Synthesis and Characterization of a Neodymium Zirconate Pyrochlore Doped with Ytterbium: $(Yb_xNd_{1-x})_2Zr_2O_7$ ($x = 0.1, 0.25$ and 0.4)

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Abstract: This study deals with the solid state synthesis of neodymium zirconates, doped with ytterbium, with the chemical formulas of: $(Yb_xNd_{1-x})_2Zr_2O_7$, ($x = 0.1, 0.25$ and 0.4). These materials are proposed as high-level radioactive waste confinement materials. Neodymium is employed as an actinide surrogate. The synthesis process consists in successive calcination steps at: 600, 1,200, 1,300 and 1,400 °C. The end-products have a sintered density of 6,368, 6,543 and 6,674 kg/m³, for: $(Yb_{0.1}Nd_{0.9})_2Zr_2O_7$, $(Yb_{0.25}Nd_{0.75})_2Zr_2O_7$ and $(Yb_{0.4}Nd_{0.6})_2Zr_2O_7$, respectively. The pyrochlores X-ray diffraction patterns of an fcc pyrochlore type lattice: $Fd\bar{3}m$, have been identified. The differential thermal analysis of these zirconates confirms their thermal stability. The materials do not show any phase transition against heating, until 1,650 °C, and under cooling. For the whole, the measured microhardnesses (< 120 HV) and fracture toughness' ($< 1.57 \times 10^6$ N/m²) reveal a brittle mechanical behaviour of the studied pyrochlores.

Key words: Zirconate pyrochlore, sintering, differential thermal analysis (DTA), scanning electron microscope (SEM), X-ray diffraction (XRD).

1. Introduction

Natural pyrochlores and associated rocks of the same mineral group have the empirical chemical formula of $(Na, Ca)_2Nb_2O_6(OH, F)$. In general, it is a green or brown mineral [1].

The pyrochlore group comprises cubic oxides with the general formula $A_{2-m}B_2X_{6-w}Y_{1-n} \cdot pH_2O$. Both “A” and “B” sites can accommodate a large range of elements, particularly actinides and lanthanides elements, and are frequently sources of high rare-earth elements (REE) concentrations [2, 3]. The betafite subgroup includes minerals in which Ti predominates in the ‘B’ site [4, 5]. Pyrochlore can also host mixed-valence metals such as Fe^{2+} and Fe^{3+} and Nb^{4+}

and Nb^{5+} [6, 7].

In recent years, basic pyrochlores, with the general formula of $A_2B_2O_7$, have been of great interest in many research fields. In these minerals, “A” is generally a trivalent lanthanide, and “B” is generally: Zr, Hf, Ce, Ti, etc. “B” is a tetravalent cation which is smaller than the cation “A”. Due to the extensive compositional range of the compounds that exhibit the pyrochlore structure; there are a variety of actual and potential applications for these materials.

These compounds exhibit a defect fluorite-type structure or an ordered pyrochlore-type structure, which is mainly governed by the ionic radius ratio of A^{3+} and B^{4+} [8].

The ideal pyrochlore structure possesses a cubic symmetry with space group $Fd\bar{3}m$, and there are eight molecules per unit cell. Pyrochlore structure ($Fd\bar{3}m$)

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can be derived from the fluorite structure (*Fm3m*) by ordering the cation sublattice and creating ordered oxygen vacancies in such a way that coordination of “A” atoms remains cubic, as in fluorite, but coordination of “B” cations decreases to octahedral. Ordering causes the pyrochlore unit cell to double with respect to the fluorite unit cell [9].

Pyrochlores materials have many applications such as solid electrolytes in solid oxide fuel cells, catalysts, nuclear waste forms, inert matrix fuel, high-temperature thermal barrier coating materials, etc. [10-22].

The pyrochlore are confinement materials suitable for geologic disposal. There are chemically durable and radiation-resistant. They have interesting physical and chemical properties, such as a high-melting point, a high thermal expansion coefficient, a low-thermal conductivity, a high thermal stability and a high-radiation stability [8, 18].

