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From design to characterization of zirconium nitride/silicon nitride nanocomposites

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ABSTRACT

ZrN/Si₃N₄ nanocomposites have been prepared by chemically crosslinking two polysilazanes with a zirconium-based compound and subsequent heat-treatment at temperatures ranging from 1000 to 1600 °C. The polymer synthesis has been systematically investigated using FT-IR, solid-state NMR, and elemental analyses. Then, the pyrolysis under ammonia at 1000 °C triggering the thermo-chemical polymer-to-ceramic conversion was examined, leading to X-ray amorphous ceramics with yields governed by the chemistry of the neat polysilazane. Investigations of the structural evolution of the single-phase amorphous ceramic network above 1000 °C by X-ray diffraction and Raman spectroscopy pointed out that the ZrN phase already segregated at 1400 °C and formed highly crystalline ZrN/Si₃N₄ nanocomposites at 1600 °C. HRTEM investigations validated the unique nanostructural feature of the nanocomposites made of ZrN nanocrystals distributed in α- and β-Si₃N₄ phases. Our preliminary investigations of the optical properties showed that these structural changes allowed tuning the optical properties of ZrN/Si₃N₄ nanocomposites.

1. Introduction

Materials discovery plays a key role in the innovation cycle of energy conversion, transmission and storage technologies [1]. Among the different types of materials with high potential in energy-related fields, advanced ceramics - inorganic and non-metallic solids that represent an “advancement” over traditional ceramics (*e.g.*, porcelain) - exhibit unique and/or superior functional attributes that can be “precisely specified” by careful synthesis, processing and quality control. Because of the attention to microstructural design and the large possibilities of element combination which are known to enhance performance and to generate new physical phenomena, ceramics prepared at nanoscale, *i.e.*, nanoceramics [2], represent high value-added products that recently demonstrated attractivities in the energy fields [3–9]. Such nanoceramics can represent also a nanoscaled component of composite materials to form nanocomposites with completely novel property combinations, owing to the synergetic effects between the different components.

The synthesis of nanosized ceramics is quite challenging,

particularly, *via* traditional powder route. In this regard, the PDC (Polymer-Derived Ceramics) route provides a flexible way to tailor the chemical composition of these ceramics at the molecular level. Several Si₃N₄-based nanocomposites have successfully been synthesized lately, covering a wide range of important applications. For instance, SiC/Si₃N₄ nanocomposite consists of a promising material for many engineering applications, such as turbine engines, high-performance cutting tools, and wear-resistant parts owing to their excellent mechanical properties and high oxidation and corrosion tolerance [10,11]. Another impactful research area is catalysis [12], which includes Transition Metal (TM) or TM Nitrides (TMN)/Si₃N₄ such as Co/Si₃N₄ [13], TiN/Si₃N₄ [14,15] and VN/Si₃N₄ [16] compounds. In particular, TiN/Si₃N₄ nanocomposites [15] demonstrated strong synergy between the nanoscaled TiN, the Si₃N₄ matrix and the Pt nanoparticles, which were homogeneously deposited onto the nanocomposite support in a second synthesis step. This resulted in excellent catalytic performances for dehydrogenation of sodium borohydride in water.

ZrN catalysts have been recently reported to outperform platinum (Pt) in alkaline conditions for oxygen reduction reactions (ORR) [17].

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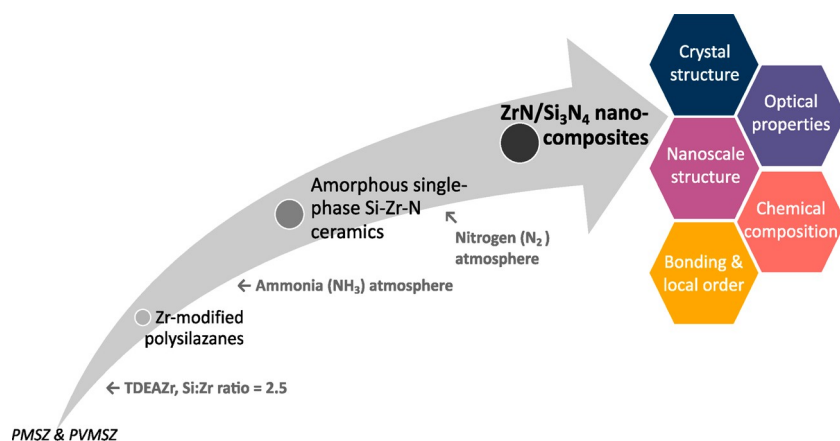


Fig. 1. Schematic diagram of the general process of designing ZrN/Si₃N₄ nanocomposites from Zr-modified polysilazanes and provided chemical, structural and optical fingerprints.

However, the synthesis of nanoscaled ZrN is highly challenging. In our process, the fact that nanoscaled ZrN is embedded in a covalently-bonded Si₃N₄ matrix – the latter acting as a support - will prevent pronounced coarsening and the damage of the dispersed nanoscaled ZrN, thus providing materials with high and constant performance even when exposed to high temperatures and/or harsh environmental conditions. Furthermore, based on our recent study, the TMN (TM Ti, Zr, Hf) nanophase can be accessible [15], as required for catalysis applications. Aside from their catalytic potential, TMN display unique optical properties and electronic structure intended – for instance - towards long-lasting, bio- and CMOS-compatible plasmonic and metasurface applications as well as an emerging class of nanophotonic materials [18]. For instance, ZrN and ZrN/SiO_xN_y have previously been shown to be effective plasmonic materials in the visible range, providing a low-cost alternative to gold and silver as well as wider application in harsh environments [19,20]. Thus, ZrN-based nanocomposites could offer strong interest for energy technologies through the exploitation of their optical, catalytic and electronic properties.

In this work, we have exploited the advantage of producing TMN/Si₃N₄ compounds [14,15,21–23] by the PDC route [24–37] to design ZrN/Si₃N₄ nanocomposites where their structure can be well controlled from the precursor level. Our approach involves first the synthesis of zirconium (Zr)-modified polysilazanes from liquid polysilazanes as Si₃N₄ precursors, *i.e.*, polymethylsilazane (PMSZ) and poly(vinyl-methyl-*co*-methyl)silazane (PVMSZ), which are known to deliver Si-C-N ceramics [22,38,39]. Then, we played with the reactivity of the central Si and Zr cations distributed in the polysilazane network with ammonia (used as atmosphere to form nitrides), resulting in an amorphous single-phase Si-Zr-N network at 1000 °C. The latter underwent subsequent phase separation and crystallization processes to deliver nanoscaled zirconium nitride (ZrN) clusters distributed in a Si₃N₄ matrix. At each stage of their synthesis, the materials have been systematically characterized. In addition, we provided preliminary optical property results of the nanocomposites. The present study demonstrates that the functional properties of the nanocomposites can be finely tuned by the unique chemistry of the nanocomposite precursors. The schematic representation of our approach is described in Fig. 1.

2. Experimental procedure

2.1. Materials

The synthesis of the precursor is carried out in a purified argon atmosphere passing through a column of phosphorus pentoxide and then a vacuum/argon line by means of standard Schlenk techniques. The cleaned glassware is stored in an oven at 90 °C overnight, before being

connected to the vacuum/argon line, assembled and pumped under vacuum for 30 min, and then filled with argon. All chemical products are handled in an argon-filled glove box (MBraun MB200B for PMSZ; O₂ and H₂O concentrations kept at <0.1 ppm and Jacomex for PVMSZ, Campus-type; O₂ and H₂O concentrations kept at <0.1 ppm and 0.8 ppm, respectively). Toluene (99.85 %, Extra Dry over Molecular Sieve, AcroSeal(R)) was purchased from Acros Organics™. The poly(vinyl-methyl-*co*-methyl)silazane labelled PVMSZ (commercial name: Durazane® 1800) was provided by Merck company, Germany, stored in a fridge and used as-received. FTIR (ATR/cm⁻¹): ν (N-H) = 3388 (m), ν (C-H) = 3046 (w), 3010 (vs), 2954 (s), 2895 (s), 2852 (m), ν (Si-H) = 2121 (s), δ (vinyl) = 1591 (m) + 1405 (m), δ (Si-CH₃) = 1251 (s), δ (N-H): 1166 (m), δ (C=C + N-Si-N + C-H + Si-C) = 1005-630 (vs); ¹H NMR (300 MHz, CDCl₃, δ/ppm): 0.4–0.1 (br, SiCH₃), 1.1–0.5 (br, NH), 4.9–4.4 (br, SiH), 6.3–5.7 (br, vinyl). Polymethylsilazane (PMSZ) was synthesized by ammonolysis of dichloromethylsilane (DCMS, HSiCH₃Cl₂) in accordance to procedures described in the literature. 10,14 DCMS was obtained from Sigma-Aldrich and freshly distilled from magnesium at P_{atm} before use. FTIR (ATR/cm⁻¹): ν (N-H) = 3377 (m), ν (C-H) = 2960 (s), 2860 (m), ν (Si-H) = 2105 (s), δ (CH_x) = 1464 (m) + 1377 (m), δ (Si-CH₃) = 1251 (s), δ (N-H): 1174 (m), δ (N-Si-N + C-H + Si-C) = 1005-630 (vs). Tetrakis(diethylamino)zirconium (Zr[N(CH₂CH₃)₂]₄ (99 %) (labelled as TDEAZr) was obtained from ABCR GmbH, stored in a fridge and used without further purification.

