

# Processing glass–pyrochlore composites for nuclear waste encapsulation

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## Abstract

Glass matrix composites have been developed as alternative materials to immobilize nuclear solid waste, in particular actinides. These composites are made of soda borosilicate glass matrix, into which particles of lanthanum zirconate pyrochlore are encapsulated in concentrations of 30 vol.%. The fabrication process involves powder mixing followed by hot-pressing. At the relatively low processing temperature used (620 °C), the pyrochlore crystalline structure of the zirconate, which is relevant for containment of radioactive nuclei, remains unaltered. The microstructure of the composites exhibits a homogeneous distribution of isolated pyrochlore particles in the glass matrix and strong bonding at the matrix–particle interfaces. Hot-pressing was found to lead to high densification (95% th.d.) of the composite. The materials are characterized by relatively high elastic modulus, flexural strength, hardness and fracture toughness. A numerical approach using a microstructure-based finite element solver was used in order to investigate the mechanical properties of the composites.

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## 1. Introduction

The immobilization and disposal of highly radioactive waste in glass or ceramic hosts has been investigated for many years [1,2]. It is well-known that glass waste forms represent a good compromise due to the high solubility of high level wastes (HLW) and chemical durability of glasses, their radiation resistance and the capability to be processed at reasonably low temperatures, in particular borosilicate glass compositions

[1–5]. However, many polycrystalline ceramic materials have been shown to possess higher chemical durability and radiation damage resistance than borosilicate glasses under storing conditions [1]. On the other hand, the presence of crystalline phases requires more complex processing technologies due to the necessary higher fabrication temperatures.

The present work proposes an innovative approach that has the aim of including the major advantages of glasses and ceramic waste forms: radionuclides should be incorporated within a crystalline phase, which is itself encapsulated in a glass matrix not incorporating radioactive elements. The aim is to be able to exploit both the advantages of glass waste forms and the radiation resistance of certain crystalline phases by forming

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glass–crystal composites. The new composite waste forms are proposed for immobilisation of special type of radioactive wastes, in particular waste containing high concentration of actinides coming from Pu reprocessing [6].

Many examples in literature are related to waste forms based on glass–crystalline materials, as suggested by Weber et al. [2]. In their work a material belonging to the family of Synroc (ceramic materials particularly suitable to contain actinides) is described, which has been combined with a glass in order to form a composite. Another composite is described in the work of Esh et al. [3]; where the crystalline phases are aluminosilicate zeolites which are mixed with glass frit and then hot isostatically pressed. Similar developments have been reported on hot isostatically pressed mixtures of glass and crystal forming components [4], in which most radioactive waste (95 wt%) resides in the crystalline phase encapsulated in the residual glassy phase. In related developments, Loiseau et al. [7] considered the crystallisation of zirconolite,  $\text{CaZrTi}_2\text{O}_7$ , in an aluminosilicate glass matrix: radionuclides are incorporated in the zirconolite phase, while the glass phase acts as an external protective matrix. Further work has been carried out considering sol–gel derived high silica glass as a host matrix for actinides (around 10 wt%) [8].

In relation to these alternative waste forms, sintered glasses have been long considered as a useful alternative to molten glasses as durable matrices for nuclear waste immobilisation [9–11]. Hot-pressing has been used in order to obtain high densification of glass–crystal composite mixtures but the results were not always successful in terms of final density achieved [12]. Moreover, in most cases reported, relatively high temperatures (about 1000 °C) were required and the volume fraction of waste added was relatively low (14 vol.%) [12].

Recently there has been renewed interest in using materials with fluorite and fluorite related structures such as pyrochlore ( $\text{RE}_2\text{Ti}_2\text{O}_7$  or  $\text{RE}_2\text{Zr}_2\text{O}_7$  with RE = rare earth) for accommodating radionuclides, especially actinides [13,14]. The reason of such an interest resides in the fact that certain of these materials have been shown to be very stable against heavy ion induced amorphization [13–16].