The thermodynamic stability of several lanthanide zirconates has been extensively studied (Ln = La, Pr, Nd, Sm, Gd, Ce, Eu) [18, 23, 24]. Systematic studies of rare-earth pyrochlores have shown that certain compositions (B = Zr, Hf) are stable to very high doses of alpha-decay event damage. Three different processes were observed: a radiation-induced amorphization, an order-disorder transformation, and phase decomposition. The radiation stability of these compositions is closely related to the structural distortions that occur for specific pyrochlore compositions and the effect of electronic structure on bonding [25].

The radiation resistance of Gd₂Ti₂O₇ and Gd₂Zr₂O₇ pyrochlores under two different extreme conditions: ion-beam irradiation and high pressure has been studied. It was demonstrated that the phase stability and the structural transformation processes of pyrochlore structure are strongly correlated to the energetics of defect formation, and the intrinsic properties inherently control the response of pyrochlore to extreme conditions, such as high pressure

or an intense radiation field [22].

Gadolinium zirconate (Gd₂Zr₂O₇) has been found to be an excellent pyrochlore matrix to immobilize actinides elements, especially plutonium, in view of its remarkable resistance to amorphization under ion beam irradiation [12]. From crystal chemical considerations, it is expected that large amounts of actinide elements will be incorporated in the Gd₂Zr₂O₇ matrix [8].

The synthesis of the single-phase pyrochlore Pu₂Zr₂O₇ has been reported, and this implies that, under reducing conditions, Pu can completely replace trivalent Gd in the zirconate matrix, without altering the crystal structure [26].

However, thorium element exhibits a little solubility in the pyrochlore lattice of Gd₂Zr₂O₇. The existence of the pyrochlore phase of Gd_{2-x}Th_xZr₂O_{7+x/2} occurs only for x = 0.0-0.075 (x < 0.1) [27].

Ce-pyrochlore (CaCeTi₂O₇) is a chemical analogue for CaPuTi₂O₇, which is a proposed ceramic waste form for deposition of Pu in geological repositories. It is postulated, based on the presence of Ce³⁺ in the Ce-pyrochlore, that neutron poisons such as Gd can be incorporated into the CaPuTi₂O₇ phase [3].

The helium behavior in Gd₂Ti₂O₇ and Nd₂Zr₂O₇ has been investigated with doping the matrices with the short-lived alpha-emitter ²⁴⁴Cm. Despite high damage and large amount of helium accumulated, the integrity of the studied materials was preserved during storage. It has been demonstrated that the zirconate were more radiation resistant than the titanate pyrochlore [28].

One can remark that natural old titanates pyrochlores, Th₂Ti₂O₇ and U₂Ti₂O₇, have been reported to recover easily their crystalline structure after amorphization, compared to the synthetic ones [29].

Several synthesis methods, either wet or dry methods, or alternative methods, derivate from these classical two methods have been used for the preparation of pyrochlores materials.

The chemical-coprecipitation, also called the sol-gel method, has been investigated [30-32]. The citrate gel precursor method and the acid-ethylene glycol resin

precursor method are other sol-gel techniques, cited in the literature [33, 34].

Many dry methods have been described in the literature, as the solid-state reaction method [35], the pressure less solid state synthesis [18, 22], and the high temperature solvent flux technique: “crystal growth” [29, 36].

A lot of parameters influence the materials properties. Process parameters, as temperature and pressure, play an important role in the structural stability of the materials [37, 38]. The chemical compositions of the pyrochlore, its thermodynamic behavior, conditioning its phase stability, are also important parameters for the final expected properties in studying a pyrochlore material [21, 39].