2.2. Synthesis of zirconium-modified polysilazanes

The reaction between PMSZ/PVMSZ and TDEAZr is performed in toluene at temperature of reflux (115 °C) in a three-neck round-bottom flask. In a typical experiment using PVMSZ (which can be identically applied to the polymer synthesized from PMSZ), 3.0 g of TDEAZr (7.9 mmol) is added with a syringe under argon atmosphere to a solution of 1.30 g of PVMSZ (20.20 mmol referred to the monomeric unit of PVMSZ) in 150 mL of toluene at RT under vigorous stirring. When addition has ended, the temperature is increased up to 115 °C and kept at this temperature under vigorous stirring three days. After cooling down, the solvent is extracted *via* an ether bridge (100 °C/1.5·10⁻¹ mbar) to release air- and moisture-sensitive from the zirconium-modified PVMSZ, which results in a yellow colored powder that is labelled as PVMZrS2.5 (2.5 being the Si:Zr ratio). Anal. Found (wt%): Si 19.6, Zr 19.3, C 31.2, N 16.3, H 7.2, O 6.4. [Si_{1.0}Zr_{0.31}C_{3.7}N_{1.7}.

H_{10.3}O_{0.6}]_n (Referenced to Si_{1.0} in the empirical formulae). FTIR (ATR/ cm⁻¹): ν(N-H) = 3388 (w), ν (C-H) = 3045 (w) + 2968 (vs) + 2925 (s), 2871 (s) + 2830 (m) + 2701 (w) + 2674 (w), ν(Si-H) = 2126 (s), δ (vinyl) = 1590 (m) + 1405 (m), δ(CH_x) = 1455 (m) + 1369 (m), ν(C-N) = 1290 (w), δ(Si-CH₃) = 1256 (s), δ (N-H, N-Si-N + C-H + Si-C) = 1184-

590 (vs). Based on the same synthesis procedure, the PMZrSZ2.5 is obtained as a brown powder. Anal. Found (wt %): Si 23.4, Zr 29.7, C 30.3, N 8.7, H 7.9, O 0.0. $[\text{Si}_{1.0}\text{Zr}_{0.37}\text{C}_{3.1}\text{N}_{0.8}\text{H}_{9.7}]_n$ (Referenced to $\text{Si}_{1.0}$ and oxygen content was omitted in the empirical formulae). FTIR (ATR/ cm^{-1}): $\nu(\text{N-H}) = 3382$ (m), $\nu(\text{C-H}) = 2960$ (vs) + 2923 (s) + 2868 (s) + 2831 (m) + 2699 (w) + 2681 (w), $\nu(\text{Si-H}) = 2112$ (s), $\delta(\text{CH}_x) = 1460$ (m) + 1370 (m), $\nu(\text{C-N}) = 1290$ (m), $\delta(\text{Si-CH}_3) = 1256$ (s), $\delta(\text{N-H, N-Si-N + C-H + Si-C}) = 1182$ -590 (vs).

2.3. Preparation of the ceramic nanocomposites

Polymeric powders are placed in alumina boats in the glove-box, then introduced in a sealed tube under argon atmosphere to prevent any oxygen contamination of the samples during the transfer to the furnace. Powders are then introduced under argon flow into a silica tube from a horizontal furnace (Carbolite BGHA12/450B). The tube is evacuated (0.1 mbar) and refilled with anhydrous ammonia (99.99%) to atmospheric pressure. Subsequently, the samples are subjected to a cycle of ramping of $5\text{ }^\circ\text{C min}^{-1}$ up to $1000\text{ }^\circ\text{C}$ in flowing ammonia (dwelling time of 2 h at $1000\text{ }^\circ\text{C}$). A constant gas flow (120 mL min^{-1}) is passed through the tube during the pyrolysis cycle. After cooling under argon atmosphere, ammonia-pyrolyzed samples are stored in the glove-box for characterization. Samples are labeled PVMZrSZ2.5_10 or PMZrSZ2.5_10 (according to the nature of the polymer) with 10 being the two first digits of the temperature ($1000\text{ }^\circ\text{C}$) at which the polymer has been exposed. For the high temperature ($T > 1000\text{ }^\circ\text{C}$) investigation, samples pyrolyzed at $1000\text{ }^\circ\text{C}$ are subsequently introduced in a graphite furnace (Gero Model HTK 8 for samples derived from PMSZ and VHT-GR from Nabertherm for samples derived from PVMSZ) for annealing treatments. The furnaces are pumped under vacuum (0.1 mbar), refilled with nitrogen and maintained under a constant flow of gas (200 mL min^{-1}) during the whole heat treatment. The program consists of a $5\text{ }^\circ\text{C min}^{-1}$ heating ramp up to the maximum temperature fixed in the range 1400 – $1600\text{ }^\circ\text{C}$, dwelling at the selected temperature for 2 h and cooling down to RT at $5\text{ }^\circ\text{C min}^{-1}$. Samples are labelled PVMZrSZ2.5_T or PMZrSZ2.5_T with T the two first digits of temperature at which the material has been exposed (1400 , 1500 and $1600\text{ }^\circ\text{C}$).

2.4. Material characterization

As the polymers are reactive towards moisture and oxygen, the following sample preparations were performed within a glove box. The chemical structure of the polymers was determined by transmission FTIR spectroscopy using a Nicolet Magna 550 Fourier transform-infrared spectrometer. ^1H NMR data of PMVSZ solutions in CDCl_3 were obtained using a Bruker AM 300 spectrometer operating at 300 MHz. Tetramethylsilane (TMS) was used as a reference for the NMR data. Solid-state ^{13}C CP MAS, ^{15}N CP MAS and ^{29}Si MAS NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (7.0 T , $\nu_0(^1\text{H}) = 300.29\text{ MHz}$, $\nu_0(^{13}\text{C}) = 75.51\text{ MHz}$, $\nu_0(^{15}\text{N}) = 30.44\text{ MHz}$, $\nu_0(^{29}\text{Si}) = 59.66\text{ MHz}$) using a 7 mm Bruker probe spinning at 5 kHz. ^{13}C and ^{15}N CP MAS experiments were recorded with ramped-amplitude cross-polarization in the ^1H channel to transfer magnetization from ^1H to ^{13}C and ^{15}N . (Recycle delay $\geq 3\text{ s}$, CP contact time $\leq 1\text{ ms}$, optimized ^1H spin-164 decoupling). Single pulse ^{29}Si MAS NMR spectra were recorded with a recycle delay of 60 s. Chemical shift values were referenced to tetramethylsilane for ^{13}C and ^{29}Si and CH_3NO_2 for ^{15}N . Spectra were fitted with the DMFit program [40]. Chemical analyses of the polymers were performed using a combination of several methods at Mikroanalytisches Labor Pascher (Remagen, Germany). Thermogravimetric analyses (TGA) of samples were performed in flowing ammonia (50 mL min^{-1}) at $5\text{ }^\circ\text{C min}^{-1}$ to $1000\text{ }^\circ\text{C}$ using silica crucibles (Setaram TGA 92 16.18, SETARAM Instrumentation (Caluire, France)). The phase composition of ceramic samples was determined by XRD analysis (Bruker AXS D8 Discover, $\text{CuK}\alpha$ radiation, Billerica, Massachusetts, USA). The scans were performed in the range of $2\theta \in (20^\circ; 90^\circ)$ with a step of 0.015° and

an exposure time of 0.7 s. The diffractograms were analyzed using the Diffrac EVA software with the JCPDS-ICDD database. Crystallite sizes of ZrN crystals were calculated from the FWHM of the (111) diffraction lines using the Scherrer formula while their chemical composition was measured by considering the interlayer spacing d_{111} . Raman spectroscopy microanalysis was achieved between 100 and 1500 cm^{-1} (Raman LabRAM ARAMIS) using an excitation He/Ne laser wavelength of 633 nm. For Transmission electron Microscopy (TEM, TOPCON 002B working at 200 kV) study, as-prepared nanocomposite powders were crushed under n-butanol in an agate mortar and deposited the drops onto a holey carbon membrane supported by a copper grid. The Selected Area Electron diffraction (SAED) patterns and images were recorded, using a TECNAI 30G² microscope working at 300 kV. Optical characterization was carried out by using a UV-vis diffuse reflectance spectrophotometer (Perkin-Elmer UV/Visible spectrophotometer (lambda 35)) by recording the diffuse reflectance spectra of the nanocomposites then converted to absorbance by the Kubelka-Munk function in the wavelength range of 200 – 1100 nm .

