



**HAL**  
open science

## Zirconia nanopowder synthesis via detonation of trinitrotoluene

Pierre Gibot, Loic Vidal, Lydia Laffont, Julien Mory

► **To cite this version:**

Pierre Gibot, Loic Vidal, Lydia Laffont, Julien Mory. Zirconia nanopowder synthesis via detonation of trinitrotoluene. *Ceramics International*, 2020, 46 (17), pp.27057-27062. 10.1016/j.ceramint.2020.07.182 . hal-03033101v1

**HAL Id: hal-03033101**

**<https://hal.science/hal-03033101v1>**

Submitted on 21 Dec 2020 (v1), last revised 1 Dec 2020 (v2)

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Manuscript Number: CERI-D-20-06076R1

Title: Zirconia nanopowder synthesis via detonation of trinitrotoluene

Article Type: Full length article

Keywords: A. Powders: Detonation synthesis; D. ZrO<sub>2</sub>; Transition metal oxides; B. Nanoparticles.

Corresponding Author: Dr. Pierre GIBOT,

Corresponding Author's Institution:

First Author: Pierre GIBOT

Order of Authors: Pierre GIBOT; Loic VIDAL; Lydia LAFFONT; Julien MORY

Abstract: Zirconium (IV) oxide nanopowder was successfully synthesized through the detonation of a mixture composed of 2,4,6 trinitrotoluene (TNT, C<sub>7</sub>H<sub>5</sub>N<sub>3</sub>O<sub>6</sub>) and zirconium sulphate tetrahydrate (Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O) as the energetic material and ceramic precursor, respectively. TNT, one of the most popular explosives, is a secondary energetic molecule and exhibits high stability and low sensitivity toward external stresses, making its handling safe. After detonation of the energetic material/ceramic precursor mixture and purification of the detonation soot, a crystallized zirconium oxide (ZrO<sub>2</sub>) powder composed of nanosized particles with a spherical morphology was produced and analysed by the usual characterization techniques (X-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy and nitrogen physisorption). The reaction mechanism, considering the thermochemical aspect of the explosive, is offered. This approach could provide promising opportunities for the synthesis of various nano-sized oxide ceramic powders.

# Zirconia nanopowder synthesis via detonation of trinitrotoluene

P. Gibot<sup>1\*</sup>, Loic Vidal<sup>2</sup>, Lydia Laffont<sup>3</sup>, Julien Mory<sup>4</sup>

1. Laboratoire Nanomatériaux pour Systèmes Sous Sollicitations Extrêmes (NS3E) UMR 3208  
ISL/CNRS/UNISTRA, Institut franco-allemand de recherches de Saint-Louis (ISL), 5 rue du  
Général Cassagnou, BP70034, 68301 Saint Louis - France
2. Institut de Science des Matériaux de Mulhouse (IS2M) UMR 7361 CNRS/UHA, 15 rue Jean  
Starcky, BP2488, 68057 Mulhouse - France
3. CIRIMAT, Université de Toulouse, CNRS, INP-ENSIACET, 4 allée Emile Monso, BP 44362,  
31030 Toulouse cedex 4, France
4. Laboratoire Physique des Chocs et Détonique, ISL, 5 rue du Général Cassagnou, BP70034, 68301  
Saint Louis - France

Type of article: Original paper

\*Corresponding author: Tel: +33 (0)3.89.69.58.77. Fax:+33 (0)3.89.69.50.75

E-mail: [pierre.gibot@isl.eu](mailto:pierre.gibot@isl.eu) (Pierre Gibot)

---

## Abstract

Zirconium (IV) oxide nanopowder was successfully synthesized through the detonation of a mixture composed of 2,4,6 trinitrotoluene (TNT,  $C_7H_5N_3O_6$ ) and zirconium sulphate tetrahydrate ( $Zr(SO_4)_2 \cdot 4H_2O$ ) as the energetic material and ceramic precursor, respectively. TNT, one of the most popular explosives, is a secondary energetic molecule and exhibits high stability and low sensitivity toward external stresses, making its handling safe. After detonation of the energetic material/ceramic precursor mixture and purification of the detonation soot, a crystallized zirconium oxide ( $ZrO_2$ ) powder composed of nanosized particles with a spherical morphology was produced and analysed by the usual characterization techniques (X-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy and nitrogen physisorption). The reaction mechanism, considering the thermochemical aspect of the explosive, is offered. This approach could provide promising opportunities for the synthesis of various nano-sized oxide ceramic powders.

Keywords: A. Powders: Detonation synthesis; D.  $ZrO_2$ ; Transition metal oxides; B. Nanoparticles.

---

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

## 1. Introduction

Zirconium (IV) oxide is an outstanding refractory ceramic material since it exhibits very interesting physicochemical properties, such as high melting (2700 °C) and boiling points (> 4500 °C) and high thermal and chemical inertias, particularly under alkali conditions [1]. The crystallographic structure of zirconium oxide material can be described as transitioning between three well-known crystallographic phases [2]: the monoclinic phase ( $P2_1/c$  space group) up to 1170°C, the intermediate tetragonal phase ( $P4_2/nmc$  space group) from 1170 - 2370 °C and the cubic phase ( $Fm\bar{3}m$  space group) from 2370 °C to the melting point. These last two crystal structures can be stabilized at room temperature by the addition of a weak molar percent of calcium oxide (CaO), cerium (IV) oxide ( $CeO_2$ ), magnesium oxide (MgO) or yttrium oxide ( $Y_2O_3$ ) [3]. The high diversity of the physicochemical properties and crystalline structures of this ceramic material makes it promising for a large number of applications in many areas, such as fuel cells [4], sensors [5], bioceramics [6] and catalysts [7].