New A₂B₂O₇-type oxides with varying ionic radius ratios have been synthesized. The following zirconates have been studied: (Nd_{1-x}Gd_x)₂(Ce_{1-x}Zr_x)₂O₇ [30], (Nd_{1.8}An_{0.2})Zr₂O_{7+x}, with An = Th, U, Np, Pu, Am [40], Gd_{2-y}La_yZr₂O₇, 0 < y < 2.0 [41, 42], La₂(Zr_{0.7}Ce_{0.3})₂O₇ [43], (Ln_{1-x}Yb_x)₂Zr₂O₇, Ln = Sm or Gd, with 0 < x < 1.0, [18], (Nd_{1-x}Gd_x)₂(Ce_{1-x}Zr_x)₂O₇ [31], Gd₂Zr₂O₇ [44], La₂Zr₂O₇ [22], Gd₂(Sn_{1-y}Zr_y)₂O₇ [45], La_{2-x}Gd_xZr₂O₇, x = 0.025, 0.05, 0.075 and 0.1 [34], Gd₂Ce_xZr_{2-x}O₇, 0 < x < 1.0 [46], Gd₂Zr₂O₇ [22, 35], Gd₂Zr_{2-x}U_xO_{7+y} [35].

Many titanates, stanates and zirconates-titanates have been described in the literature, namely: Gd₂Ti₂O₇ [21], (Ca_{0.87}Ce³⁺_{0.21}Ce⁴⁺_{0.86})Ti_{2.05}O₇ [3], Sm₂Ti₂O₇, Dy₂Ti₂O₇, Tb₂Ti₂O₇ [37], Zr-doped Nd₂Sn₂O₇ [47], Dy₂(Ti_{1-y}Zr_y)₂O₇, 0 ≤ y ≤ 1 [48], and CaCeZr_xTi_{2-x}O₇, x = 0.2-2.0 [19], (Na, Ca, U)₂(Nb, Ti, Ta)₂O₆ [49].

The crystallographic structure of a A₂B₂O₇ compound is generally cubic. But, the pyrochlore structure occurs only when the ionic radius ratio of R(A)/R(B) vary from 1.46 to 1.78, at the atmospheric pressure [8].

The phase stability for any A₂B₂O₇ pyrochlore compound (where A is a trivalent rare-earth cation ranging in size from Lu³⁺ to La³⁺, and B is a tetravalent cation ranging in size from Ti⁴⁺ to Pb⁴⁺) is not well characterized. It was demonstrated that rare earth

containing titanates, A₂B₂O₇ pyrochlore, trend to decrease in stability with decreasing R_A/R_B, due to increasing propensity to disorder and a more energetically favorable fluorite structure [50].

In the present paper, we have synthesized by a dry metallurgical method a neodymium (Nd) zirconate doped with ytterbium (Yb), with the chemical formula of: (Yb_xNd_{1-x})₂Zr₂O₇, (x = 0.1, 0.25 and 0.4). Neodymium is employed as an actinide surrogate. The physical and microstructural characteristics of the materials were determined, namely the geometrical and Archimede densities, the microstructure and the phase identification, by scanning electron microscopy (SEM) and X ray diffraction analysis (XRD). The phase stability of these zirconates has been investigated by differential thermal analysis (DTA). The mechanical behaviour of the materials has been studied by measuring the microhardnesses and the fracture toughness.

2. Experiments

Three chemical compositions of neodymium zirconate pyrochlores were synthesized: (Yb_xNd_{1-x})₂Zr₂O₇, (x = 0.1, 0.25 and 0.4, respectively), by the dry route of synthesis.

The pure metallic oxides: ZrO₂ (99.978 %), Alfa Aesar, Yb₂O₃ and Nd₂O₃ (99.95% and 99.999%, respectively), Aldrich, were dried one night at 873 K, then 8 hours at 1,000 °C, and one second night at 873 K. An agath hand-milling was performed between each drying step.

For each chemical composition, a stoichiometric mixture of the three oxides was prepared in a batch of 40 g. It was milled in a RMO 29207 Retsch miller during 2 h with ethylene glycol, Fluka Chemie (puriss p.a) in a 1:1 ratio, and then dried in a steamroom at 523 K, during 2 h. Pellets of 14.5 mm of diameter with various heights were prepared by uniaxial compaction in a Sodemi RD 20 DE press, at an average pressure of 7 tf with a compaction cycle of 90 s. About 0.5 wt.% of zinc stearate, Aldrich, was added as an organic

lubricant. The materials were dried in air, in a high temperature Carbolite Furnace RHF-1600, following the above steps: 10 min at 120 °C, 10 min at 493 K, 30 min at 673 K, 2 hours at 773 K and at 873 K. The calcinated materials density was then deduced.