3. Results and discussion

3.1. Nanocomposite precursor design

As described in the experimental section, the synthesis of the nanocomposite precursors consists in performing the reaction between polysilazanes as Si_3N_4 precursors and a low molecular weight compound (tetrakis(diethylamino)zirconium, TDEAZr) acting both as a ZrN precursor and a crosslinker at reflux of toluene (staying then three days). Zr-modified polysilazanes called polyzirconosilazanes, are thus generated. To understand and control the chemistry behind the precursor synthesis, we have synthesized two representative polyzirconosilazanes labelled PMZrSZ2.5 and PVMZrSZ2.5 (2.5 indicates the Si:Zr atomic ratio) from PMSZ and PVMSZ, respectively. Both propose a controlled Si:Zr molar ratio which is fixed at 2.5 according to the quantity of TDEAZr added to PMSZ and PMVSZ solutions at RT prior to thermolysis. The elemental analysis data of PMZrSZ2.5 $[\text{Si}_{1.0}\text{Zr}_{0.37}\text{C}_{3.1}\text{N}_{0.8}\text{H}_{9.7}]_n$, and PVMZrSZ2.5 $[\text{Si}_{1.0}\text{Zr}_{0.31}\text{C}_{3.7}\text{N}_{1.7}\text{H}_{10.3}\text{O}_{0.6}]_n$ samples prove that the precursor synthesis proceeded as planned; in particular for the PMZrSZ2.5 sample: the Si:Zr ratio measured by elemental analysis (2.7) is close to the one fixed during the synthesis (2.5). The non-negligible deviation between the Si:Zr ratio measured (3.3) and the one fixed (2.5) for PVMZrSZ2.5 indicates that the TDEAZr introduced during the polymer synthesis did not completely react with PVMSZ. Most probably, the steric hindrance imposed by vinyl groups in PVMSZ limits the reaction of the latter with TDEAZr in comparison to PMSZ, which does not exhibit organic groups with such a steric hindrance per monomeric units. This is confirmed by the use of perhydropolysilazane (PHPS, $[\text{SiH}_2\text{NH}]_n$) as a Si_3N_4 precursor: a Si:Zr ratio of 2.5 has been measured (*results not published*). Beside this, carbon and hydrogen content significantly increased (more limited for the nitrogen content) in PMZrSZ2.5 and PVMZrSZ2.5 compared to neat polysilazanes ($[\text{Si}_{1.0}\text{C}_{1.5}\text{N}_{1.1}\text{H}_{5.5}]_n$ for PVMSZ (Referenced to $\text{Si}_{1.0}$ and oxygen content - 0.4 wt% - was omitted in the empirical formulae)) suggesting the presence of side groups such as $-\text{N}(\text{R})_2$ ($\text{R} = \text{CH}_2\text{CH}_3$) units as in general shown with polysilazanes containing amino groups [39,41,42]. This could explain the extremely high sensitivity of these precursors to oxygen. In order to obtain a complete view of the precursor structure, the Zr-modified polysilazanes have been characterized by infrared and solid-state NMR spectroscopies.

The FTIR spectra of PMZrSZ2.5 and PVMZrSZ2.5 (See Fig. 1SI in ESI) display the characteristic absorption bands of neat PMSZ and PVMSZ, which share many features in common given their similar chemical structure: the stretching of N-H bonds at 3382 – 3388 cm^{-1} coupled to NH deformations at 1182 – 1184 cm^{-1} , the stretching of CH— bonds in CH_x groups at 2960 – 2968 and 2850 – 2871 cm^{-1} . The bands at 2112 – 2126 cm^{-1} and at 1256 cm^{-1} are attributed to stretching of Si-H bonds and deformations of SiC—H₃ units, respectively. Below ~ 1000

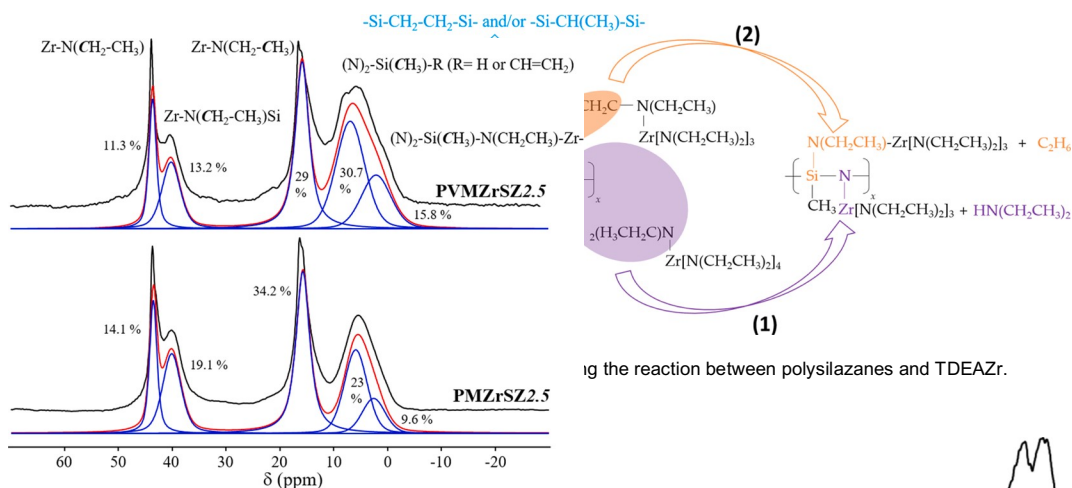


Fig. 3. Experimental and simulated ^{13}C CP MAS NMR spectra recorded for PMZrSZ2.5 and PVMZrSZ2.5.

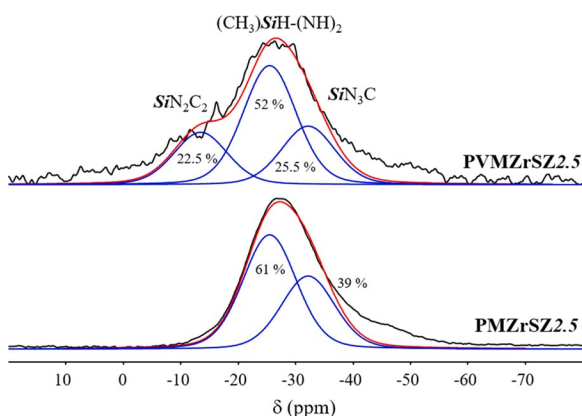


Fig. 4. (a) Experimental and simulated ^{29}Si MAS NMR spectra recorded for PMZrSZ2.5 and PVMZrSZ2.5.

cm^{-1} , absorption bands attributed to the stretching and deformation vibrations involving Si-C, Si-N, C-H, and C-C bonds, overlap and cannot be assigned unambiguously.

The main changes in both synthesized materials (PMZrSZ2.5 and PVMZrSZ2.5) occur in the intensity of the main reaction sites as highlighted in Fig. 2. Hence, the bands assigned to N-H and SiH bonds tend to shrink, with the band assigned to N-H bonds decreasing the most. Moreover, the bands assigned to the vibration of C-H bond in the vinyl groups present only in PVMZrSZ2.5 decrease in intensity in the FTIR spectrum of PVMZrSZ2.5, suggesting that polymerization of the vinyl groups (reaction (3) in Fig. 2) and/or the hydrosilylation reaction

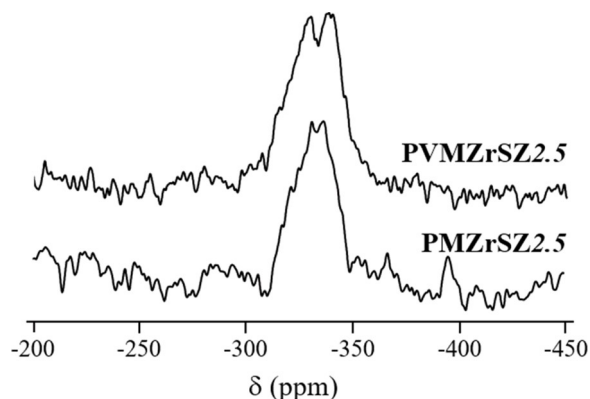


Fig. 5. Experimental ^{15}N CP MAS NMR spectra recorded for PMZrSZ2.5 and PVMZrSZ2.5.

between SiH and SiHC units, leading to the formation of carbasilane bonds (SiCCSi) reaction (4) in Fig. 2 occur during the reaction. Parallel to the aforementioned events, a set of broad bands in the range of $2670\text{--}2860\text{ cm}^{-1}$ appears for both samples: they are attributed to the vibration of C-H bonds from TDEAZr's ethyl groups. The N-C bonds in $\text{NC-H}_2\text{CH}_3$ groups are responsible for the weakly intense band at 1290 cm^{-1} . At around 1370 cm^{-1} , another set of bands that can be ascribed to C-H band deformation appears.

As expected, FTIR spectroscopy tends to corroborate the involvement of NH and SiH groups in polysilazanes during the reaction of the latter with TDEAZr through the occurrence of the mechanism already identified during the reaction between PMSZ and tetrakis(dimethylamino) titanium ($\text{Ti}[\text{N}(\text{CH}_3)_2]_4$) labelled TDMATi [14,23]:

- those involving -NH units in both polysilazanes and $\text{-N}(\text{CH}_2\text{CH}_3)_2$ groups in TDEAZr to form -N-Zr- bonds releasing ethylamine according to the reaction (1) in Fig. 2.
- those involving the silicon centers of polysilazanes and $\text{-N}(\text{CH}_2\text{CH}_3)_2$ groups in TDEAZr causing the consumption of Si-H groups while forming $\text{-Si-N}(\text{CH}_2\text{CH}_3)\text{-Zr-}$ bridges in the obtained precursor and the concomitant evolution of ethane according to the reaction (2) in Fig. 2.

To achieve an in-depth understanding of the local carbon, nitrogen and silicon environments in the polymer, we investigated ^{13}C , ^{29}Si and ^{15}N via solid-state NMR spectroscopy of both polymers (Figs. 3–5). The cross-polarization (CP) technique has been used for ^{13}C and ^{15}N NMR experiments to obtain spectra with reasonable acquisition times and signal-to-noise ratios. Deconvolution of signals has been done for ^{13}C and ^{29}Si spectra of the PVMZrSZ2.5 and PMZrSZ2.5 samples, allowing reaching the site fraction of the different environments. Note that Table 1 summarizes the main findings regarding the chemical

Table 1

Summary of the NMR spectroscopy data of the PVMZrSZ2.5 and PMZrSZ2.5 samples.