To satisfy these numerous applications, synthesizing a tunable zirconium (IV) oxide material that exhibits distinct physical surface properties (i.e., particle size, specific surface area, and porosity) or particles with various morphologies has become paramount. Thus, as a large number of these properties strongly depend of the synthesis conditions, many processes have been developed, including sol-gel without ultrasound assistance [8,9], coprecipitation [10,11], hydrothermal [12], mechanochemical [13], microwave [14], Pechini [15] and combustion methods [16]. More recently, an unconventional dynamic method based on the detonation of highly energetic materials (EM) or explosives to generate precursors for powder preparation has been published in the literature. This method combines high temperatures (> 1000 °C) and pressures (> GPa) for short times, thus producing (metastable) materials at nanoscales. The nanometric dimensions of the materials are assured by a cooling bath surrounding the energetic charge. The first example of successful detonation synthesis was reported for nanodiamonds using a mixture of two common secondary explosives, 2,4,6 trinitrotoluene (TNT) and 1,3,5 trinitro-1,3,5-triazine (RDX) [17]. From these initial results, some researchers have used RDX and ammonium nitrate ( $NH_4NO_3$ ), an inorganic energetic molecule; or a mixture of both as the detonation source for producing single ( $Al_2O_3$ ,  $ZrO_2$ ,  $B_2O_3$ ,  $TiO_2$ ,  $ZnO$ ,  $CeO_2$ )

[18-25] or mixed oxide ceramics ( $Gd_2O_3/CeO_2$ ,  $LiMn_2O_4$ ,  $MnFe_2O_4$ ,  $SrAl_2O_4$ ) [26-29]. The ammonium nitrate-based explosive emulsion approach was patented by [30,31], and Innovnano markets an as-detonated yttria-stabilized zirconia material [30-32]. These authors claim many advantages regarding the detonation method, such the synthesis of a pure material consisting of particles with a spherical morphology and of nanometric size. For example, Bukaemskii synthesized a nanosized zirconia powder from a mixture of zirconium hydroxide ( $Zr(OH)_x$ ) and RDX as the zirconium precursor and explosive molecule, respectively [33]. Cubic 5-6 nm- sized  $ZrO_2$  particles were successfully produced without the assistance of a stabilizing compound, as used in previous studies. Recently, non-oxide ceramics have also be prepared via the explosive route [34-36]. For example, Örnek et al. have successfully demonstrated the synthesis of nanoscale metastable boron nitride phases (w-BN and e-BN) from the detonation of an hexagonal boron nitride phase (h-BN) mixed with an explosive emulsion [34,35]. Langenderfer and co-workers have synthesized silicon carbide nanoparticles by submitted a pre-ceramic polymer (polycarbosilane) to the high pressures and temperatures generated by the detonation of a 2,4,6-trinitrotoluene and 1,3,5-trinitro-1,3,5-triazine energetic mixture [36]. Succinctly, the literature cited above evidences the high potential of this approach given the possibility of producing nano-sized materials, of stabilizing metastable phases and that for different kinds of materials.

Herein, a zirconium (IV) oxide nanopowder was detonation-synthesized using a mixture of 2,4,6 trinitrotoluene (TNT) and zirconium (IV) sulfate tetrahydrate as the explosive substance and zirconium source, respectively. TNT has the advantage of being less sensitive to mechanical stimuli than RDX, thus contributing to operator safety during the handling of these explosive compositions [37]. For example, the impact and friction sensitivities of TNT are 15 J and 353 N, respectively, compared to 7.4 J and 120 N for RDX. Finally, the as-detonated product was submitted to a series of analyses for characterization.

## 2. Experimental section

Zirconium sulfate tetrahydrate ( $Zr(SO_4)_2 \cdot 4H_2O$ , 99%) was purchased from Alfa Aesar. The energetic mixture of 2,4,6 trinitrotoluene or 2-methyl-1,3,5-trinitrobenzene (TNT,  $C_6H_2(NO_2)_3CH_3$ ) and 1,3,5-

1 trinitro-2-[2-(2,4,6-trinitrophenyl)-ethenyl] benzene or hexanitrostilbene (HNS,  $((\text{NO}_2)_3\text{C}_6\text{H}_2\text{CH})_2$ )  
2 (99.65/0.35 wt. %) was provided by Titanobel. Estane 5703, a polyester type thermoplastic  
3 polyurethane, was obtained from Lubrizol Advanced Materials, Inc. Hydrochloric acid (37%) was  
4 obtained from Prolabo.  
5  
6  
7  
8  
9

## 10 **2.1. Preparation of the zirconium-based energetic charge**

11 The zirconium sulfate hydrate material was covered by an Estane 5703 polymer layer using a  
12 dissolution/precipitation synthesis method. Using vigorous stirring (600 rpm), 1.54 g of Estane 5703  
13 was dissolved in 200 mL of acetone. Then, 29.64 g of zirconium salt was dispersed in the solution, and  
14 the mixture was stirred to obtain a homogeneous solution. Then, 460 mL of heptane was added (the  
15 first 280 mL added drop-by-drop) to the previous solution and maintained under stirring conditions to  
16 precipitate the polymer. Acetone was removed using a rotating evaporator (50 °C, 100 mbars), and the  
17  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ /Estane 5703 granules (95/5 weight ratio) were separated by filtration followed by  
18 washing with heptane. The  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ /Estane 5703 powder was mixed with the 2,4,6  
19 trinitrotoluene/1,3,5-trinitro-2-[2-(2,4,6-trinitrophenyl)-ethenyl] benzene explosive substance at a  
20 10:90 weight ratio using a Turbula mixer (model T2A – W.A. Bachofen) at 23 rpm for 20 min. The  
21 mixture was preheated at 70 °C (30 min.) and pressed at 765 bars for 10 min. Cooling was performed  
22 at 230 bars to 8 °C before releasing the mould. Cylindrical pellets (L = 50 mm,  $\text{Ø}$  = 45 mm) with a  
23 density of  $1.703 \pm 0.002$ , corresponding to 98% of the theoretical maximum density (TMD), were thus  
24 obtained. Two pellets were glued, placed in a plastic bag containing demineralized water and hung in  
25 the centre of a detonation chamber. Water was used to cool the detonation products extremely rapidly.  
26 A booster (graphite/wax/1,3,5-trinitro-1,3,5-triazinane secondary explosive 0.5/5/94.5 wt%, 55 g,  $\text{Ø}$  =  
27 28.4 mm, L = 57.5 mm) and an electric initiator (SA4000, Davey Bickford) were used to complete the  
28 energetic train. After detonation, the soot was filtered to remove plastic and metal fragments, washed  
29 with 2 mol/L hydrochloric acid to dissolve the rust from the detonation chamber and calcinated at  
30 700°C for 1 hour to oxidize the carbonaceous products of the TNT detonation and polypropylene tube  
31 combustion. The oxide ceramic yield was ~ 35%.  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