The materials were then sintered three times at: 1,473 K during 40 h, at 1,573 K during 40 hours, and at 1,673 K during 48 h. Both the rates of heating and cooling were of 6°/min, respectively. Between each calcination step, a wet milling in ethylene glycol, Prolabo, followed by a steamroom drying at 423 K, was introduced. In the same time, the compaction operation was repeated with zinc stearate as lubricant.

The determination of the particles densities (ρ) before the heat treatments was performed using the Archimedes method. The powders densities were calculated on green materials, and after each calcination step; and the materials XRD diagrams were determined with a monochromatic Cu K α Philips X'Pert Pro diffractometer, using Philips X'Pert Plus 2001 software [50]. A nickel crystal was employed as an internal standard. The analysis parameters were: a scan step size of 0.02, a time per step of 0.5, for 2 θ varying from 5 to 100 degrees, I = 40 mA, V = 40 kV, λ = 1.54 nm. In order to eliminate systematic errors in the scattering angles, the observed angles were corrected with those obtained with silicon standard. The X-ray diffraction patterns were indexed and were used to refine lattice parameters employing the software X'Pert Plus Version 1.0 supplied by Philips, Netherlands [50]. Crystalline structure, lattice parameters, densities, and porosities were calculated.

Specific area measurements were made using a sorption/desorption B.E.T Micromeritics Flowsorb II 2300, with nitrogen gas at -196 °C, on sintered powder samples weighing 15 g. Grains and pores distribution of the matrices was performed with a scanning electron microscope: Philips XL 30, equipped with an EDX, ESEM-FEG probe. Either secondary electrons or back scattered electrons modes were used, with 10-15 keV energy.

Both Vickers indentations and the fracture toughness measurements are performed as mechanical characterizations of the materials. An average Vickers microhardness was measured, three times for each sample, using a 368-372 Reichert-Austria apparatus, equipped with a 68-309.1 Reichert-Austria camera. The equipment was calibrated using the formula:

$D = 1,854 F / (0.159 x)^2$, for Vickers microhardness, where F , the applied force = 8.3 kgF, x is the number of graduations in measuring the diagonal mark with a graduation length of 0.159 μ m.

The fracture toughness tests were performed with a 10 t instron universal testing machine. The strength at the compression was of 200 N. The differential thermal analysis (DTA) was performed with a Setaram instrument, in the range temperature of 25-1,650 °C.

3. Results and Discussion

3.1 Materials Densities

For the three studied compositions of (Yb, Nd) zirconates, the water immersion densities, and the green (d_g) and sintered (d_s) densities, for the three sintering steps, are given in Table 1.

The geometrical green densities (d_g) are lower than the water immersion densities of the corresponding no compacted powders. The sintered densities increase with increasing the calcination steps. There are greater than the water immersion densities of the corresponding milled materials.

Table 1 Variations of the materials densities (10³ kg/m³) during the heating treatments.

(Yb _x Nd _{1-x}) ₂ Zr ₂ O ₇	x = 0.1	x = 0.25	x = 0.4
R _(Yb, Nd) /R _{Zr}	1.523	1.4972	1.4714
d_g	5.836	5.792	5.407
ρ_g	5.602	5.743	5.537
ρ_1	5.805	5.578	5.770
ρ_2	5.899	5.728	5.679
ρ_3	5.539	5.728	5.679
d_{s1} (1st sintering at 1,273 K)	5.249	4.970	5.594
d_{s2} (2nd sintering at 1,473 K)	5.857	5.947	6.120
d_{s3} (3rd sintering at 1,673 K)	6.368	6.543	6.674

The final densities (d_{s3}) are representative of the lanthanides zirconates pyrochlore densities. They decrease with increasing the content of Nd. The best sintered material is that of the composition: (Yb_{0.4}Nd_{0.6})₂Zr₂O₇ (6674 kg/m³).

Liu, et al. [18] report the decrease of the relative densities when the content of both Nd and Ce increases, for (Nd_{1-x}Gd_x)₂(Ce_{1-x}Zr_x)₂O₇ solid solutions, with $0 \leq x \leq 1$.