Nucleus	Assignment	δ (ppm)	Deconvoluted fraction (%)	
			PVMZrSZ2.5	PMZrSZ2.5
^{13}C	(N) ₂ -Si(CH ₃)-N(CH ₂ CH ₃)-Zr-	2	15.8	9.6
	(N) ₂ -Si(CH ₃)-R (R = H or CH = CH ₂)	5	30.7	23.0
^{29}Si	Zr-N(CH ₂ -CH ₃)	16	29.0	34.2
	Zr-N(CH ₂ -CH ₃)Si	39	13.2	19.1
	Zr-N(CH ₂ -CH ₃)	42	11.3	14.1
^{15}N	SiN ₂ C ₂	-13.5	22.5	—
	(CH ₃)SiH-(NH) ₂	-25.5	52.0	61.0
	SiN ₃ C	-32.5	25.5	39.0
^{15}N	HNSi ₂	-335	*	*
	N-CH ₂ CH ₃	-345	*	—

* Signal identified but not quantified.

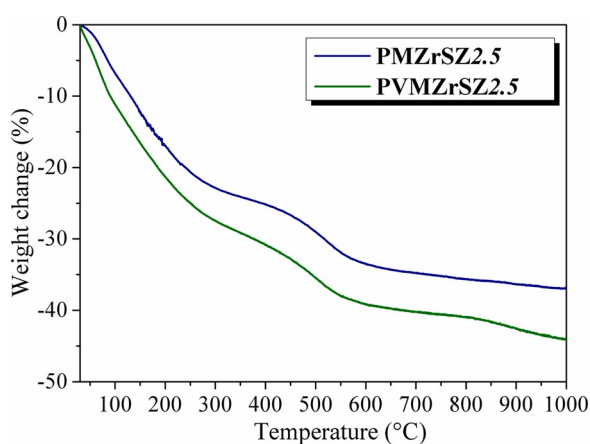
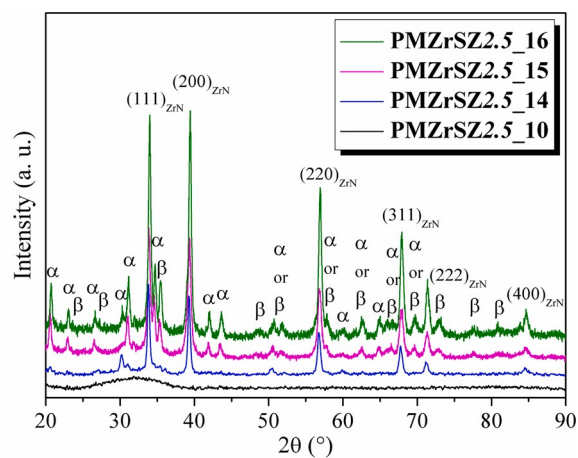


Fig. 6. TG curves recorded during decomposition of PMZrSZ2.5 and PVMZrSZ2.5 samples in flowing ammonia.

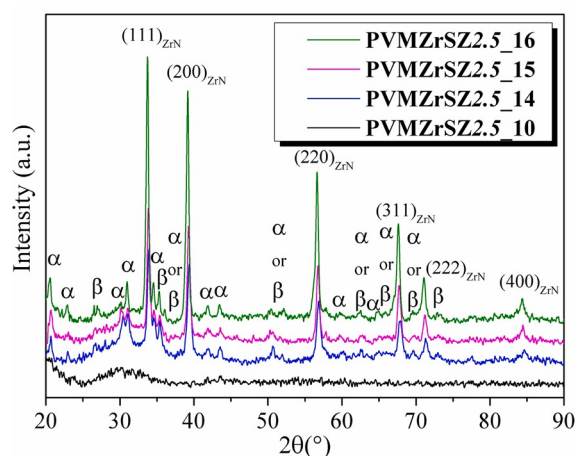
environments and the quantified deconvoluted signals (^{13}C and ^{29}Si) from the NMR analyzed samples.

The solid-state ^{13}C CP MAS NMR spectra (Fig. 3) exhibit four signals at around 5, 18, 39 and 42 ppm; the first one – very broad – being deconvoluted into two signals, one at 2 ppm and another one at 5 ppm.

^{13}C NMR signals around 0 ppm are generally assigned to carbon atoms of aliphatic groups bonded to a silicon atom, *i.e.* in this case SiCH₃ units as identified in PVMSZ (See Fig. 2SI in ESI) [38,39]. The presence of two signals can be due to the two types of SiCH₃ unit-containing environments shown in Fig. 2: SiCH₃ groups can be in SiCN₃ environments (*i.e.*, Si environment in the chain of the type ₂(RN)-Si(CH₃)-N(CH₂CH₃)-Zr- because of the reaction of -SiH units with TDEAZr, reaction (2), Fig. 2) and in SiCRN₂ environment (with R = H (*i.e.*, Si environment in the monomeric unit of the type Si(CH₃)(H)(NH)₂ in PMSZ and PVMSZ) or R = C (*i.e.*, Si environment in the monomeric unit of the type Si(CH₃)(CH₂CH₂)(NH)₂ of PVMSZ). Signals around 16 ppm can possibly be attributed to carbon atoms linked to another aliphatic carbon, in this case CH₃ environments of the N(CH₂CH₃) groups present in TDEAZr. The resonances at 39 and 42 ppm are assigned to carbon atoms linked to nitrogen; thereby N(CH₂CH₃) units in two types of environments [14,40]. Based on our previous report [23], resonances at 39 and 42 ppm are assigned to Zr-N(CH₂CH₃) units as side groups, *i.e.*, Si₂N-Zr-(N(CH₂CH₃)₂)_n units (1 ≤ n ≤ 3) and as bridges, *i.e.*, ₂(RN)-Si(CH₃)-N(CH₂CH₃)-Zr- units resulting from the reaction between SiH groups and TDEAZr, respectively. Consistently, the sum of both Zr-NCH₂- signals around 40 ppm is more or less equal to the Zr-N(CH₂CH₃) one around 16 ppm. At a given Si:Zr ratio (2.5), the relative proportion of the signal at 42 ppm compared to the one at 39 ppm is



(a)



(b)

Fig. 7. XRD patterns of ceramics derived from PMZrSZ2.5 (a) and PVMZrSZ2.5 (b) samples prepared in flowing ammonia (up to 1000 °C) then in flowing nitrogen (1400-1600 °C).

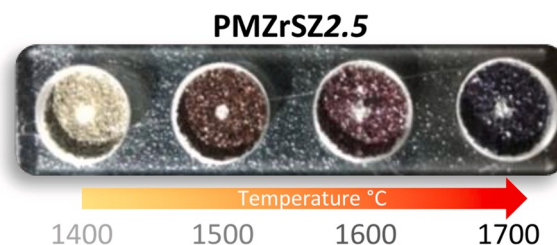
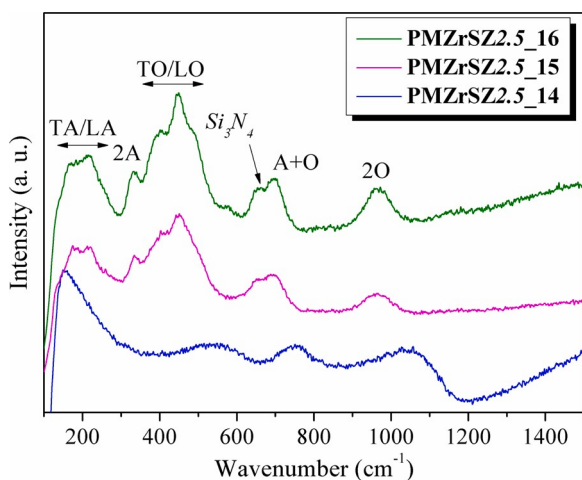
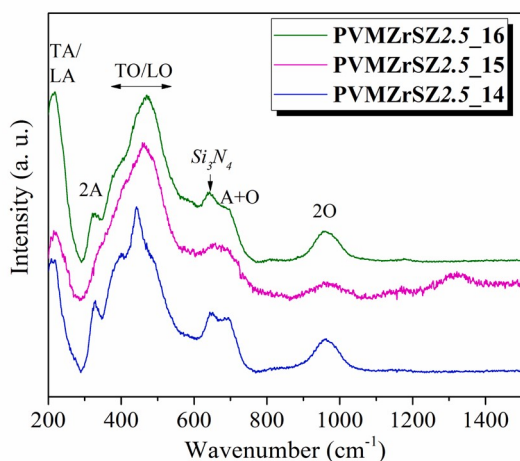


Fig. 8. PMZrSZ2.5_14, PMZrSZ2.5_15, PMZrSZ2.5_16, and PMZrSZ2.5_17 samples from left to right.

higher in PVMZrSZ2.5 (0.856) in contrast to PMZrSZ2.5 (0.738). This means that the reaction involving Si-H bonds is more efficient in the latter which is related to the fact that vinyl groups - imposing a certain steric hindrance in PVMSZ - are absent in the monomeric unit of PMSZ. Indeed, the ^{13}C signals at 124 and 138 ppm (See Fig. 3SI in ESI) in the PVMZrSZ2.5 spectrum assigned to vinyl groups are already present in PVMSZ (See Fig. 3SI in ESI). Residual vinyl groups - which have been identified by FTIR in the sample - can provide a source of latent reactivity during the further thermo-chemical conversion of the PVMZrSZ2.5 sample (*See later*). To complete our investigation, the experimental solid-state ^{29}Si MAS NMR spectra of PMZrSZ2.5 and PVMZrSZ2.5 have



(a)



(b)

Fig. 9. Raman spectra of ceramics derived from PMZrSZ2.5 (a) and PVMZrSZ2.5 (b) samples prepared in flowing ammonia (up to 1000 °C) then in flowing nitrogen (1400–1600 °C).

been recorded at 7 T (Fig. 4).

