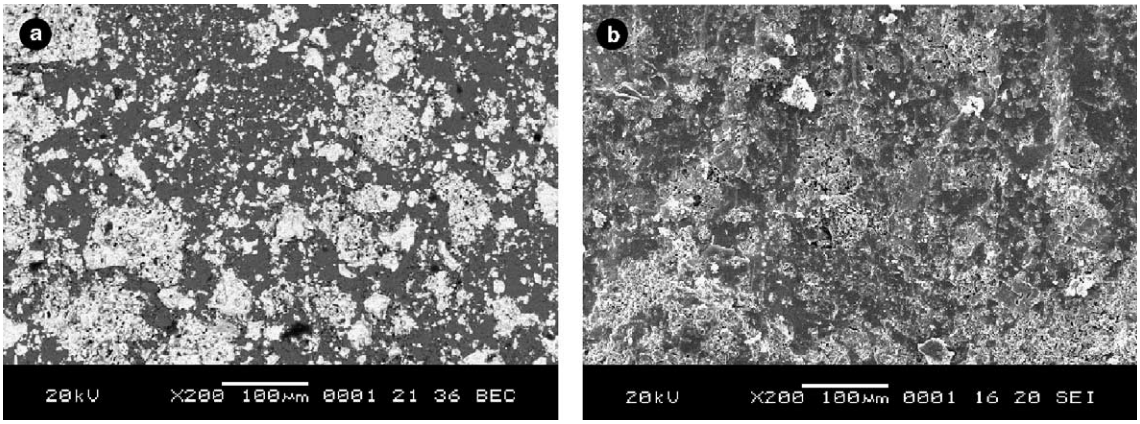

Fig. 5. SEM micrographs of a hot pressed composite containing 40 vol.% $La_2Zr_2O_7$ in lead silicate glass matrix: (a) polished surface, showing a high inclusion content and low porosity; some agglomerates of lanthanum zirconate are visible; however no significant interconnection between the inclusions is detected; (b) fracture surface, showing the absence of pull-out and secondary microcracks, indicating the strong interfacial bond.

[30,31] for $La_2Zr_2O_7$ encapsulation. It has been shown that for relatively low PbO concentration, lead is a network modifier, thus decreasing the chemical resistance of silicate glasses [54]. Even if lead-containing glass matrices may offer the possibility of self-shielding from radiation, the introduction of pyrochlore phases in a more durable borosilicate glass [22,45] is undoubtedly advantageous. The polished surface of a soda borosilicate glass matrix composite, shown in Fig. 7(a), demonstrates the high degree of homogeneity of inclusions' distribution in the matrix achieved. The fracture surface of the borosilicate glass matrix composite with 30 vol.% $La_2Zr_2O_7$ is shown in Fig. 7(b). Although the matching of the thermal expansion coefficients in this composite is not as close as that between $La_2Zr_2O_7$ and lead silicate glass (see Tables 1 and 2), there is no evidence of secondary cracks due to residual thermal stresses. Moreover, the borosilicate glass/pyrochlore bonding is found to be strong, leading to the absence of particle pullout during fracture. The fracture lines in Fig. 7(b) may suggest that the fracture propagated by direct particle cutting. Such mechanism is known for its advantageous toughening effect in brittle matrix composites [55,56], which could cause the composites to be more fracture resistant than the monolithic glass matrix. As shown in Fig. 7(b), porosity remains within the pyrochlore particles, since the processing temperature is not high enough for a significant sintering of $La_2Zr_2O_7$, and there is no glass infiltration into the $La_2Zr_2O_7$ agglomerates. This result is in agreement with the previous investigation using lead silicate glass matrix [31].

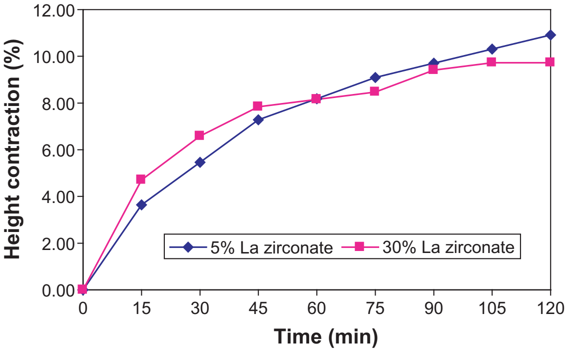

Fig. 6. Heating microscopy plots in terms of relative longitudinal contraction of cylindrical samples of 5 and 30 vol.% $La_2Zr_2O_7$ containing borosilicate glass matrix composites, sintered at 630 and 650 °C, respectively.