Our results are comparable with those of these last authors [18, 31] which have synthesized by a wet method, a Nd and a Sm-zirconate doped with Yb and Gd. They found similar densities compared to our values, namely: 6,263 kg/m³ for (Nd_{0.9}Gd_{0.05}Yb_{0.05})₂Zr₂O₇, and 6,467 kg/m³ for (Sm_{0.9}Gd_{0.05}Yb_{0.05})₂Zr₂O₇.

Wiss, et al. [28] report similar sintered densities for Nd₂Zr₂O₇ (6,135 kg/m³) and Gd₂Zr₂O₇ (5.7 kg/m³); and Yates, et al. [51] report a very close calculated density for Nd₂Zr₂O₇ (6,360 ± 1 kg/m³) compared to that we found for (Yb_{0.1}Nd_{0.9})₂Zr₂O₇ (6,368 kg/m³). This is due to the chemical compositions of both pyrochlores, which are similar.

However, Wiss, et al. [28], which have studied the helium behavior in Gd₂Ti₂O₇ and Nd₂Zr₂O₇ zirconates, have report lower densities of the materials, namely: 5,700 and 6,135 kg/m³, respectively for Gd and Nd zirconates.

3.2 Phase Identification and Microstructure

A typical diffractogram of each kind of synthesized zirconate is given in Fig. 1. The crystallographic parameters calculated from the diffractograms are given in Table 2.

The Fig. 1 reveals the X-ray diffraction patterns of a pyrochlore type lattice: Fd-3m fcc, which has been identified to the structure of Sm₂Zr₂O₇ zirconate pyrochlore ceramic (JCPDS pattern 00-024-1012 [50]). (Yb_xNd_{1-x}) substituent confers to the studied (Yb_xNd_{1-x})₂Zr₂O₇ pyrochlores a structure with a lattice parameter which is close to that of Sm. One can

observe the presence of typical super-lattice peaks at 2θ values of about 14° (111), 28° (311), 29° (222), 33° (400), 37° (331), 45° (511), 48° (440), 50° (531), 57° (622), 60° (444) and 71° (800), using Cu K α radiation [35, 48, 52-56].

A secondary faced centered cubic phase is matched for the three compositions (Yb_xNd_{1-x})₂Zr₂O₇ (x=0.1, 0.25 and 0.40). It has been identified to a lanthanide zirconium oxide, with a Fm-3m fcc phase, which is close to the Ho_{0.5}Zr_{0.5}O_{1.75} phase (01-078-1294 [50]). Ho positions are replaced by Yb and Nd atoms. One can observe the presence of typical peaks at 2θ values of about 29.8° (111), 34.5° (200), 49.5° (220), 58.8° (311) and 82.9° (420), using Cu K α radiation.

Fig. 1 XRD patterns of the pyrochlores (Yb_xNd_{1-x})₂Zr₂O₇ (x = 0.1, 0.25 and 0.4). (a) (Yb_{0.1}Nd_{0.9})₂Zr₂O₇, (b) (Yb_{0.25}Nd_{0.75})₂Zr₂O₇ and (c) (Yb_{0.40}Nd_{0.60})₂Zr₂O₇.

Table 2 The microstructural data of the synthesized zirconates (Yb_xNd_{1-x})₂Zr₂O₇.

(Yb _x Nd _{1-x}) ₂ Zr ₂ O ₇	x = 0.1	x = 0.25	x = 0.4
$R(\text{Yb}_x\text{Nd}_{1-x})/R(\text{Zr})$	1.5230	1.4972	1.4714
Phase identification [50]	98 % fcc pyrochlore (00-024-1012)	87 % fcc pyrochlore (00-024-1012)	61 % fcc pyrochlore (00-024-1012)
	and 2% fcc (01-078-1294)	and 13% fcc (01-078-1294)	and 39% fcc (01-078-1294)
	$a_{\text{pyroc}} = 10.5940$ (10.5900) $a_{\text{fcc}} = 5.20095$ (5.20000)	$a_{\text{pyroc}} = 10.5929$ (10.5900) $a_{\text{fcc}} = 5.19519$ (5.20000)	$a_{\text{pyroc}} = 10.5574$ (10.5900) $a_{\text{fcc}} = 5.21071$ (5.20000)
Lattice parameters (Å)			
TD (kg/m ³)	6,577	6,676	6,841
d_s (kg/m ³)	6,368	6,543	6,674
d_{rel} (%TD)	96.82	98.01	97.56
p (%)	3.18	1.99	2.44
SEM average grain size (μm)	3.0	1.5	0.9