In both samples, the ^{29}Si MAS spectra exhibit a main broad resonance centered at around -28 ppm that can be simulated with two or three components for PMZrSZ2.5 and PVMZrSZ2.5 respectively. The main signal at -25.5 ppm (is consistent with previously published results and attributed to silicon atoms in a SiHCN_2 , i.e., $(\text{CH}_3)\text{SiH}(\text{NH})_2$, environment [41–43]. The second signal at -32.5 ppm could correspond to SiN_3C , i.e., $2(\text{RN})\text{-Si}(\text{CH}_3)\text{-N}(\text{CH}_2\text{CH}_3)\text{-Zr}$, environments highlighting reactions between Si-H units and $\text{N}(\text{CH}_2\text{CH}_3)_2$ groups (reaction (2), Fig. 2). For PVMZrSZ2.5, an additional signal is observed at -13.5 ppm, which can be assigned to SiN_2C_2 units. This chemical shift indicates that this sample is preferentially composed of six- and eight-membered Si-N rings [44]. The small signal present in both samples around -48 ppm can be attributed to Si_3N_4 groups [45], confirming the occurrence of a reaction between Si-H units and $\text{N}(\text{CH}_2\text{CH}_3)_2$ groups. The solid-state ^{15}N CP MAS NMR spectra (Fig. 5) of the same polymers display a very broad signal centered at 335 ppm, implying the presence of HN-Si environments in the silazane backbone in both samples [19, 46]. Moreover,

more resolution is observed in the PVMZrSZ2.5 spectrum, indicating the presence of a second contribution around -345 ppm that would correspond to $\text{N}(\text{CH}_2\text{CH}_3)$ environment.

The combination of multinuclear solid-state NMR data with the results derived from elemental analyses and FTIR allows for a comprehensive understanding of the chemistry behind the reaction between PMSZ/PVMSZ and TDEAZr. Two reactions depicted in Fig. 2 and involving TDEAZr occur during the synthesis of PMZrSZ2.5 and PVMZrSZ2.5. Zr atoms are homogeneously distributed within the PMSZ/PVMSZ structures as bridges i.e. those involving $-(\text{Si-N})_n\text{-Zr}$ units, which are built by the reaction between $-\text{N}(\text{CH}_2\text{CH}_3)_2$ from TDEAZr and $-\text{NH}$ groups from PMSZ/PVMSZ; and those involving $\text{N}_2\text{Si}(\text{CH}_3)\text{-N}(\text{CH}_2\text{CH}_3)\text{-Zr}$ units, which arise due to the reaction between $-\text{SiH}$ (from PMSZ/PVMSZ) and $-\text{N}(\text{CH}_2\text{CH}_3)_2$ (from TDEAZr) moieties. The latter seems to be particularly active in the studied polymeric systems. As-formed units should allow building the polymer network of the samples and increase the degree of cross-linking of the polymeric backbone, which is a pre-requisite to limit the weight loss occurring during the further polymer-to-ceramic conversion. It should be pointed out that a third mechanism – involving TDEAZr not as a reagent but as a catalyst – occurred the hydrosilylation of vinyl groups of PVMSZ. Thus, once these precursors have been synthesized, the subsequent thermo-chemical conversion up to 1000 °C will occur in ammonia to deliver single-phase amorphous ceramics labelled as PMZrSZ2.5_10 and PVMZrSZ2.5_10 samples.

3.2. Ceramic conversion

The conversion of PMZrSZ2.5 and PVMZrSZ2.5 into their single-phase amorphous ceramic derivatives (i.e., PMZrSZ2.5_10 and PVMZrSZ2.5_10 samples) has been monitored by thermogravimetric analysis (TGA) as shown in Fig. 6.

The TG curves of the PMZrSZ2.5 and PVMZrSZ2.5 samples display a marked three-step weight loss in the temperature range 30–1000 °C. The first weight loss from 30 to 250 °C; a second one from 250 to 600 °C; and the third weight loss from 600 to 1000 °C. Whereas PMZrSZ2.5 is decomposed with a weight loss much lower than that measured for PMSZ in the same conditions (85.25 % of weight loss at 1000 °C), the PVMZrSZ2.5 sample undergoes a weight loss measured at 1000 °C higher than that measured for PMSZ (32.8 % of weight loss at 1000 °C) in flowing ammonia.

In both systems, the degree of crosslinking of the polymers after modification with Zr is higher than in neat polysilazanes according to the identified formation of bridged bonds such as direct bonds $-\text{N-Zr}$ (reaction (1) in Fig. 2) and $-\text{Si-N}(\text{CH}_3)\text{-Zr}$ (reaction (2) in Fig. 2). Such units are expected to reduce the segment mobility of PMSZ and PVMSZ hindering depolymerization reactions in the polysilazane network in the low temperature regime of the polymer-to-ceramic conversion; thereby, reducing the weight loss at low temperature. This clearly happens with PMZrSZ2.5. However, a high cross-linking is not the only prerequisite for a high yield polymer-to-ceramic conversion of preceramic polymer. Another important issue is a sufficient latent reactivity of the precursors, i.e., the ability to undergo cross-linking reactions during the heat treatment. This is particularly the case when $-\text{Si-H}$, $-\text{N-H}$ and vinyl groups are present in the polymer structure like in PVMSZ, which lead to dehydrocoupling and hydrosilylation reactions [47, 48]. Because they reacted with TDEAZr during the polymer synthesis, the availability of such units is significantly reduced in the PVMZrSZ2.5 sample compared to PVMSZ. Furthermore, the highest weight loss recorded for PVMZrSZ2.5 is most probably a consequence of the presence of $-\text{N}(\text{CH}_2\text{CH}_3)_2$ as side groups in its structure. Such groups are unable to undergo cross-linking reactions and are decomposed during the polymer-to-ceramic conversion. Thus, PVMZrSZ2.5 exhibits a more pronounced weight loss than PVMSZ because $-\text{N}[(\text{CH}_2\text{CH}_3)_x]_y$ units ($x = 1$ or 2 and $y = 1 \rightarrow 3$) are highly reactive with ammonia to release amines

as gaseous by-products via transamination reactions.

After the thermo-chemical conversion of the precursors at 1000 °C

(dwelling time of 2 h) in flowing ammonia, the XRD patterns of the PMZrSZ2.5_10 and PVMZrSZ2.5_10 samples reveal that these ‘SiZrN’

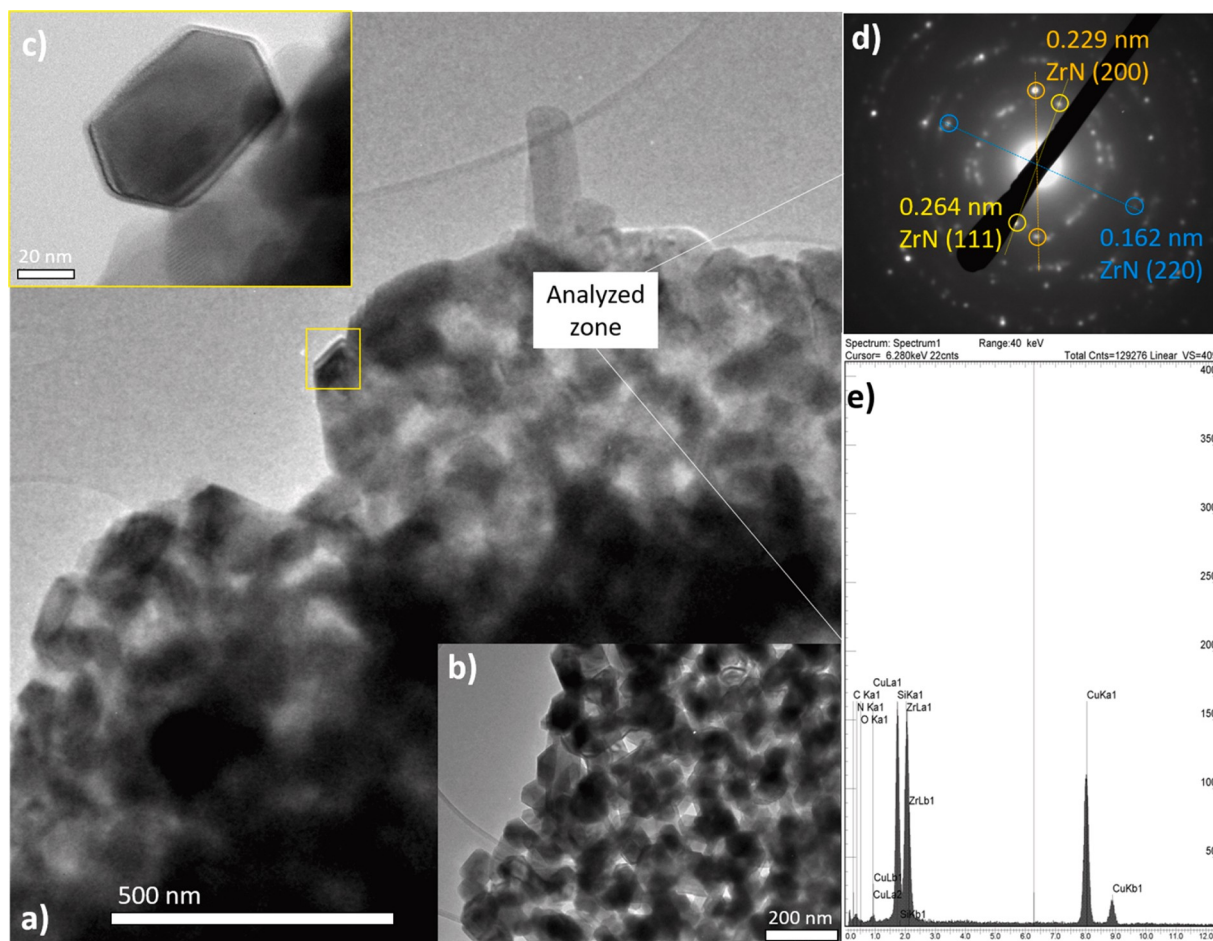


Fig. 10. (a,b) Low magnification TEM image of the surface of the PMZrSZ2.5_16 sample, c) TEM image of a ZrN nanocrystal, d) Selected area electron diffraction pattern and e) EDS map of the analyzed zone.

ceramics are amorphous as indicated by the diffuse XRD peaks composing the patterns (black lines in Fig. 7). Thus, higher temperatures have been applied to generate the title materials.