## 2.2. Characterization techniques

X-ray powder diffraction (XRD) was recorded on a D8 Advance diffractometer (Bruker, Billerica, MA, USA) using Cu-K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) equipped with a Lynxeye detector and operating at 40 kV and 40 mA in the range  $2\theta = 20\text{--}80^\circ$  with a  $2\theta$  step size of  $0.02^\circ$ . Fourier Transform Infra-Red (FT-IR) spectroscopy analysis of the sample was conducted using a Bruker Tensor 27 spectrometer. The spectrum was recorded in the transmission mode (KBr pellets) with a wavenumber range of  $4000\text{--}450 \text{ cm}^{-1}$  and by superposing 16 scans. The resolution was fixed at  $4 \text{ cm}^{-1}$ . The structure and microstructure of the product was determined using a JEM 2100F transmission electron microscope (JEOL, Tokyo, Japan) at an acceleration voltage of 200 kV and equipped with an energy dispersive spectrometer. The diffraction pattern of the investigated material was obtained using the selected area electron diffraction mode or by Fast Fourier transform of the high-resolution transmission electron microscopy images. Nitrogen sorption measurements at  $-196^\circ\text{C}$  were carried out on an ASAP2020 surface area analyser (Micromeritics, Norcross, GA, USA) with the sample outgassed at  $200^\circ\text{C}$  under vacuum for 6 hours. The specific surface area was determined according to the Brunauer–Emmett–Teller method within the 0.05–0.20 relative pressure domain. The particle size distribution of the powder, which as previously dispersed in chloroform (0.1 g/L), was determined by dynamic light scattering using a Zetasizer nanoZS apparatus (Malvern Instrument, Worcestershire, United Kingdom).

## 3. Results and Discussion

The XRD pattern of the product synthesized by the detonation of a TNT/Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O (90/10 wt%) energetic charge is displayed in Figure 1 (top). All the diffraction peaks could be assigned to the single zirconium (IV) oxide phase (ZrO<sub>2</sub>) except for the two thick and low intensity peaks located at  $\sim 21^\circ$  and  $\sim 26\text{--}27^\circ$ , which were assigned to an impurity from the white paint covering the inner wall of the detonation tank (Figure 1 top, symbol star). The impurity was identified as silica in quartz form (JCPDS 01-087-2096). Note that a sand blasting operation is planned in the near future to remove this impurity. Regarding the zirconia phase, both polymorphs were detected, including the monoclinic and



1 tetragonal structures described as  $P2_1/a$  and  $P4_2/nmc$  space groups, and were identified by the JCPDS  
2 card No 37-1484 and No 72-7115, respectively. Taking into account the relative intensity of the  
3 diffraction peaks described in both crystallographic reference cards, a preferential orientation/growth  
4 of the crystallite was observed at  $2\Theta = 35\text{--}36^\circ$ , which may correspond to the (002) and (110) Miller  
5 planes of the monoclinic and tetragonal phases, respectively. To date, the reaction mechanism is not  
6 yet well-understood, and an investigation is in progress.  
7  
8  
9

10 The volume percent ( $V_m$ ) of the monoclinic structure was determined using formula (1) by Schmid et  
11 al. [38] as given below:  
12

$$13 \quad V_m = \frac{1.311 \cdot X_m}{1 + 0.311 \cdot X_m} \quad (1)$$

14 where  $X_m$ , the ratio of integrated intensities (noted I) of specific (hkl) diffraction peaks, was specified  
15 by formula (2):  
16

$$17 \quad X_m = \frac{I_{m(-111)} + I_{m(111)}}{I_{m(-111)} + I_{m(111)} + I_{t(101)}} \quad (2)$$

18 A volume fraction of ~52% monoclinic phase was calculated (45% of  $X_m$  weight fraction), making  
19 this structure the majority in the  $ZrO_2$  powder.  
20

21 Figure 2 shows the FTIR spectrum of the product synthesized by the detonation of the  
22 TNT/ $Zr(SO_4)_2 \cdot 4H_2O$  (90/10 wt. %) energetic charge, magnified on the  $500\text{--}1000\text{ cm}^{-1}$  domain  
23 characterizing the metal-oxygen bonds vibration. The wavenumbers identifying each infrared vibration  
24 band are reported on the spectrum. The intense vibration band at  $505\text{ cm}^{-1}$  was assigned to the Zr-O  
25 bond vibration in the tetragonal structure, while the bands at  $578$  and  $744\text{ cm}^{-1}$  were correlated to  
26 zirconia material in the monoclinic phase [39]. This result supports the previous structural result  
27 (XRD) that showed the coexistence of both zirconia phases. An overview of the spectrum; i.e. over  
28  $1000\text{ cm}^{-1}$  is shown on Supporting information. The different visible vibration bands were associated  
29 with the vibrational modes of hydroxyl groups (-OH) or water molecules, both physisorbed on the  
30 surface of the material. Traces of the silica impurity were also observed.  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