One can remark that the ratio of the fcc fluoride structure to that the fcc pyrochlore structure increase with the amount of Yb in the material from 2% for (Yb_{0.1}Nd_{0.9})₂Zr₂O₇ to 87% for (Yb_{0.25}Nd_{0.75})₂Zr₂O₇ to 61% for (Yb_{0.40}Nd_{0.60})₂Zr₂O₇. This signify that the Yb atoms are in tetravalent oxidation states that lead to an oxygen deficient solid solution of the material, when increasing the amount of Yb atoms in the fcc structure. This may favors the fcc fluorine structure. These oxidation phenomena are favored during heating, and have been reported for some actinides doped zirconates [57, 58].

This solubility limit of Nd in (Yb_xNd_{1-x})₂Zr₂O₇ pyrochlore phase, when the amount of Nd increase leads to the formation of a secondary fcc fluoride phase. This result is analogous to that reporting the solubility limit of Ce in the pyrochlore lattice of Gd₂Zr₂O₇, which leads to the formation of a secondary fcc fluoride phase [46].

The solubility limit of uranium in Gd-zirconate has been also reported to be less than 10 %. Above this limit, an fcc fluoride phase form, and U is solubilized in the Zr sites of the pyrochlore structure [35].

The ionic radius ratio of $R(\text{Yb}_x\text{Nd}_{1-x})/R(\text{Zr})$ vary from 1.4714 to 1.5230. This interval is included in that of the formation of pyrochlore crystal, which is in the range of 1.46 to 1.78, at the atmospheric pressure [8]. The ionic radius of Zr⁴⁺ is 0.72 Å in six-coordinated; however, the ionic radius of Nd³⁺ and Yb³⁺ are 1.109

and 0.985 Å in an eight-fold coordination, respectively [59].

Both the lattice parameters and theoretical densities, calculated from the XRD measurements are satisfactory results. For the three studied chemical compositions, the lattice parameters are close to those given in the JCPDS data of Fd-3m pyrochlore structure, and the relative densities are higher than 96 %.

As for the materials densities, Yates, et al. [51] report a very close calculated lattice parameter for Nd₂Zr₂O₇ (10.678 ± 0.002 Å) compared to that we found for (Yb_{0.1}Nd_{0.9})₂Zr₂O₇ (10.5940 Å). This is due on one hand to the employed milling methods employed in the synthesis process, and on the other hand to the chemical compositions of both pyrochlores, which are similar each other.

Lui, et al. [59, 60] which have synthesized by a wet method, a Nd and Sm-zirconate doped with Yb and Gd. They found similar lattice parameters and theoretical densities, compared to our values, namely: 10.6253 Å (6,504 kg/m³) for (Nd_{0.9}Gd_{0.05}Yb_{0.05})₂Zr₂O₇ and 10.5740 Å (6,723 kg/m³) for (Sm_{0.9}Gd_{0.05}Yb_{0.05})₂Zr₂O₇.

Mandal et al. [27] which have synthesized by a dry method, a thorium-doped Gd zirconate, Gd_{1.8}Th_{0.2}Zr₂O_{7.1}, found a lattice parameter of 10.5422 Å and a volume cell of 1,173 Å³.

Fig. 2 shows juxtaposed XRD diagrams for one of the three studied pyrochlores, for the three heating treatments. They show that the skeletal of pyrochlore

Fig. 2 XRD patterns of (Yb_xNd_{1-x})₂Zr₂O₇ (x = 0.1, 0.25 and 0.4) pyrochlores for the three sintering temperatures.

structure forms below 1,200 °C, for the whole of the materials. At 1,200 and 1,300 °C, several chemical intermediates, with the general formulas of REEO₂, REE₂Zr₂O₄, REE₃ZrO₄, have been identified [51]. REE may be Yb, Nd, or a combination of the two present lanthanides.