3.3. High-Temperature phase and microstructure evolution

The amorphous PMZrSZ2.5_10 and PVMZrSZ2.5_10 samples have been annealed at 1400 °C, 1500 °C, and 1600 °C for 2 h in nitrogen atmosphere in order to explore their high-temperature behaviour with respect to crystallization, phase separation and microstructure evolution.

Fig. 8 shows the changes in the colour of the samples produced from PMZrSZ2.5: PMZrSZ2.5_14, PMZrSZ2.5_15, PMZrSZ2.5_16. Note that the PMZrSZ2.5_17 sample is also presented although not being investigated in the following section.

The change in the color of the sample directly reflects the crystallization evolution of the samples derived from PMZrSZ2.5. Fig. 7 shows the XRD pattern evolution for ceramics derived from PMZrSZ2.5 (a) and PVMZrSZ2.5 (b) samples. Samples already crystallize after annealing at 1400 °C (PMZrSZ2.5_14 and PVMZrSZ2.5_14). Main sharp peaks corresponding to nanocrystalline phases appear at 33.8 °, 39.3 °, 56.75 °, 67.75 °, 71.15 ° and 84.5 °. The peaks matched with the rock salt ZrN phase (ICDD PDF number: 04-004-2860) in the cubic Fm-3 m space group. The crystallite sizes calculated at the dominant (111) peak were found to be 22.2 nm (PMZrSZ2.5_14) and 18.8 nm (PVMZrSZ2.5_14).

Annealing treatment also induces nucleation of α (ICDD PDF number: 04-005-5074) and β (ICDD PDF number: 04-033-1160) -Si₃N₄ in the PVMZrSZ2.5_14 sample, whereas there is only a very small contribution

from crystalline silicon nitride in PMZrSZ2.5_14. Based on the Si-Ti-N systems that demonstrated a strong effect of the Ti content of the polymers on the crystallinity extent of the derived Si₃N₄ matrix [14], nucleation of Si₃N₄ already occurred at 1400 °C in the samples derived from PVMSZ, most probably because of the lowest Zr content in the material. After heat-treatment at 1500 °C, the XRD patterns show similar ZrN XRD peaks (in terms of FWHM and intensity) and the ZrN phase seems to be not affected by the increase of the annealing temperature. The ZrN crystallite calculated at the dominant (111) peak was found to be 22.2 nm (PMZrSZ2.5_15) and 20.8 nm (PVMZrSZ2.5_15); values close to those calculated for the samples prepared at 1400 °C. The continuous increase of the annealing temperature confirms the extended crystallization of the different constitutive phases as shown through the sharper and more intense ZrN peaks along with XRD peaks of α - and β -Si₃N₄ in the XRD patterns of samples annealed at 1600 °C (PMZrSZ2.5_16, ZrN crystallite size = 25.2 nm and PVMZrSZ2.5_16, ZrN crystallite size = 23.1 nm). It should be pointed out that the diffraction patterns in Fig. 7 do not indicate sample oxidation, which is generally evidenced by the broad shoulders of the ZrN (111) and (220) peaks [19]. For a better understanding of the structure and phase evolutions during annealing, the samples have been investigated by Raman spectroscopy (Fig. 9).

As illustrated in Fig. 9, the Raman spectra of the samples are characteristic of the face-centered cubic (fcc) ZrN phase through the presence of the low frequency (below 380 cm⁻¹; acoustic phonons) peaks - having the tendency to red-shift to higher frequency from 1400 to 1500 °C that could attest the improved crystallinity of the materials as well as the creation of N vacancies [49] in the nanocomposites - and high frequency (above 380 cm⁻¹; optical phonons) mode [50]. Interestingly,

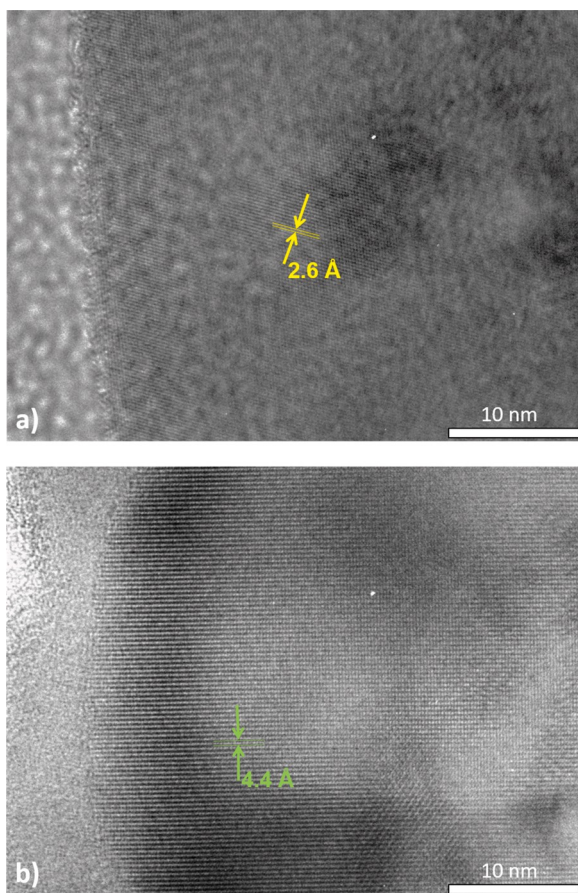
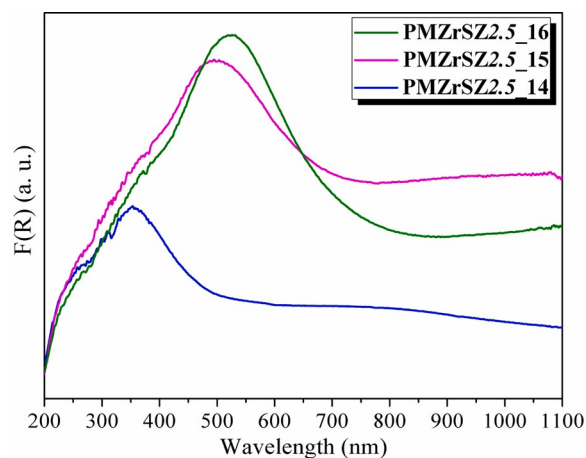


Fig. 11. HRTEM images of the PMZrSZ2.5_16 sample representing the fringe network of the ZrN (a) and α -Si₃N₄ (b) structures.

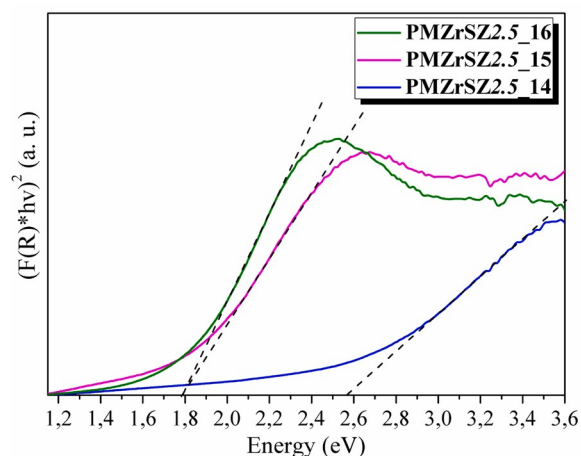
there are one peak in the region 300–410 cm^{-1} between the acoustic and optic modes that tends to increase in intensity with the increase of the temperature of pyrolysis. It represents a low-frequency second-order acoustic mode (2A) and it is an indication of ZrN with less stoichiometric defects [51]. It should be mentioned that the Raman peak at 660 cm^{-1} - attributed to Si₃N₄ [52] and present in all spectra of the samples derived from PVMSZ, and in PMZrSZ2.5_15 and PMZrSZ2.5_16 samples - indicated that the Si₃N₄ crystallization occurred in such samples as observed in the XRD patterns.

The Raman spectrum of the PMZrSZ2.5_14 sample is quite different from other spectra. In particular, the bands in the high frequency mode above 380 cm^{-1} are shifted to higher frequencies most probably because of the poor crystallinity of the Si₃N₄ phase. The corresponding Raman peak is absent in the PMZrSZ2.5_14 sample, indicating that a crystallization of the Si₃N₄ matrix in all samples derived from PVMSZ, as well as in the PMZrSZ2.5_15 and PMZrSZ2.5_16 samples, most likely imposes a constraint state which affects the band positions of the ZrN phase in the Raman spectra. Therefore, based on the combination of XRD and Raman spectroscopy, we can conclude that the structure of ZrN/Si₃N₄ nanocomposites can be finely tailored through the chemistry of precursors from nanoscaled ZrN crystals distributed in an amorphous Si₃N₄ (PMZrSZ2.5_14 sample) to nanoscaled ZrN crystals distributed in a highly crystallized Si₃N₄ matrix (PMZrSZ2.5_16 and PMZrSZ2.5_16 samples).