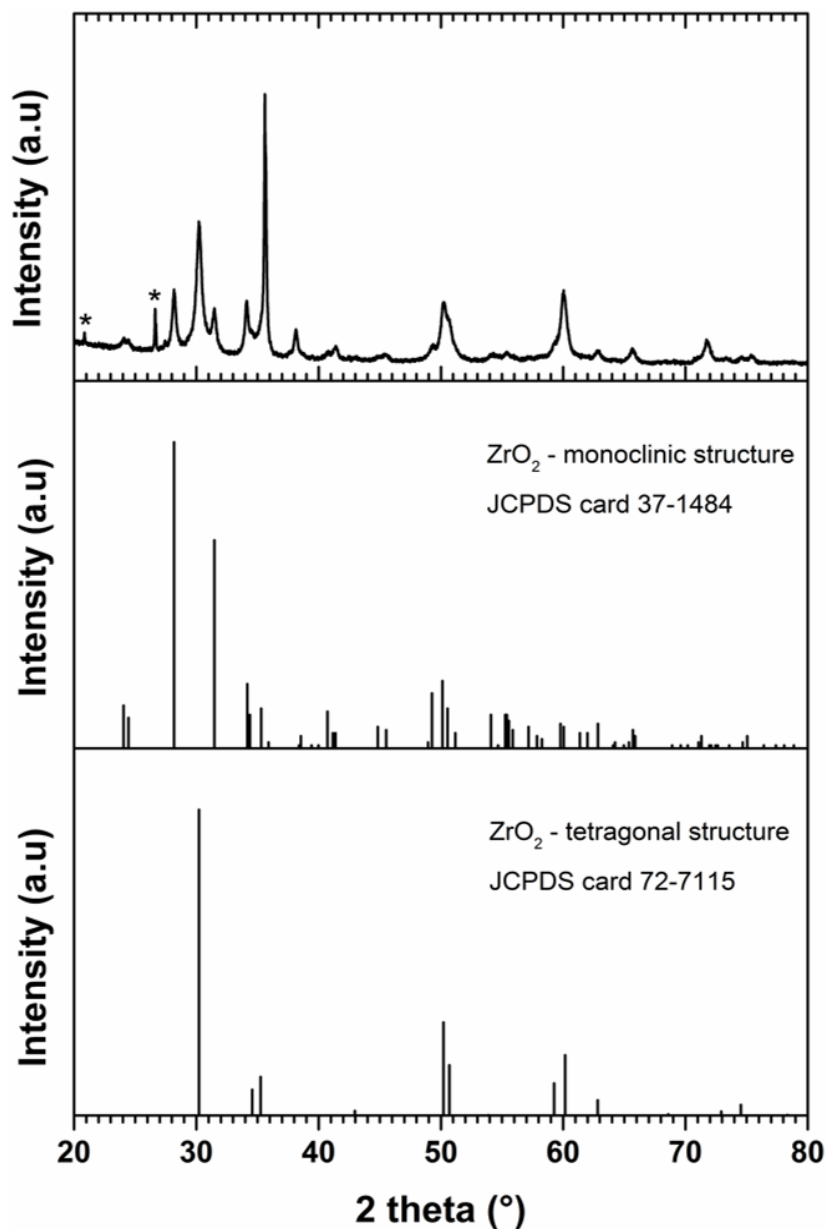
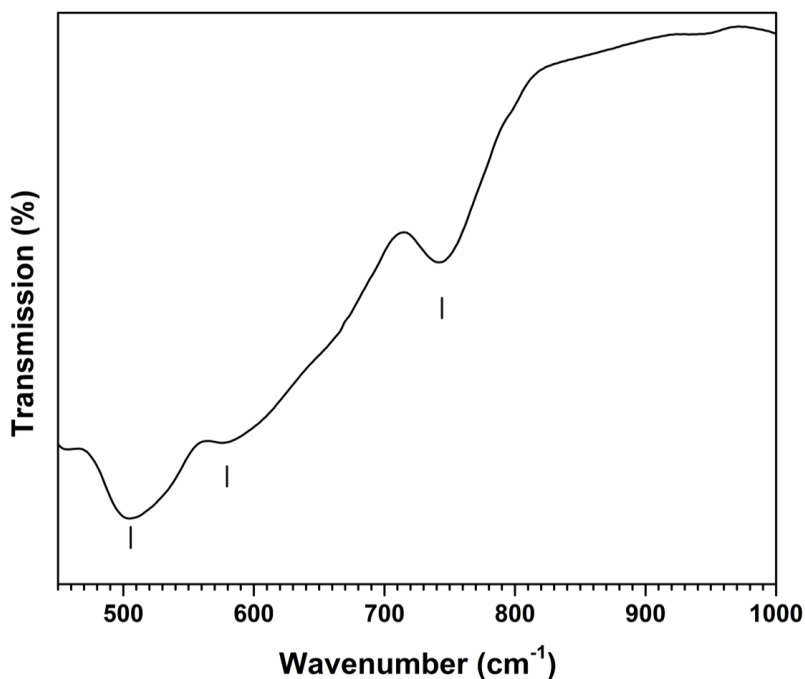
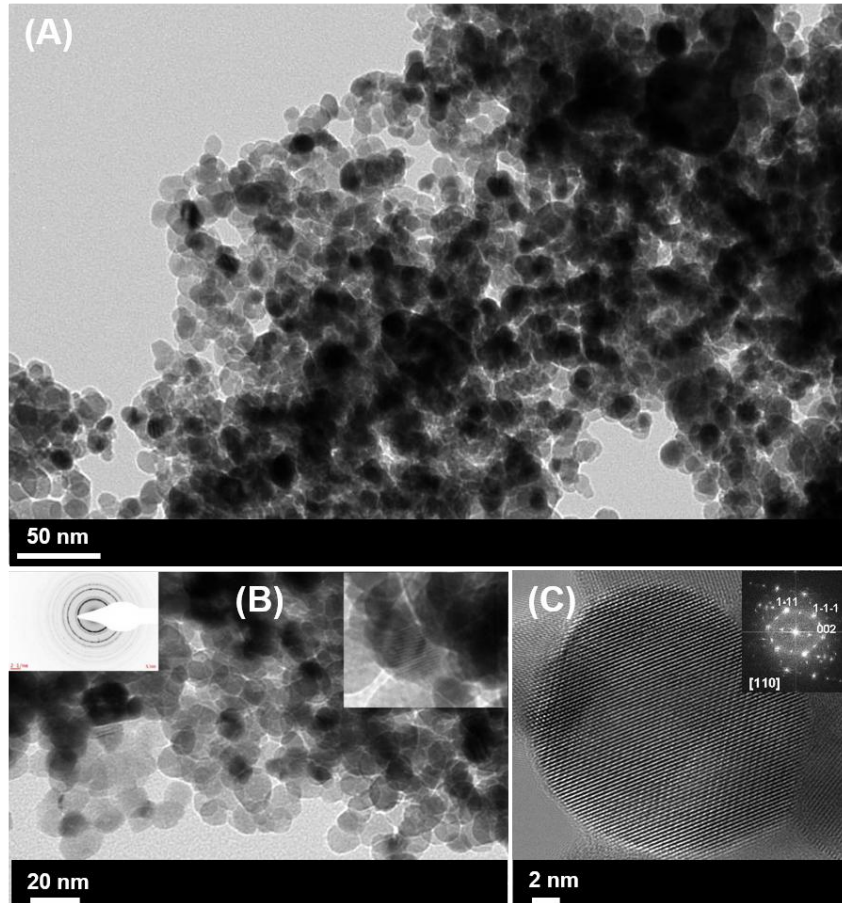