Based on those findings, an approach for actinides waste immobilisation is being developed by our group [17–19]: the primary immobilization of radioactive waste is achieved within a pyrochlore phase, which is itself encapsulated into a silicate glass matrix. The use of sintered silicate glass for the matrix has the important advantage of allowing relatively low processing temperatures (<700 °C) which are much lower than those required for densification of pyrochlore crystalline ceramics (about 1200 °C). Moreover, the mechanism of encapsulation itself permits lower processing temperatures than those required for activating the crystallisa-

tion of the crystalline host phase from the glass phase, like in traditional glass-ceramics, which occurs usually at temperature >1000 °C [1,20]. In addition, the present concept avoids the risk of devitrification and phase separation, which have been reported to occur in traditional glass melting processes [1]. In our previous studies with lead silicate glass matrix, the use of lanthanum zirconate ( $\text{La}_2\text{Zr}_2\text{O}_7$ , pyrochlore structure) has been proposed as host phase for actinides not only due to the radiation resistance exhibited by this compound [13] but also because it has a thermal expansion coefficient very close to that of the lead silicate glass used as matrix. The use of an alternative glass matrix based on a soda borosilicate glass of low sintering temperature has been preliminary explored [18]. The main reason to investigate a borosilicate glass matrix is the intrinsic high chemical durability of this glass, which is higher than that of the lead silicate glass used earlier [17].

In this study we investigate composite materials constituted by a soda borosilicate glass matrix incorporating  $\text{La}_2\text{Zr}_2\text{O}_7$  particles. Hot-pressing was the technique adopted for fabricating composites. For the first time, a series of mechanical tests has been conducted on the composite waste form to confirm the suitable mechanical behaviour that this material shows, relevant for nuclear waste encapsulation, which must be resistant to impact loads or thermomechanical stresses. The use of a 2D finite element microstructural model is introduced to characterize the mechanical properties of the composites.

## 2. Experimental procedure

### 2.1. Starting materials

The lanthanum zirconate powder was prepared from commercial powders of  $\text{La}_2\text{O}_3$  (Alpha Aesar 99.99% purity) and  $\text{ZrO}_2$  (Alpha Aesar 99.978% purity). The synthesis of the lanthanum zirconate powder involved mixing, cold pressing and sintering and it has been described elsewhere [17]. Final products of the process were sintered pellets of lanthanum zirconate, from which powders with two different average particle sizes were produced. A first series of pellets was crushed using a mortar and a pestle, while a second one was put into a gyro mill and milled for 30 s. Time of milling was optimised in order to avoid or at least minimize the risk of contamination from the mill. The powder obtained by milling was analyzed by X-ray diffraction (XRD), using a Philips PW 1719 instrument ( $\text{CuK}\alpha$  radiation, 40 kV of voltage) as well as by differential thermal analysis (DTA) and thermogravimetry analysis (TGA) using a heating rate of 10 °C/min. The aim of these analyses was to check the absence of any other crystalline phases or contaminations in the powder and to investigate

Table 1  
Physical properties of  $\text{La}_2\text{Zr}_2\text{O}_7$  [17]

Property	$\text{La}_2\text{Zr}_2\text{O}_7$
Density ( $\text{g}/\text{cm}^3$ )	6.05
Melting point ( $^\circ\text{C}$ )	2300
Linear thermal exp. coeff. ( $10^{-6} \text{K}^{-1}$ )	9.1
Young's modulus (GPa)	175
Hardness (GPa)	9.9
Fracture toughness ( $\text{MPa m}^{1/2}$ )	1.1
Poisson's ratio	0.24

Table 2  
Composition and properties of the soda borosilicate glass matrix [10]

Composition	wt%
$\text{SiO}_2$	56.7
$\text{B}_2\text{O}_3$	12.4
$\text{Al}_2\text{O}_3$	2.6
$\text{Na}_2\text{O}$	17.5
$\text{CaO}$	4.1
$\text{MgO}$	2.1
$\text{TiO}_2$	4.6
Density ( $\text{g}/\text{cm}^3$ )	2.57
Linear thermal exp. coeff. ( $10^{-6} \text{K}^{-1}$ )	10.6
Transformation point ( $^\circ\text{C}$ )	537
Young's modulus	74
Poisson's ratio	0.23

thermal stability. Table 1 presents the most relevant physical and mechanical properties of  $\text{La}_2\text{Zr}_2\text{O}_7$  [17].