3.4. $Gd_2Zr_2O_7$/lead silicate glass composites

The results for $Gd_2Zr_2O_7$ containing lead silicate glass matrix composites are found to be very promising, since pressureless sintering at temperatures as low as 600 °C led to a relatively high densification (82.4%) for 10 vol.% inclusion content. The appearance of the polished surface in Fig. 8(a) is consistent with the low porosity of the samples. Unlike the composites containing $La_2Zr_2O_7$, some indication of particle debonding and pullout is visible on the fracture surface, shown in Fig. 8(b). This is probably due to the fact that the inclusions have a slightly higher thermal expansion coefficient than the matrix, thus developing residual tensile stresses along the interface upon cooling from the processing temperatures, which may exceed the strength of the interfacial bonding. If required, the pull-out of the inclusions could be minimized, for example introducing a glass with a higher thermal expansion coefficient, like the above described

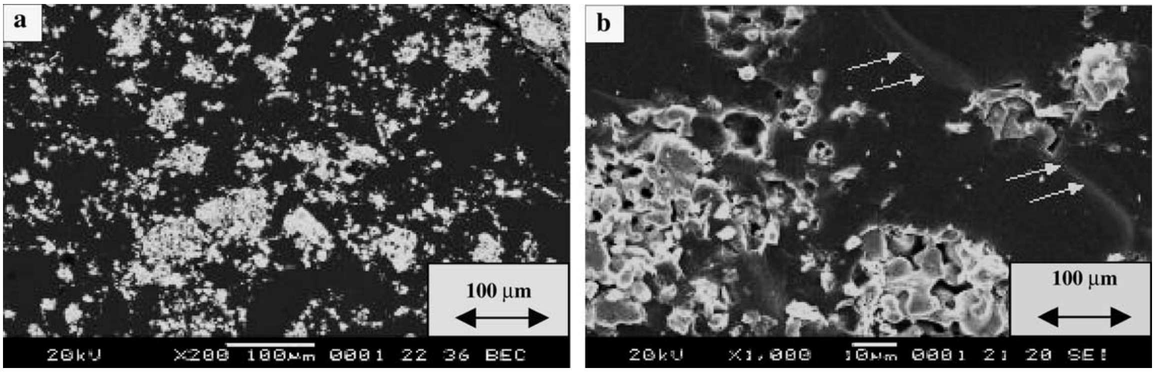

Fig. 7. SEM micrographs of a hot-pressed composite containing 30 vol.% $La_2Zr_2O_7$ in VG98 borosilicate glass: (a) polished surface showing a good distribution of the inclusions; (b) fracture surface, showing the absence of particle pull-out and microcracks; the fracture lines, marked by arrows, suggest that the fracture propagated by direct particle cutting.