Figure 1: XRD patterns of the zirconium (IV) oxide sample ( $ZrO_2$ ) synthesized via detonation of a 2,4,6 trinitrotoluene/zirconium-salt (90/10 wt. %) explosive charge. Monoclinic and tetragonal structures are given for the XRD peak attribution.



**Figure 2: FTIR spectrum of the  $ZrO_2$  powder synthesized via detonation of a 2,4,6 trinitrotoluene/zirconium-salt (90/10 wt. %) explosive charge.**

The as-detonated zirconia powder was imaged by transmission electron microscopy (TEM) and high resolution (HR)-TEM analysis in order to reveal the morphology, structure and crystalline degree of the particles. Representative views are displayed in Figure 3. At low magnification, the TEM bright-field images clearly showed highly agglomerated particles exhibiting a nanometric dimension (Figure 3A). At an intermediate magnification, as shown in Figure 3B, the nanoparticles adopted a spherical morphology with a shape factor close to one. The particle dimensions were definitively at the nanoscale, and the particle size distribution appeared to be narrow with the main size range of approximately 25–30 nm. In the insert in Figure 3B, a selected area electron diffraction pattern (SAED) obtained on the nanoparticles confirmed the crystallinity of the powder due to the presence of rings. The HRTEM image shown in Figure 3C highlights the diffraction planes present in a particle. The Fast Fourier transform (insert of Figure 3C) of the HRTEM image of one nanoparticle is indexed using the monoclinic structure with a space group  $P2_1/a$  corresponding to  $ZrO_2$  zirconia.



**Figure 3: (A, B) TEM and (C) high resolution (HR) TEM images of the ZrO<sub>2</sub> powder synthesized via detonation of a 2,4,6 trinitrotoluene/zirconium-salt (90/10 wt%) explosive charge.**

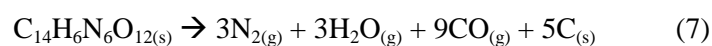
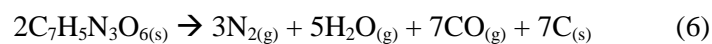
Nitrogen adsorption analysis provided textural properties data for the as-detonated ZrO<sub>2</sub> sample. In particular, the specific surface area (S), taking into account the Brunauer-Emmett-Teller (BET) model, was determined to be ~32 m<sup>2</sup>/g. Assuming the zirconia powder was composed of monodisperse dense spherical particles and knowing its density ( $\rho = 5890 \text{ kg/m}^3$ ), the average particle size ( $\varnothing$ ) was estimated using the following formula (5) [40]:

$$\varnothing = \frac{6}{\rho \times S_{\text{BET}}} \quad (5)$$

The average particle size was thus calculated to be approximately 32 nm, which is in good agreement with the trend observed by the microscopic analysis.

Based on the results determined above, a discussion is attempted in order to elucidate some points regarding the present synthesis method, namely the composition of the detonation soot, the particles size as well as the structure of the detonation products.

The detonation soot's composition is dependent on the reaction mechanism. The chemical decomposition mechanism taking place during the zirconia ceramic detonation synthesis was quite complex since the initial explosive mixture consisted of several ingredients, including explosive substances, such as 2,4,6 trinitrotoluene (TNT, C<sub>7</sub>H<sub>5</sub>N<sub>3</sub>O<sub>6</sub>) and hexanitrostilbene (HNS, C<sub>14</sub>H<sub>6</sub>N<sub>6</sub>O<sub>12</sub>), and the inert zirconium salt (Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O). Estane polymer was voluntarily discarded to simplify the reactive system. To investigate the detonation process, the decomposition reaction of the mixture may consider the sum of the decomposition chemical reactions of each ingredient independently. Based on the chemistry of the explosives, including the thermochemical aspect [41], the decomposition reaction of both explosive molecules, TNT and HNS, considering the Kistiakowsky-Wilson rules (the oxygen balance of TNT and HNS are much lower; i.e., -74.00 and -67.60 wt%, respectively), could be described by reactions (6) and (7) below:

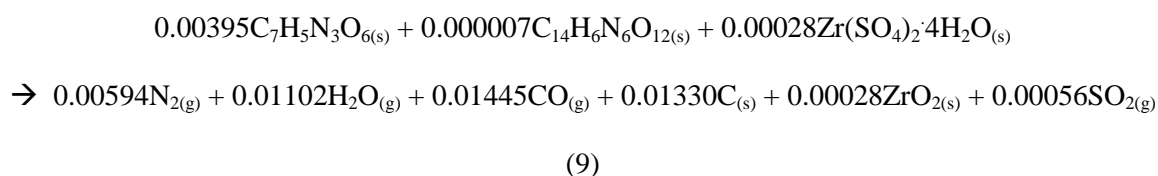


Note that negative oxygen balances will lead to the formation of a carbon solid phase since the amount of oxygen within the molecules was not enough to completely oxidize the compounds considered [41].

The thermal decomposition reaction of the Zr-salt inert compound could be represented by equation (8):



Finally, the global detonation reaction could be summarized by equation (9) based on the reaction of 1 g of mixture and taking into account the weight percentage of each of the three ingredients comprising the zirconium-doped explosive mixture (89.68, 0.32 and 10 wt. % for TNT, HNS and Zr(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, respectively):



Note that only carbon and zirconia solid phases were formed during the detonation, in line with the results obtained from the different characterization techniques shown previously. These two species were found in the detonation soot and were accompanied by impurities, such as iron oxide (Fe<sub>2</sub>O<sub>3</sub>) and

1  
2 silicium oxide ( $\text{SiO}_2$ ), originating from the roost and paint covering the inner wall of the detonation  
3 chamber. Most of the impurities were discarded during the purification process.