Fig. 3 shows typical SEM microstructures of (Yb_xNd_{1-x})₂Zr₂O₇ (x = 0.1, 0.25 or 0.40). The observed grains are inhomogeneous, and the average grain size is about 3 μm. The contrast in brightness between the grains reveals the presence of secondary phases at the interfaces.

Yates, et al. [51] have synthesized a neodymium zirconate Nd₂Zr₂O₇ by both a solid state and a sol gel method with a homogeneous microstructure with continuous connectivity of the Nd₂Zr₂O₇ phase, and a microstructure revealing a final average grain size in the range of 1.34-3.4 μm, and average pore sizes around 400 nm.

These last described results are better than ours, because of the high sintering temperature of 1,650 °C and sintering time of 4 h, which may excessively coarsen the Nd₂Zr₂O₇ from its initial nanometer particle size.

As well as for the microhardness, the measured values of fracture toughness of the three studied zirconates are weak values. One can conclude that these materials are not mechanically resistant against strong constraints.

(a)

(b)

(c)

Fig. 3 SEM micrographs of the synthesized pyrochlores. (a) (Yb_{0.1}Nd_{0.9})₂Zr₂O₇, (b) (Yb_{0.25}Nd_{0.75})₂Zr₂O₇ (c) (Yb_{0.40}Nd_{0.60})₂Zr₂O₇.

Table 3 The mechanical properties of the synthesized zirconates (Yb_xNd_{1-x})₂Zr₂O₇ (x = 0.1, 0.25 and 0.40).

(Yb _x Nd _{1-x}) ₂ Zr ₂ O ₇	x = 0.1	x = 0.25	x = 0.4
R(Yb _x Nd _{1-x})/R(Zr)	1.5230	1.4972	1.4714
D (HV)	120	115	118
Fracture toughness (10 ⁶ N/m ²)	1.57	1.57	1.24

3.3 Mechanical Properties

The mechanical properties of $(Yb_xNd_{1-x})_2Zr_2O_7$ ($x = 0.1, 0.25$ or 0.40) are given in Table 3.

Vicker's hardnesses are medium values, showing the brittle mechanical behaviour of these materials. The microhardness values decrease from $(Yb_{0.1}Nd_{0.9})_2Zr_2O_7$ to $(Yb_{0.4}Nd_{0.6})_2Zr_2O_7$ and $(Yb_{0.25}Nd_{0.75})_2Zr_2O_7$ materials. The lowest amounts of Yb content in the pyrochlore (in $(Yb_{0.4}Nd_{0.6})_2Zr_2O_7$) gave the lowest microhardnesses.

The specific surface areas are good values (Table 4.). The synthesized materials are less porous. Tong et al. [61] gave a value of $11.33 \text{ m}^2 \text{ g}^{-1}$ in a lanthanum zirconate $Ln_2Zr_2O_7$, and a better value than our results, for neodymium zirconate $Nd_2Zr_2O_7$, which is $3.48 \text{ m}^2/\text{g}$.

Typical DTA graphs of the materials are given in Fig. 4. For the three chemical compositions, the DTA analyses show similar graphs. The error on the temperatures intervals does not exceed 2° . For the three steps of sintering, one can note two endothermic phase transitions located around $1,473 \text{ K}$ and $1,687 \text{ K}$, for the first sintering step; and around $1,664 \text{ K}$ for the second step. In the first calcination, the two transformations correspond to the addition of the two lanthanides successively, on the skeleton of the zirconia oxide structure. In the second calcination, one can observe the formation of the cubic crystal at $1,664 \text{ K}$, being in mind that this compound has been calcinated only at $1,573 \text{ K}$ [29]. In the third calcination, the pyrochlore phase, identified by XRD analysis is thermally stable and does not show any phase transition against heating until $1,923 \text{ K}$, and also under cooling. This confirms the thermal stability of the synthesized pyrochlores materials.