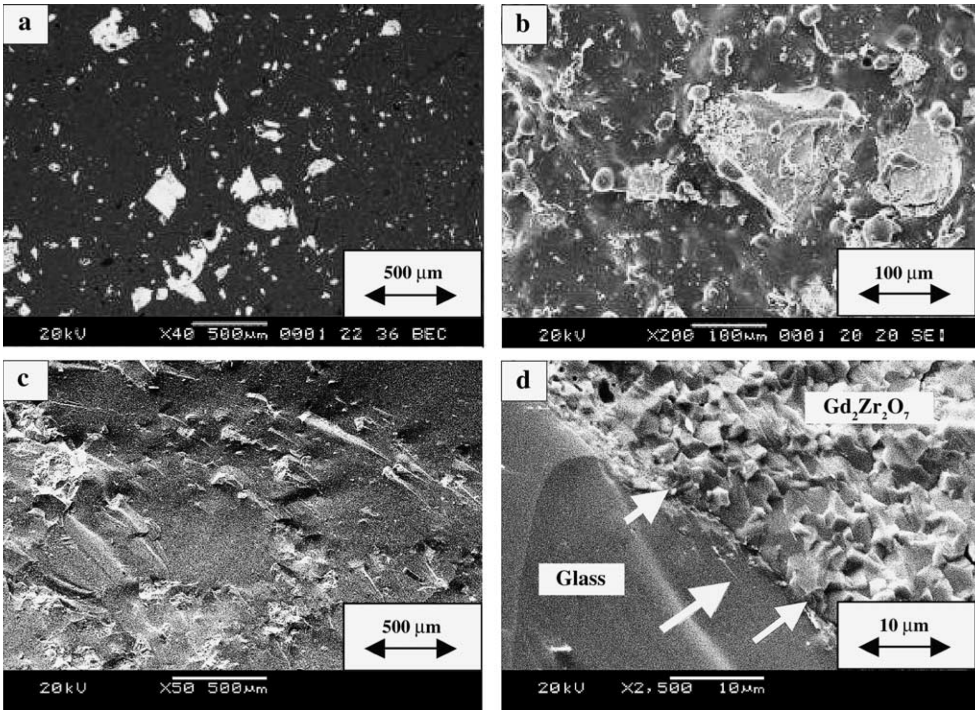

Fig. 8. SEM micrographs showing the microstructure of composites containing 10 vol.% $Gd_2Zr_2O_7$ in lead silicate glass matrix: (a) sintered sample,polished surface showing high density of the sample; (b) sintered sample, fracture surface showing a certain debonding and pull-out of the particles; (c) hot pressed sample, fracture surface showing homogeneous distribution of inclusions in a fully dense matrix; (d) $Gd_2Zr_2O_7$ particle/glass interface (marked by arrows) in a hot-pressed sample indicating good bonding.

VG98 borosilicate glass. However $Gd_2Zr_2O_7$ particle pull-out was not observed in fracture surfaces of hot-pressed samples, as shown in Fig. 8(c). This SEM micrograph indicates that particle cutting is the main fracture propagation mechanism. Moreover, evidence of a strong interface in the hot-pressed sample may be inferred from high-magnification SEM micrographs, as shown in Fig. 8(d). The hot-pressed samples containing 10 vol.% $Gd_2Zr_2O_7$ reached excellent densification (91.5% theoretical density), slightly lower than that of samples with $La_2Zr_2O_7$ inclusions developed earlier [31]. An increase of the processing temperature or of the holding time should lead to a higher densification in these composites. Nevertheless, the manufacturing of highly dense $Gd_2Zr_2O_7$ containing composites was demonstrated for the first time in this study to be feasible. In fact, only slight corrections of the processing route for the $La_2Zr_2O_7$ containing composites developed earlier [31] are needed for the encapsulation of the more radiation resistant $Gd_2Zr_2O_7$ phase in the same glass matrix.

4. Conclusions

Glass matrix composites containing pyrochlore crystalline phases were developed as possible alternative nuclear waste froms. The pyrochlore phases may act as an optimum host for specific actinides (mainly Pu). Glass matrix composites were manufactured by powder mixing, followed by (i) cold pressing and pressureless sintering (at temperatures $\leqslant 750$ °C) or (ii) hot-pressing at lower temperatures ($\leqslant 620$ °C). The pyrochlore crystalline structures were thermally stable in the range of temperatures used. The hot-pressing route was found to be the most attractive, since it leads to a relatively good densification even with a high loading of lanthanum zirconate particles in lead silicate glass matrix (40 vol.%). The feasibility of producing highly dense borosilicate glass matrix composites containing $La_2Zr_2O_7$ was also demonstrated. The composites exhibited a homogeneous microstructure and high structural integrity. The absence of microcracks, due to the close matching of the thermal expansion coefficient of inclusions and matrix, together with a strong interfacial bonding, suggests that the composites should have high mechanical and impact strength. As recently discussed, $La_2Zr_2O_7$ is the most radiation sensitive of the Zr–pyrochlore compositions [57]. Therefore, lead silicate glass matrix composites containing the more radiation 'tolerant' gadolinium zirconate phase were fabricated for the first time in this study. Slight modifications of the process developed earlier for the composites with lanthanum zirconate inclusions are needed in order to obtain highly dense samples. Future experimental work should be focused on determining the chemical durability (leaching resistance) of the composites produced and its dependence on composite composition and manufacturing route.

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