The soda borosilicate glass used has been employed in previous studies on the immobilization of nuclear waste [10]. The glass was available as a fine powder of mean particle size  $<20 \mu\text{m}$ . This glass powder is characterized by a relatively low sintering temperature and has a high thermal expansion coefficient, which is very similar to that of lanthanum zirconate [17]. Table 2 shows a summary of relevant physical properties of the soda borosilicate glass used.

## 2.2. Preparation of composite samples

Two series of composite samples were obtained, containing 5 vol.% and 30 vol.%  $\text{La}_2\text{Zr}_2\text{O}_7$ . The powders of  $\text{La}_2\text{Zr}_2\text{O}_7$  and glass were weighted in the correct proportions for each composition and placed in plastic bottles. The mixed powders were added with a small amount of ethanol (5 ml for 10 g of composite powder) and then mixed for 30 min in a tubular mixer. The content of the bottles was poured into a glass petri dish, which was subsequently placed on a hot plate at  $40^\circ\text{C}$  for 50 min in order to completely eliminate residues of alcohol. After drying, the mixtures were crushed again with mortar and pestle in order to remove agglomerates resulting from the drying process.

Uniaxial hot-pressing was applied to produce samples containing 5 and 30 vol.%  $\text{La}_2\text{Zr}_2\text{O}_7$  inclusions. Discs of 38 mm diameter and 3 mm thickness were obtained by using a custom-made facility, which has been described previously [21]. A graphite die was used and covered with a thin layer of boron nitride powder in order to facilitate removal of samples after hot-pressing. A pressure of 5 MPa was applied when the sample reached the temperature of  $620^\circ\text{C}$ . The holding time was chosen to be 1 h, accordingly to the aim of reducing the processing time. The heating rate was held constant at  $100^\circ\text{C}/\text{h}$  and the samples were left to cool down slowly in the hot-press after the sintering period.

## 2.3. Characterization of the composites

The density of all samples was determined geometrically and by the Archimedes method and subsequently related to the theoretical density in order to obtain the porosity. The theoretical density of the composites was calculated using the rule of mixtures.

Small fragments of hot-pressed samples were crushed into powder for XRD analysis. Fractured surfaces and polished samples were analyzed by scanning electron microscopy (SEM). For preparing fracture surfaces, samples were manually broken using a hammer. For polishing, selected samples were mounted in a resin matrix, ground with SiC paper and then polished with 3 and  $1 \mu\text{m}$  diamond paste.

The hot-pressed discs were polished up to  $1 \mu\text{m}$  diamond finish, and subsequently cut in order to obtain bars of 33–38 mm length, 4 mm width and 3 mm height. These bar specimens were subjected to mechanical tests in order to determine the flexural strength, using the three-point bending test, as well as the hardness and indentation fracture toughness by Vickers indentations. For the three-point bending test, the following parameters were used: distance between supports = 20 mm, test speed =  $0.500 \text{ mm}/\text{min}$ . For the Vickers indentation test, a load of 5 kg was applied for 10 s. The Young modulus of elasticity was measured on prismatic bars using the Grindosonic<sup>®</sup> or impulse excitation technique. In this method, the test sample is subjected to an initial deformation by means of a light mechanical impulse. The sample acts as a spring-mass system and produce a transient mechanical vibration. The frequency of this vibration is related to the mass, shape and dimensions of the sample and to the Young's modulus of elasticity of the material.

## 2.4. Numerical model

For the first time here, a numerical approach has been adopted in order to obtain a model for prediction of mechanical properties and fracture behaviour that may be used in the future design of this kind of composite waste forms. With this aim, the hot-pressed sample

with 30 vol.% pyrochlore phase was investigated using a microstructure-based finite element solver named OOF [22,23]. This code operates on data obtained from 2-D images of the microstructure (e.g. SEM micrographs) under investigation. Currently OOF performs microstructural thermoelastic calculations in two dimensions working in plane stress or plain strain. It works *in tandem* with a second program, called PPM2OOF, which creates data file for OOF by graphically combining data from an image with user-specified properties [22,23]. Examples of this kind of approach applied to a variety of materials including glass composites can be found in the literature [24–26].