3.4 FTIR Spectroscopy

The FTIR spectra of the three synthesized pyrochlores according to the sintering temperature are similar each other. They could be represented on Fig. 5.

The absorption bands recorded by FTIR of solid materials in the range $100\text{--}1,000 \text{ cm}^{-1}$ are usually assigned to interparticle vibrations within the crystal lattice. For $A_2B_2O_7$ pyrochlore molecules, the absorption band observed around 600 cm^{-1} is due to the stretching vibration mode of the B cation with oxygen:

Fig 4 DTA diagrams of $(Yb_{0.1}Nd_{0.9})_2Zr_2O_7$ at different sintering steps. (a) DTA diagram of $(Yb_{0.1}Nd_{0.9})_2Zr_2O_7$ sintered at $1,473 \text{ K}$, (b) DTA diagram of $(Yb_{0.1}Nd_{0.9})_2Zr_2O_7$ sintered at $1,573 \text{ K}$, (c) DTA diagram of $(Yb_{0.1}Nd_{0.9})_2Zr_2O_7$ sintered at $1,673 \text{ K}$.

Fig. 5 FTIR spectra of (Yb_{0.1}Nd_{0.9})₂Zr₂O₇ at the different sintering steps.

Table 4 Changes in the specific surface area of (Yb_xNd_{1-x})₂Zr₂O₇ pyrochlores (x = 0.1, 0.25 or 0.40) as a function of the sintering temperature.

(Yb _x Nd _{1-x}) ₂ Zr ₂ O ₇	x = 0.1	x = 0.25	x = 0.4
Sintering temperature (K)	Surface area (m ² /g)		
1273	13.256	13.155	12.987
1473	12.337	12.178	12.098
1673	11.181	11.069	10.899

BO (in our case: Zr-O) in the octahedron BO₆ [60-62].

The skeleton of pyrochlore is already formed at 1,000 °C. The absorption band appearing around 500 cm⁻¹ corresponds to the stretching vibration mode of the cation A with oxygen: AO (in our case: Yb-O or Nd-O). This band often appears around 520 cm⁻¹ [8]. In our case, and for the three studied chemical compositions, it appears at 525.1, 524.7 and 523.6 cm⁻¹, for the heating treatments of 1,273, 1,473 and 1,673 K, respectively.

We noted a slight shift towards lower frequencies when the temperature increases. The FTIR spectra show that the frequency decreases almost linearly with the raise of the sintering temperature.

4. Conclusions

In this study, we successfully synthesise three neodymium zirconates: (Yb_xNd_{1-x})₂Zr₂O₇, with x = 0.1, 0.25 and 0.4 by a dry milling method. The main physical and crystallographic characteristics of the materials were reached.

The final materials densities are representative of the lanthanides zirconates pyrochlore densities. They decrease with increasing the content of Nd. The best sintered material is that of the composition: (Yb_{0.4}Nd_{0.6})₂Zr₂O₇ (6,674 kg/m³). The XRD analysis gives patterns of a pyrochlore type lattice: Fd-3m fcc, which has been identified to the structure of a pyrochlore zirconate. A secondary faced centered cubic phase appear for the three compositions (Yb_xNd_{1-x})₂Zr₂O₇ (x = 0.1, 0.25 and 0.40). It has been identified to a lanthanide zirconium oxide, with an Fm-3m fcc phase. The observed microstructure reveals inhomogeneous grains, with average grains size about 3 micrometers. Vicker's hardnesses are medium values, showing the brittle mechanical behaviour of these materials. The measured values of fracture toughness of the three studied zirconates are also weak values. Thus, these pyrochlores are not mechanically resistant against strong constraints. The DTA analysis proves the thermal stability of the synthesized pyrochlores materials. The specific surface areas of the materials show that there are less porous, and the FTIR analysis confirms the appearance of the skeleton of the pyrochlore since 1,273 K.

One can conclude that the fabricated materials are well densified, and show good crystalline and microstructural structures, despite a brittle mechanical resistance. Further investigations are needed with loading the pyrochlores with uranium or thorium, in order to perform the durability tests of these potential candidates' materials for the sequestration of high level radioactive waste.

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