4 Regarding the particles size of the as-detonated zirconia powder, the detonation approach is known to  
5 generate high pressures (GPa) and temperatures ( $> 1000\text{ }^\circ\text{C}$ ) that are suitable to the gasification of the  
6 precursors and the formation of crystalline phases during the subsequent condensation step [19, 30-33,  
7 37, 41]. More, the extremely high cooling rate of the detonation gaseous products, estimated as high as  
8  $10^9\text{ }^\circ\text{C}/\text{sec}$ . due to the rapid expansion of the chemical species, impedes the growth of particles  
9 produced and consequently leads to the formation of materials of nanoscale dimension [21-36]. The  
10 use of water to cool down the detonation products (see Experimental section) efficiently also acts to  
11 stop the growth of condensed species and thus controls the particles size in the nanoscale.  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21

22 Concerning the structure of the as-detonated zirconia powder, monoclinic and tetragonal phases were  
23 prepared. The metastable cubic structure was not identified. Based on the work of Bukaemskii [33],  
24 the cubic phase is favoured for the smallest particles due to a layer-by-layer growth model where  
25 surface layers are preferentially made of high-temperature phases. Particles smaller than  $\sim 10\text{ nm}$   
26 would adopt a cubic structure moving gradually towards the tetragonal and finally the monoclinic  
27 phases as the particle growths. As, in the present work, the as-detonated  $\text{ZrO}_2$  particles exhibit a  
28 particle size ranging from 25 to 30 nm, the cubic structure was not favoured. Now, regarding the  
29 formation of both monoclinic and tetragonal phases, it can be explain by a mitigation of the shock  
30 wave during its dissipation in all the volume of the detonation chamber [33]. It can be speculate that  
31 this mitigation leads to the coexistence of reaction zones where pressures and temperatures are  
32 different. Highest pressures and highest temperatures domains (close to the central axis of the  
33 cylindrical charge) would promote the formation of the metastable tetragonal phase at the expense of  
34 the monoclinic one which might rather originate from the zone located at the edge of the charge [33-  
35 35]. Currently, it has not be possible to distinguish the crystalline structure of the  $\text{ZrO}_2$  material as  
36 function of the particles size.  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57

#### 58 **4. Conclusion**

59  
60  
61  
62  
63  
64  
65

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

In summary, a zirconia nanopowder ( $ZrO_2$ ) was synthesized via a detonation process using 2,4,6 trinitrotoluene (TNT) as the high energetic molecule mixed with zirconium sulfate. TNT is one of the energetic materials with the lowest sensitivity compared to other high explosives that can be used in such a process, and therefore, it is seen as a promising compound for future development. In addition, as the melting point of TNT is low (80.8 °C), it can be used in melting or casting processes to lead to more homogeneous explosive/ceramic precursor mixtures. In the present work, purified soot was composed of  $ZrO_2$  particles exhibiting well-defined microstructural properties (spherical morphology, nanoscale particles size, narrow particles size distribution). However, the simultaneous synthesis of two zirconia polymorphs could be a disadvantage for many applications, which may be able to be overcome by adding stabilizing ingredients, such as yttrium, cerium, or calcium oxides, in the initial detonative mixture. Successful synthesis of mixed oxides has been demonstrated in the previous literature. Finally, the present investigation confirmed that explosive synthesis routes are efficient and suitable for producing nanosized ceramics powders.

## Acknowledgements

The French National Centre for Scientific Research (CNRS), French German Research Institute of Saint-Louis (ISL, Saint-Louis, France) and University of Strasbourg (UNISTRA, Strasbourg, France) are acknowledged by the authors for funding. The authors thank E. Fousson (ISL, Saint-Louis) and D. Spitzer (director of NS3E laboratory, Saint-Louis) for the help in the explosion experiments and the incentives to develop this research topic, respectively.

## References

- [1] Handbook of Chemistry and Physics, 84<sup>th</sup> ed., The Chemical Rubber Co, Ohio, 2003-2004.
- [2] G. Beranger, J. Favereon, G. Moulin, Zircon-Céramique fonctionnelle, Techniques de l'ingénieur, 2008.
- [3] J.M. Haussonne, C. Carry, P. Bowen, J. Barton, Céramiques et Verres, Principes et techniques d'élaboration, 1<sup>st</sup> ed., Presses polytechniques et universitaires romandes, Lausanne, 2005.
- [4] B.C.H. Steele, A. Heinzl, Materials for fuel-cell technologies, Nature. 414 (2001) 345-352.
- [5] S.A. Ghom, C. Zamani, S. Nazarpour, T. Andreu, J.R. Morante, Oxygen sensing with mesoporous ceria-zirconia solid solutions, Sens. Actuators B. 140 (2009) 216-221.