As a preliminary investigation in the present work, the OOF model was used to calculate the Young's modulus of the glass–pyrochlore composite and the numerical results were validated with experimental data.

### 3. Results and discussion

#### 3.1. Characterization of the starting powders

XRD analysis showed that the milled ceramic powder consisted of lanthanum zirconate of pyrochlore structure and that there were no traces of contamination, as shown in Fig. 1. In addition, it was found by DTA that the powder was thermally stable until at least 900 °C, and it did not transform to another structure over the temperature range of interest for this study (<700 °C, results not shown here but reported elsewhere [17]). Moreover weight loss does not take place during heating the lanthanum zirconate powders up to 900 °C in air, as revealed by TGA. The glass particles showed an average size of 20 µm, with a very wide particle size

distribution, which is expected to affect the particles' packing and their final densification. The crushed (mortar and pestle) and milled (gyro milled) powders of lanthanum zirconate have both a bimodal size distribution and similar average particle size: 10 µm for the crushed powder and 6 µm for the milled powder. It follows that the two lanthanum zirconate powders are finer than the glass powder, which is likely to improve the final particle packing in the composite mixture. For hot-pressing experiments powders with average particle size 10 µm were used.

#### 3.2. Characterization of glass–pyrochlore composites

Fig. 1 shows a comparison between XRD patterns of a hot-pressed (620 °C for 1 h) composite containing 30 vol.% pyrochlore produced in this study and of a composite fabricated by pressureless sintering at 650 °C for 2 h. The XRD patterns are also compared to the spectrum of the original milled powder of lanthanum zirconate. It is seen that no new crystalline phases have formed during the heat-treatment, indicating that no devitrification process occurred in the glass matrix at the working temperatures. Moreover, the heat-treatment has not transformed the crystalline pyrochlore structure of the initial lanthanum zirconate particles, since all the main XRD peaks are present.

It is well-known that a high content of rigid inclusions can be detrimental to effective sintering of glass particles [27]. Nevertheless, the use of the hot-pressing technique has allowed the fabrication of composites containing 5 and 30 vol.% pyrochlore inclusions with a high degree of densification. The densities measured by the Archimedes method were in all cases >95% of the theoretical density. Fig. 2 shows that there is a fairly

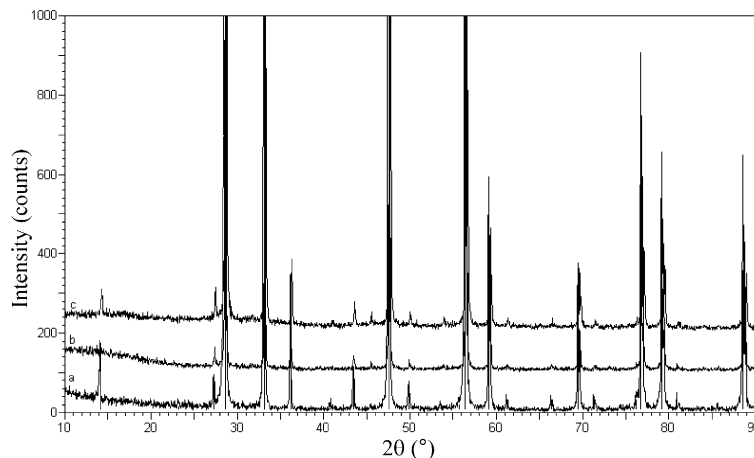


Fig. 1. XRD patterns of (a)  $\text{La}_2\text{Zr}_2\text{O}_7$  powder as milled in a gyromill for 30 s; (b) borosilicate glass composite containing 30 vol.%  $\text{La}_2\text{Zr}_2\text{O}_7$ , obtained by cold-pressing and sintered at 650 °C for 2 h; and (c) borosilicate glass composite containing 30 vol.%  $\text{La}_2\text{Zr}_2\text{O}_7$ , obtained by hot-pressing at 620 °C for 1 h. No extra crystalline peaks due to devitrification of the glass matrix are detected.