In order to assess the micro-/nanostructure of the latter, the PMZrSZ2.5_16 sample was further studied by means of HRTEM (Fig. 10a–d), in which the size population range of ZrN nanocrystals has been measured. The TEM micrographs (Fig. 10a and b) are consistent with the XRD data of the same sample: they indicate the formation of a highly crystallized material. The TEM micrograph, in Fig. 10c shows



(a)



(b)

Fig. 12. (a) Plot of $F(R)$ obtained from UV-vis diffused reflectance versus wavelength and (b) $(F(R) \cdot h\nu)^2$ function versus photon energy ($h\nu$) for PMZrSZ2.5_14, PMZrSZ2.5_15 and PMZrSZ2.5_16.

that the crystalline ZrN nanoparticles display a generally hexagonal shape which renders the generation of a particle size distribution highly complex from a series of low-magnification TEM images. The latter demonstrated that the particle size remains distributed over a relatively large range of diameter (See Fig. 4S1 in ESI). The corresponding SAED pattern (Fig. 10d) and the EDS image (Fig. 10e) generated from the highlighted region align with standards for the lattice spacing of the ZrN (111), (200) and (220) planes, and confirm the presence of Zr and Si.

At higher magnification (Fig. 11), the HRTEM images show fringe spacing of 0.26 and 0.44 nm, corresponding to the d-spacing of the lattice plane of the ZrN and α -Si₃N₄ structures.

3.4. Optical properties of nanocomposites

The optical property is studied thoroughly due to the variable range of possible applications such as in LEDs, lasers, solar cells, photocatalysts, etc. One of the most important parameters for determining the applicability of the title nanocomposites is their optical band gap (E_g), which means the minimum energy of light to be incident for the material to absorb the light and produce an electron - hole pair [53].

As a preliminary investigation, UV-vis spectroscopy was employed to examine the tuning of the ZrN/Si₃N₄ nanocomposite optical band gap.

Fig. 12 shows the optical properties of the samples derived from PMZrSZ2.5:PMZrSZ2.5_14, PMZrSZ2.5_15, and PMZrSZ2.5_16 over the UV–vis range (200–1100 nm).

Fig. 12a plots the Kubelka-Munk function $F(R)$ [54] versus wavelength calculated from the recorded diffused reflectance spectra. The latter are characterized by a deep maximum of absorption in the UV (PMZrSZ2.5_14, 352 nm) and visible (PMZrSZ2.5_15 and PMZrSZ2.5_16, 498 and 524 nm, respectively) domains. Interestingly, Fig. 12a reveals the opportunities of tuning the optical properties as the annealing temperature increases, the position of the maximum of absorption increases and shifts towards higher wavelengths in line with the crystallization of the samples. The Kubelka-Munk method promotes the transformation of the measured diffuse reflectance and the extraction of the band gap (E_g) values with best accuracy [54,55]. After the Kubelka-Munk treatment shown in Fig. 12b, E_g value can be determined by extrapolating the linear least squares fit of $(F(R)hv)^2$ to zero, in a “ $(F(R)hv)^2$ versus E ” plot. Thus, by this method, the assignment of the optical band gap can be made (Fig. 12b) and we observed a decrease of the E_g values from 2.58 eV for PMZrSZ2.5_14 to 1.7 eV for PMZrSZ2.5_15 and PMZrSZ2.5_16. If we consider the PMZrSZ2.5_17 sample (samples annealed at 1700 °C), the band gap continues to decrease until reaches a value of 1.52 eV (See Fig. 5SI in ESI), unveiling the more conducting character of the latter. The calculated values are much lower than those found for bulk silicon nitride (5.0 eV) [56] and zirconium nitride (2.84–4.75 eV depending on the reactive gas) [57]. Thus, the crystallization of the different phases composing the nanocomposites, as well as their likelihood towards polymorphism (α - or β -Si₃N₄) and the increase in ZrN crystal size gives the annealing temperature a strong effect on the optical bandgap of the nanocomposites. This is especially compelling since it shows the possibility to tune the onset of the reflectance to the desired UV–vis wavelength. The reduced band gap of ZrN/Si₃N₄ nanocomposite prepared in the high temperature range (1600–1700 °C) is expected to improve their photocatalytic activities due the increase of their absorbance range from UV to visible in solar spectrum. Further works devoted to the photocatalytic activity of those materials are under investigation and will be published separately.

4. Conclusion

To summarize, we reported the synthesis of zirconium-modified polysilazanes by chemically modifying two polysilazanes, a polymethylsilazane (PMSZ) and a poly(vinylmethyl-co-methyl)silazane (PVMSZ), using tetrakis-(diethylamino)zirconium Zr[N(CH₂CH₃)₂]₄ with an atomic Si:Zr ratio of 2.5. The role of the chemistry behind the synthesis of these polymers was discussed based on complementary characterization tools, such as FTIR, solid-state NMR spectroscopy and elemental analyses. It corroborated our finding on Ti-modified polysilazanes: reactions mainly involved N–H and SiH– bonds in polysilazanes and N(CH₂CH₃)-based groups in Zr[N(CH₂CH₃)₂]₄ with a stronger contribution of Si–H bonds during the polymer synthesis and an important role of steric hindrance imposed by the vinyl groups in PVMSZ. Polymerization and/or hydrosilylation of vinyl groups present in PVMSZ could also occur during the synthesis of the polymers. Thus, the incorporation of Zr increased the crosslinking degree of the polysilazanes and introduced side groups that affected the weight change during the polymer-to-ceramic conversion under ammonia at 1000 °C, generating materials that were predominantly amorphous. Subsequent pyrolysis in the temperature range 1400–1600 °C under nitrogen allowed the precipitation of zirconium nitride nanocrystals embedded in a Si₃N₄ matrix. The crystallization (α - and β -Si₃N₄) of the latter closely depends on the Zr content of the considered polymers. HRTEM investigations highlighted the distribution of hexagonal faceted ZrN nanocrystals in the α - and β -Si₃N₄ matrix after heat-treatment at 1600 °C. The unique nano- and microstructural feature allowed tuning the ZrN/Si₃N₄ nanocomposite optical band gap as an interesting mean to explore the photocatalytic properties of these materials.

Data availability

Raw data and other supplementary material are available at the following repository: osf.io/7zpcj.

No data was used for the research described in the article.

Data will be made available on request.

No data was used for the research described in the article.

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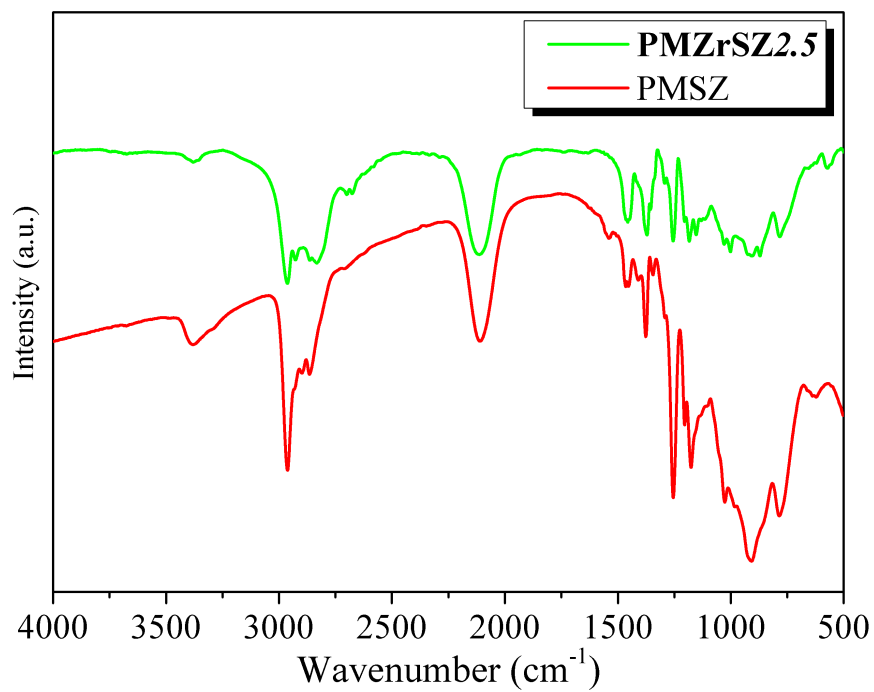
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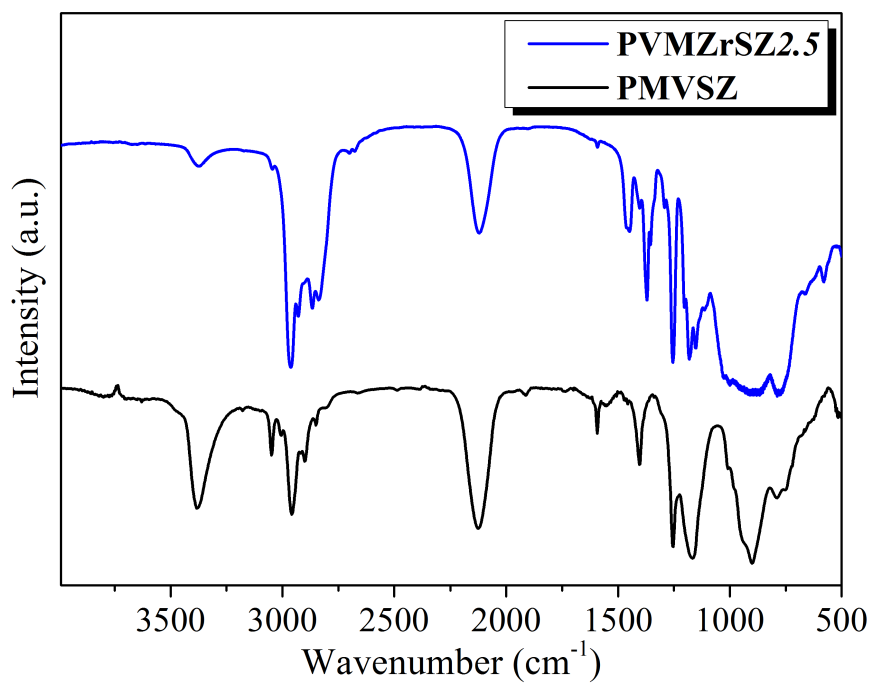
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ESI



(a)



(b)

Fig. 1SI. FTIR spectra of (a) PMSZ and the derived **PMZrSZ2.5** and (b) PMSZ and the derived **PMVZrSZ2.5**.