- [6] C. Piconi, G. Maccauro, Zirconia as a ceramic biomaterial, *Biomaterials*. 20 (1999) 1-25.
- [7] Y. Li, D. He, Z. Cheng, C. Su, J. Li, Q. Zhu, Effect of calcium salts on isosynthesis over  $ZrO_2$  catalysts, *J. Mol. Catal. A: Chem.* 175 (2001) 267-275.
- [8] J. Yan, X. Li, S. Cheng, Y. Ke, X. Liang, Facile synthesis of titania–zirconia monodisperse microspheres and application for phosphopeptides enrichment, *Chem Commun.* (2009) 2929-2931.
- [9] J. Judes, V. Kamaraj, Sol-gel preparation and characterization of ceria stabilized zirconia minispheres, *J. Sol-Gel Sci. Technol.* 49 (2009) 159-165.
- [10] H. Chen, A. Yin, X. Guo, W. Dai, K. Fan, Sodium hydroxide-sodium oxalate-assisted co-precipitation of highly active and stable  $Cu/ZrO_2$  catalyst in the partial oxidation of methanol to hydrogen, *Catal. Lett.* 131 (2009) 632-642.
- [11] M. Dechamps, B. Djuricic, S. Pickering, Structure of zirconia prepared by homogeneous precipitation, *J. Am. Ceram. Soc.* 78 (1995) 2873-2880.
- [12] T.M. Arantes, G.P. Mambrini, D.G. Stroppa, E.R. Leite, E. Longo, A.J. Ramirez, E.R. Camargo, Stable colloidal suspensions of nanostructured zirconium oxide synthesized by hydrothermal process, *J. Nanopart. Res.* 12 (2010) 3105-3110.
- [13] A. Dodd, P. McCormick, Synthesis of nanocrystalline  $ZrO_2$  powders by mechanochemical reaction of  $ZrCl_4$  with  $LiOH$ . *J. Eur. Ceram. Soc.* 22 (2002) 1823-1829.
- [14] Y. T. Moon, D. K. Kim, C. H. Kim, Preparation of monodisperse  $ZrO_2$  by the microwave heating of zirconyl chloride solutions, *J. Am. Ceram. Soc.* 78 (1995) 1103-1106.
- [15] C. Lin, C. Zhang, J. Lin, Phase transformation and photoluminescence properties of nanocrystalline  $ZrO_2$  powders prepared via the Pechini-type sol-gel process, *J. Phys. Chem. C* 111 (2007) 3300-3307.
- [16] I.O. Fabregas, D.G. Lamas, Parametric study of the gel-combustion synthesis of nanocrystalline  $ZrO_2$ -based powders, *Powder Technol.* 214 (2011) 218–228.
- [17] V. N. Mochalin, O. Shenderova, D. Ho, Y. Gogotsi, The properties and applications of nanodiamonds, *Nat. Nanotechnol.* 7 (2012) 11-23.
- [18] S. Cudzilo, A. Maranda, J. Nowaczewski, R. Trebinski, W.A. Trzcinski, Detonative synthesis of inorganic compounds, *J. Mater. Sci. Lett.* 9 (2000) 1997-2000.
- [19] A.A. Bukaemskii, Explosive synthesis of ultra-disperse aluminium oxide in an oxygen-containing medium, *Combust. Explos. Shock Waves.* 37 (2001) 594-599.
- [20] R. Y. Li, X. J. Li, H. H. Yan, J. Peng, Experimental Investigations of the controlled explosive synthesis of ultrafine  $Al_2O_3$ , *Combust. Explos. Shock Waves.* 49 (2013) 105-108.
- [21] Y. Qu, X. Li, X. Wang, D. Liu, Detonation synthesis of nanosized titanium oxide powders, *Nanotechnology.* 18 (2007) 205602-205607.
- [22] Y.D. Qu, X.J. Li, H.H. Yan, X. Ouyang, Selective synthesis of  $TiO_2$  nanopowders, *Glass Phys. Chem.* 34 (2008) 637-639.
- [23] H. Yan, T. Zhao, X. Li, B. Zhao, Slurry explosive detonation synthesis and characterization of 10 nm  $TiO_2$ , *Ceram. Int.* 42 (2016) 14862–14866.
- [24] X. Xie, X. Li, H. Yan, Detonation synthesis of zinc oxide nanometer powders, *Mater. Lett.* 60 (2006) 3149-3152.



- 1 [25] Z. W. Han, S. Xu, L.F. Xie, Y.C. Han, Study on the application of emulsion explosives in synthesizing  
2 nanostructured ceria, *Combust. Explos. Shock Waves*. 50 (2014) 477-482.
- 3 [26] O. Vasylykiv, Y. Sakka, Nanoexplosion synthesis of multimetal oxide ceramic nanopowders, *Nano Lett.* 5  
4 (2005) 2598-2604.
- 5 [27] X. Xie, X. Li, Z. Zhao, H. Wu, Y. Qu, W. Huang, Growth and morphology of nanometer  $\text{LiMn}_2\text{O}_4$  powder,  
6 *Powder Technol.* 169 (2006) 143-146.
- 7 [28] X.H. Wang, X.J. Li, H.H. Yan, L. Xue, Y.D. Qu, G.L. Sun, Nano- $\text{MnFe}_2\text{O}_4$  powder synthesis by detonation  
8 of emulsion explosive, *Appl. Phys. A*. 90 (2008) 417-422.
- 9 [29] X. Li, Y. Qu, X. Xie, Z. Wang, R. Li, Preparation of  $\text{SrAl}_2\text{O}_4$ :  $\text{Eu}^{2+}$ ,  $\text{Dy}^{3+}$  nanometer phosphors by  
10 detonation method, *Mater. Lett.* 60 (2006) 3673-3677
- 11 [30] C. Da Silva, J. Manuel, A. Dos Santos; E. Marisa, Nanometric-sized ceramic materials, process for their  
12 synthesis and uses thereof. United States Patent 8,557,215. 2013.
- 13 [31] A. Dos Santos, E. Marisa, C. Da Silva, J. Manuel, C. Lagoa, A.L. Cia, Process for nanomaterial synthesis  
14 from the preparation and detonation of an emulsion, products and emulsions thereof. United States Patent  
15 9,115,001. 2015.
- 16 [32] <http://www.innovnano.pt/>
- 17 [33] A.A. Bukaemskii, Nanosize powder of zirconia. Explosive method of production and properties, *Combust.*  
18 *Explos. Shock Waves*. 37 (2001) 481-485.
- 19 [34] M. Ornek, K. M. Reddy, C. Hwang, V. Domnich, A. Burgess, S. Pratas, J. Calado, K. Y. Sie, S. L. Miller,  
20 K. J. Hemker, R. A. Haber, Observations of explosion phase boron nitride formed by emulsion detonation  
21 synthesis, *Scr. Mater.* 145 (2018) 126-130.
- 22 [35] M. Ornek, C. Hwang, K. Y. Xie, S. Pratas, J. Calado, A. Burgess, V. Domnich, K. J. Hemker, R. A. Haber,  
23 Formation of metastable wurtzite phase boron nitride by emulsion detonation synthesis, *J. Am. Ceram. Soc.* 101  
24 (2018) 3276-3281.
- 25 [36] M. J. Langenderfer, W. G. Fahrenholtz, S. Chertopalov, Y. Zhou, V. N. Mochalin, C. E. Johnson,  
26 Detonation synthesis of silicon carbide nanoparticles, *Ceram. Int.* 46 (2020) 6951-6954.
- 27 [37] R. Meyer, J. Kohler, A. Homburg, *Explosives*, 6<sup>th</sup> ed., Wiley-VCH, Weinheim, 2007.
- 28 [38] H.K. Schmid, Quantitative analysis of polymorphic mixes of zirconia by X-ray diffraction, *J. Am. Ceram.*  
29 *Soc.* 70 (1987) 367-376.
- 30 [39] M. Aflaki, F. Davar, Synthesis, luminescence and photocatalyst properties of zirconia nanosheets by  
31 modified Pechini method, *J. Molecular Liquids* 221 (2016) 1071-1079.
- 32 [40] S. Lowell, J.E. Shields, M.A. Thomas, M. Thommes, *Characterization of porous solids and powders:*  
33 *surface area, pore size and density*, 1<sup>st</sup> ed. Kluwer Academic Publishers, The Netherlands, 2004.
- 34 [41] J. Akhavan, *The chemistry of explosives*, 2<sup>nd</sup> ed., Royal Society of Chemistry, United Kingdom, 2004.
- 35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