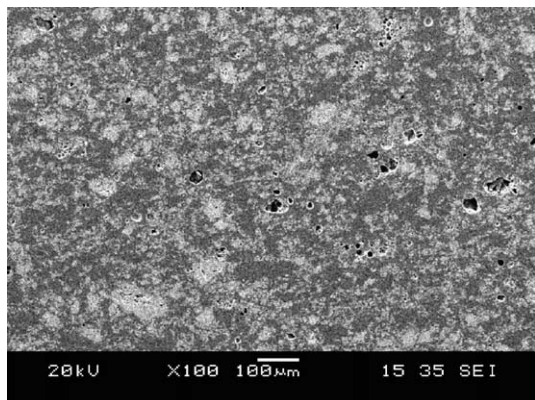


Fig. 2. SEM image of the polished surface of a borosilicate glass composite containing 30 vol.%  $\text{La}_2\text{Zr}_2\text{O}_7$  obtained by wet mixing and hot-pressing at 620 °C for 1 h.

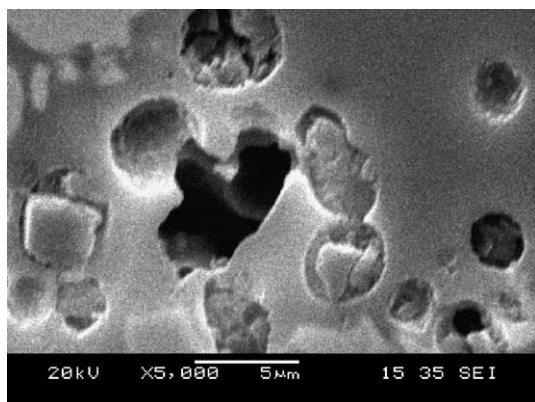


Fig. 3. SEM image of the polished surface of a borosilicate glass composite containing 30 vol.%  $\text{La}_2\text{Zr}_2\text{O}_7$  obtained by wet mixing and hot-pressing at 620 °C for 1 h, at high magnification. It provides evidence of the residual porosity inside the pyrochlore phase.

homogeneous distribution of the pyrochlore particles in the matrix. The inclusions are isolated, with little or no interconnection between them: this is very important regarding the leaching behaviour of the composite, since considerable interconnection of the host phase could lead to unacceptable loss of actinides from the pyrochlore phase during possible contact with water. At high magnifications, as shown in Fig. 3, it is possible to observe residual porosity inside the pyrochlore agglomerates, which is in agreement with previous results [17,18]. The residual porosity located between the primary lanthanum zirconate particles inside the large agglomerates is caused by the fact that no significant densification of the pyrochlore particles occurs during hot-pressing, as expected due to the relatively low temperature used (620 °C).

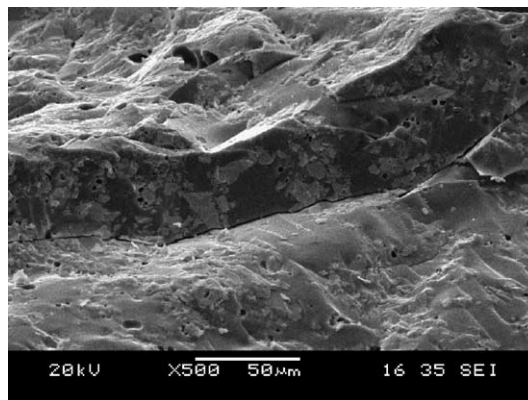


Fig. 4. SEM image of the fracture surface of a hot-pressed borosilicate glass composite containing 30 vol.%  $\text{La}_2\text{Zr}_2\text{O}_7$  obtained at 620 °C for 1 h.

By analysing fracture surfaces, it is observed that the fracture behaviour of the hot-pressed samples is clearly transgranular, where the fracture has proceeded through both the glass matrix and the lanthanum zirconate particles, as shown in Fig. 4. This indicates that there is a strong bonding at the interface between the glass matrix and the pyrochlore particles. The image (Fig. 4) illustrates that the advancing crack directly cuts the pyrochlore particles without deflection at the pyrochlore particle–glass interfaces. Debonding or pull-out of the  $\text{La}_2\text{Zr}_2\text{O}_7$  particles is not observed either. Particle cutting is a mechanism known for its advantageous reinforcing and toughening effect in some ceramic–glass systems [28], which should render the composites more fracture resistant than the monolithic glass matrix. This was confirmed in the present composites by mechanical tests (see next section). The crack propagation observed is expected because of the close matching of the thermal expansion coefficients of the two phases, which suppress significant development of residual thermal stresses in the composites upon cooling from the processing temperature. The strong bonding at the glass matrix–pyrochlore particle interface coupled with the absence of residual stresses and microcracks are favourable features regarding the long-term maintenance of the mechanical strength and chemical stability of the samples, which are of primary importance for nuclear waste forms.