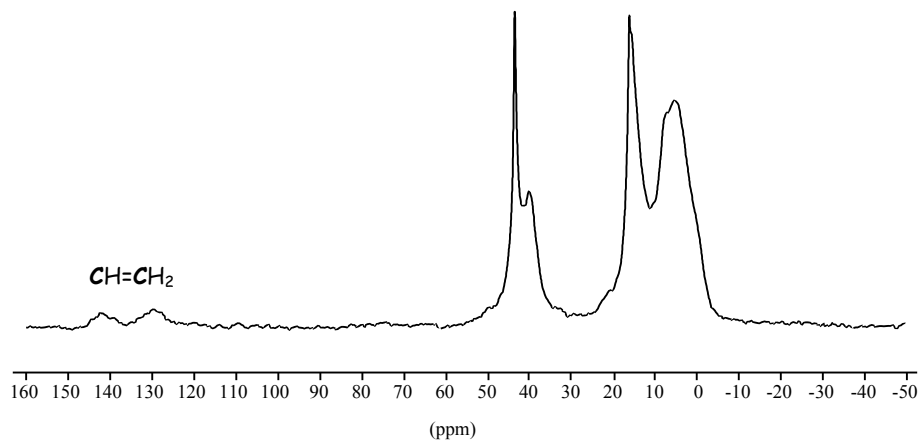


Fig. 2SI. Experimental ^{13}C CP MAS NMR recorded for the **PVMZrSZ2.5** sample from -50 to 160 ppm.

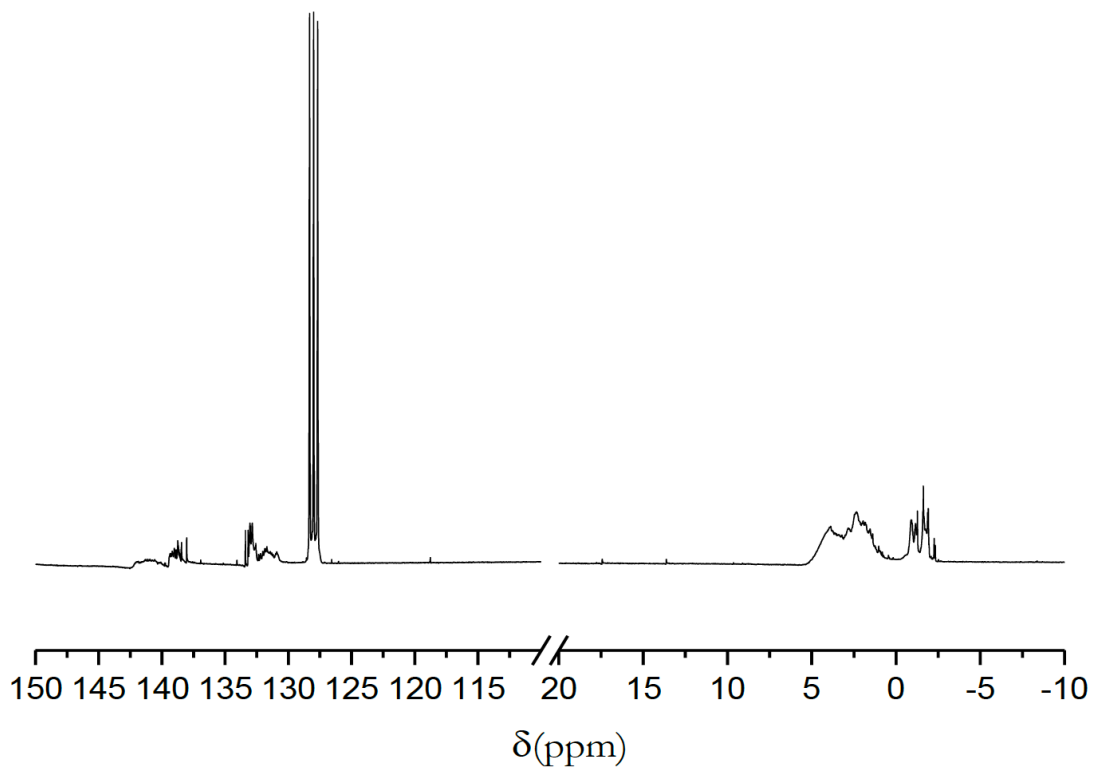


Fig. 3SI. Liquid-state ^{13}C NMR spectrum of PVMSZ.

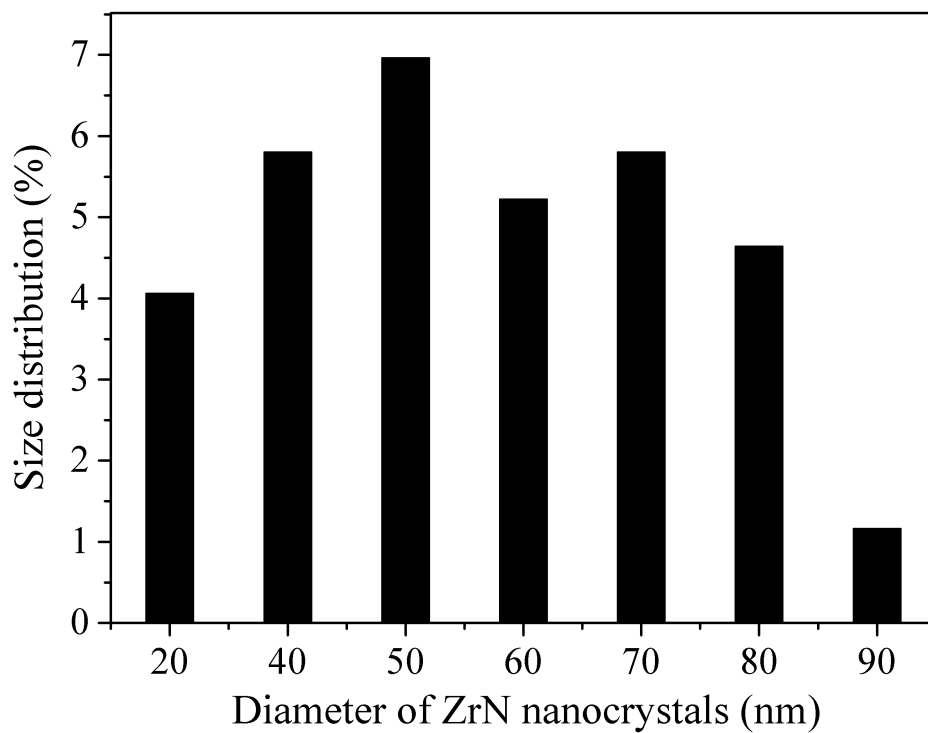


Fig. 4SI. Size distribution of ZrN nanocrystals calculated based on 62 measurements.

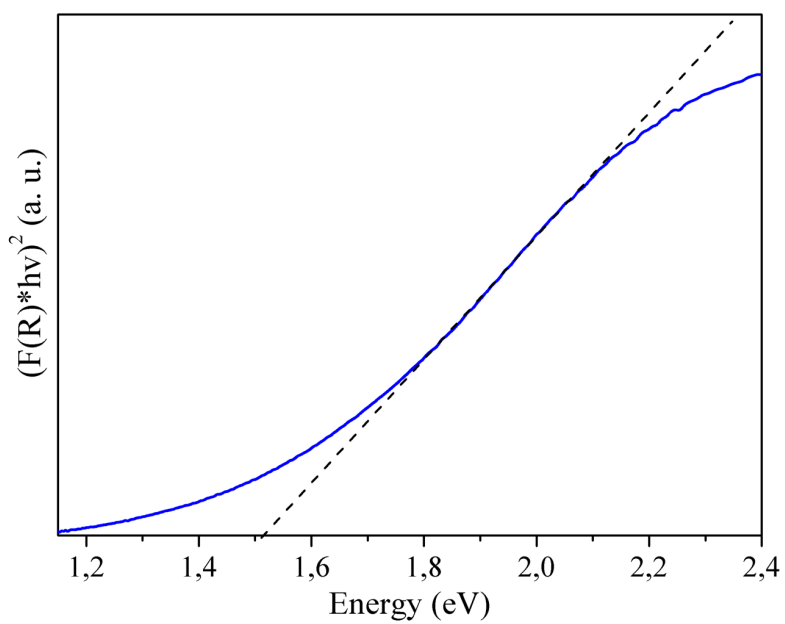


Fig. 5SI. $(F(R) \cdot h\nu)^2$ function versus photon energy ($h\nu$) for **PMZrSZ2.5_17**.