## Zirconia nanopowder synthesis via detonation of trinitrotoluene

P. Gibot<sup>1\*</sup>, Loic Vidal<sup>2</sup>, Lydia Laffont<sup>3</sup>, Julien Mory<sup>4</sup>

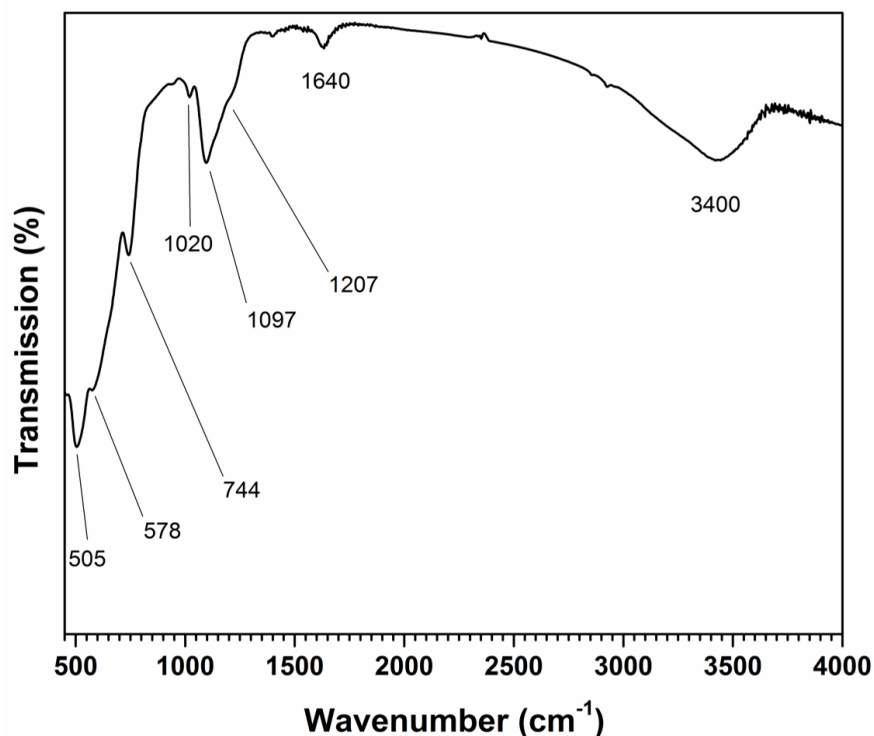
1. Laboratoire Nanomatériaux pour Systèmes Sous Sollicitations Extrêmes (NS3E) UMR 3208 ISL/CNRS/UNISTRA, Institut franco-allemand de recherches de Saint-Louis (ISL), 5 rue du Général Cassagnou, BP70034, 68301 Saint Louis - France
2. Institut de Science des Matériaux de Mulhouse (IS2M) UMR 7361 CNRS/UHA, 15 rue Jean Starcky, BP2488, 68057 Mulhouse - France
3. CIRIMAT, Université de Toulouse, CNRS, INP-ENSIACET, 4 allée Emile Monso, BP 44362, 31030 Toulouse cedex 4, France
4. Laboratoire Physique des Chocs et Détonique, ISL, 5 rue du Général Cassagnou, BP70034, 68301 Saint Louis - France

Type of article: Original paper

\*Corresponding author: Tel: +33 (0)3.89.69.58.77. Fax:+33 (0)3.89.69.50.75

E-mail: [pierre.gibot@isl.eu](mailto:pierre.gibot@isl.eu) (Pierre Gibot)

## Supporting Information



**Figure 1:** FTIR spectrum of the ZrO<sub>2</sub> powder synthesized via detonation of a 2,4,6 trinitrotoluene/zirconium-salt (90/10 wt. %) explosive charge.

As mentioned in the main text, the active domain located at 500-800 cm<sup>-1</sup> corresponds to Zr-O bonds vibrations modes. The second ones observed at 1000–1300 cm<sup>-1</sup> is attributed to silicon-oxygen bonds (impurity from the set-up). The IR vibration bands at 1020, 1097 and 1207 cm<sup>-1</sup> were associated with the asymmetrical stretching vibration of the Si-O-Si functional entity (impurity inherent to the detonation chamber) following longitudinal and transverse optical components [1]. Finally, the bands observed at 1640 cm<sup>-1</sup> and approximately 3400 cm<sup>-1</sup> were attributed to the vibrational modes of hydroxyl groups (-OH) or water molecules, both physisorbed on the surface of the material.

[1] R.M. Ameida, C.G. Pantano, Structural investigation of silica gel films by infrared spectroscopy, J. Appl. Phys. 68 (1990) 4225.