### 3.3. Mechanical properties

The microstructural homogeneity and high density (>95% of theoretical) achieved in samples prepared by hot-pressing were expected to result in favorable mechanical properties of the composite. Mechanical tests were conducted on samples with 30 vol.% pyrochlore. The Grindosonic<sup>®</sup> test was used to determine the

Young's modulus, which was found to be:  $E = 94.9 \pm 0.5$  GPa. The result is in good agreement with the rule of mixtures, considering that the sample has approximately 5% porosity.

The flexural strength determined on at least five samples by the three-point bending test was found to be:  $\sigma_{\text{flex}} = 116 \pm 20$  MPa. This is a relatively high value, compared with that of hot-pressed borosilicate glass ( $\approx 60$  MPa [29]), and it anticipates a favourable mechanical behaviour of the glass–pyrochlore composite material.

The hardness determined by Vickers indentation was found to be:  $H = 5.4 \pm 0.3$  GPa. The hardness of the original sintered borosilicate glass [29] has been slightly improved by the presence of the pyrochlore phase. Many indentations (15) were produced in order to determine the indentation fracture toughness ( $K_{\text{IC}}$ ) of the composite, which was calculated by means of the following equation [30]:

$$\left(\frac{3K_{\text{IC}}}{Ha^{1/2}}\right)\left(\frac{H}{3E}\right)^{2/5} = 0.129\left(\frac{c}{a}\right)^{-3/2}, \quad (1)$$

where  $H$  = hardness;  $a$  = half diagonal length,  $c$  = radial crack length,  $E$  = Young's modulus.

By using this equation, a fracture toughness  $K_{\text{IC}} = 1.80 \pm 0.14$  MPa  $\sqrt{\text{m}}$  was calculated. This value is considerably higher than that of plain borosilicate glass, which has been measured to be of the order of 0.7 MPa  $\sqrt{\text{m}}$  [29,31]. This result is very important, as it demonstrates that the pyrochlore particles impart some degree of toughening to this material and hence the composite should exhibit a higher tolerance to fracture in comparison to the plain borosilicate glass matrix. Possible toughening mechanisms in this type of composites containing a particulate phase of high Young's

modulus well bonded to a low-modulus matrix are load transfer and direct particle cutting [28,29,32]. These mechanisms are supported by SEM micrographs of the advancing cracks produced by indentations, as illustrated in Fig. 5. Cracks propagate in transgranular manner, i.e. without deflection along the interface but rather cutting through the lanthanum zirconate particles. The brittleness index ( $B = H/K_{\text{IC}}$ ) of the composite material has a value  $B = 2.99 \mu\text{m}^{-1/2}$ , more than 50% lower than that of the plain borosilicate glass [33]. Thus, it is possible to conclude that in general the composite material developed here will behave in a less brittle manner than monolithic borosilicate glass waste forms, a fact that has implications regarding the better resistance of the material to possible impact loads and thermal shock damage during storage.

#### 4. Numerical modelling

In the present investigation, the Young's modulus of the hot-pressed  $\text{La}_2\text{Zr}_2\text{O}_7$ -borosilicate glass composites was studied for the first time by using the OOF numerical code, and the numerical results were compared with the experimentally obtained values. The preliminary results reported in this work should be followed in future by the investigation of other properties of the material, in particular mechanical and fracture properties, for which OOF is a very useful predictive tool [22–26].

One of the SEM pictures of the composite microstructure was chosen as input image for the code PPM2OOF. The necessary properties (thermal expansion coefficient, Young's modulus, Poisson's ratio) of the lanthanum zirconate inclusions and the glass matrix, both considered as isotropic constituents, were taken from Tables 1 and 2, respectively. The only simplification made in creating the finite element mesh was that of omitting residual pores, and this choice was made due to the fact that porosity is rather low ( $\approx 5\%$ ), making it easier to evaluate its effect on material properties by analytical models. A fine mesh of about 50000 nodes was created, as shown in Fig. 6. Then a simulated tensile test was performed on the mesh to determine Young's modulus, which resulted in  $E = 103.2$  GPa. This value is in good agreement with the rule of mixtures value ( $E = 104.1$  GPa), but it is higher than that obtained with the Grindosonic<sup>®</sup> method (94.9 GPa). However, the presence of the pores, which were neglected in the numerical model, could explain this difference. The application of the OOF numerical model in order to describe and interpret the fracture behaviour of the composites remains as an interesting task for future investigations. Indeed the suitability of the OOF approach to be used as a generalised tool for prediction of the mechanical behaviour of composite radioactive waste forms should be validated.

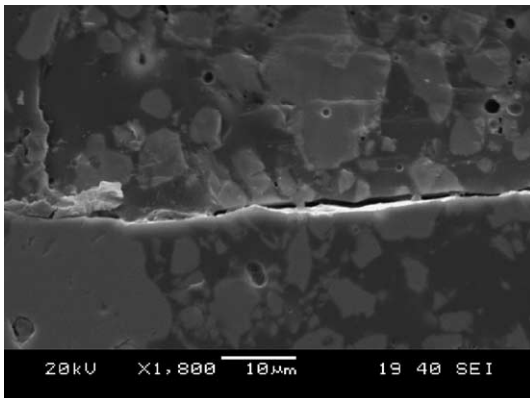


Fig. 5. SEM image of an advancing crack produced by a Vickers indentation on the surface of the borosilicate glass composite containing 30 vol.%  $\text{La}_2\text{Zr}_2\text{O}_7$ . It shows that the crack advances through both the glass matrix and the pyrochlore particles without significant crack deflection.

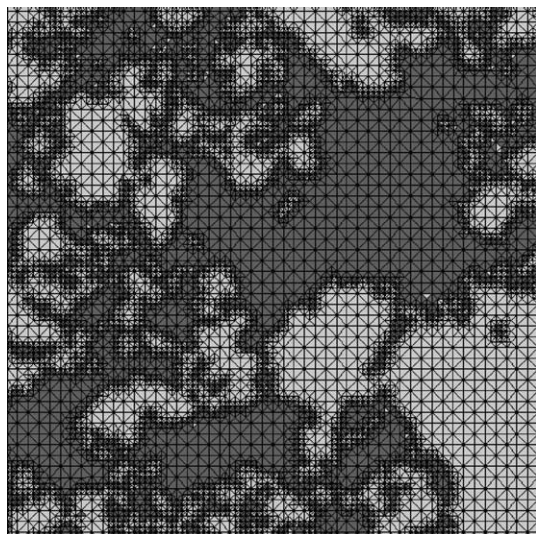


Fig. 6. Detail of the mesh created in PPM2OOF starting from an SEM image of the composite microstructure. The mesh was used to calculate the composites Young's modulus.

## 5. Conclusions

Soda borosilicate glass matrix composites containing  $\text{La}_2\text{Zr}_2\text{O}_7$  pyrochlore particles were developed as alternative nuclear waste forms. The pyrochlore phase should act as an efficient host for actinides and for Pu. The composites were manufactured by powder mixing followed by hot-pressing at 620 °C. The hot-pressing route leads to a high densification (95% th.d.) of samples with a relatively high volume fraction of lanthanum zirconate particles acting as rigid inclusions (30 vol.%). The composites were found to exhibit relatively high mechanical strength, Young's modulus as well as high hardness and fracture toughness values in comparison with monolithic borosilicate glass. The numerical approach (OOF) was used in order to evaluate the elastic properties of the composite and the result supports the experimental data. This numerical approach should be further developed in the future, especially as predictive tool for designing new compositions of the same composite or for selecting convenient modifications of the glass matrix or the pyrochlore phase. Future experimental work will be focused on determining the chemical durability of the composite and its dependence on composition and manufacturing route.

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