

Short communication

Synthesis and structural evolution of partially and fully stabilized ZrO₂ from a versatile method aided by microwave power

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ABSTRACT

We propose a simple, fast, and economical method to obtain ZrO₂ powders aided by microwave heating. Partially stabilized zirconia (tetragonal + monoclinic) undergoes transition to fully stabilized zirconia in the tetragonal phase as Gd³⁺ ions are incorporated (0.5–5 mol%) into the zirconium precursor solution and posteriorly annealed at 300, 500 and 700 °C for 15 min in an adapted household microwave oven. XRD, Rietveld refinement and Raman scattering results confirm that structural evolution of zirconia occurs due to the presence structural ordering at both long- and short-range, whose fully stabilization, and hence, the higher structural order-disorder degree, was kept only for doping content at 5% of Gd³⁺ by the elimination of secondary phase (monoclinic). TEM/HRTEM/SAED results revealed that partially and fully stabilized ZrO₂ are polycrystalline materials composed by an agglomerate of nanoparticles formed due to the fast microwave heating.

1. Introduction

The ZrO₂ polymorphism is a limiting factor for many its technological applications, mainly, at high temperatures [1–5]. Tetragonal zirconia under elevated temperatures tends to exhibit a large volume change (3–5%) along cooling process to the monoclinic phase around to 970 °C [1,4]. Therefore, one of the major challenges in the use of ZrO₂ lies in the difficulty in to obtain a stable crystalline structure, *i.e.*, fully stabilized zirconia (FSZ) [1], mainly, in the tetragonal and cubic phases which are more valuable for technological applications [6–15]. However, zirconia stabilized can be obtained by the incorporation of stabilizing agents such as divalent cations (Mg²⁺ [16], Ca²⁺ [17]) and/or trivalent rare earth cations (Y³⁺ [12,18,19], Gd³⁺ [20–22], Eu³⁺ [9,23,24], Er³⁺ [8,25] and Tb³⁺ [26,27]). Huang and co-workers [20] reported that addition of Gd³⁺ ions (5–40% mol) reduces the needed reaction temperature or duration for the formation of the ZrO₂ nanocrystals as well as the phase selective effect for the formation of cubic ZrO₂. Ilanchezhian et al. [22] verified that insertion of 3–5 wt % Gd³⁺ besides to promote the structural stabilization, promoted a blue shift effect in the absorption edge of ZrO₂ and an improvement of the dielectric properties of ZrO₂ complexes. Tamrakar and Upadhyay [28] observed that for range doping 0.5–3 mol% of Gd³⁺, only cubic ZrO₂ was obtained and the optical performance exhibited an intense UV emission up to 2.5% of Gd³⁺, whereas the red emission decreases with increasing Gd³⁺ concentration. Stabilized zirconia can be obtained by

several methods such as sol-gel [29–33], spray pyrolysis [34], co-precipitation [22,35], hydrothermal/solvothermal [8,20,36], electrochemical deposition [37] and combustion [23,26,38]. Nevertheless, most of these methods shows disadvantages related to the employed of high reaction temperatures, expensive processing techniques and long reaction times. Therefore, the main goal of present work was to find a simple and versatile method for preparing partially stabilized zirconia (pristine ZrO₂) and fully stabilized zirconia (gadolinium-doped ZrO₂) from a combination of the sol-gel process and post annealing, both performed by microwave power.

2. Experimental

Pristine and Gd-doped ZrO₂ were obtained by a two-step synthetic route, both assisted by microwave heating systems using adapted household microwave ovens (Fig. 1). Thereby, in the first microwave heating system (see Fig. 1a), the zirconium (ZrO(NO₃)₂.xH₂O - 99%, Aldrich) and gadolinium (Gd(NO₃)₃.6H₂O - 99%, Aldrich) precursors solutions (sol) were placed into sealed autoclave (Teflon® cup and a manometer). After turning on the microwave power, microwave irradiation cross in Teflon® cup, once this one not absorbing it, increasing the thermal/kinetics effects of the reaction medium to expedite the sol-gel transition (gelation). In the second microwave heating system (see Fig. 1(b)), the xerogels were placed on the alumina crucible and covered by a SiC crucible, which absorber the microwave irradiation for

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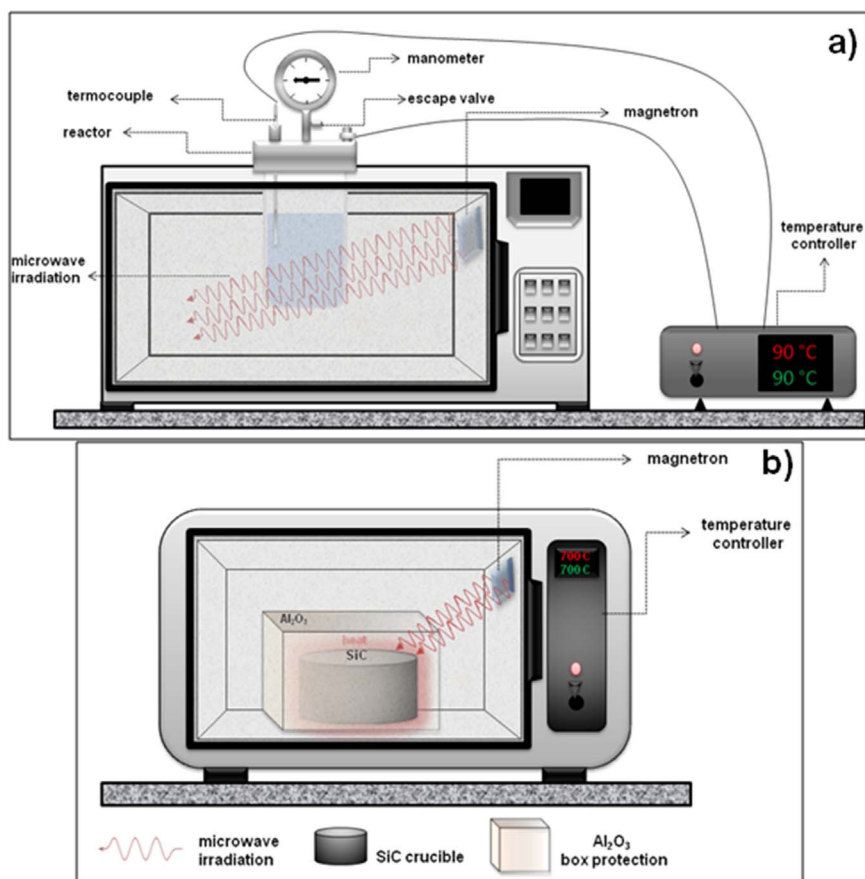


Fig. 1. Microwave heating system employed to expedite the sol-gel transition (a). Microwave heating system performed to promote the crystallization of the ZrO_2 samples (b).

transformed it in heat to promote the crystallization stage. A box protection of Al_2O_3 was placed over SiC crucible to avoid superheating. A thermocouple, not shown in the Fig. 1b, is in contact with alumina crucible to monitor the sample temperature. Details of the procedure to obtaining of the pristine ZrO_2 and Gd-doped ZrO_2 samples and the characterization techniques can be verified on the [Supplementary Material](#).

3. Results and discussion

Fig. 2 shows the Raman spectra of the pristine and Gd-doped ZrO_2 processed at 300, 500 and 700 °C and of the material untreated thermally. As can be observed in Fig. 2(a), the pristine ZrO_2 sample without microwave annealing (as-prepared ZrO_2) no exhibits a typical Raman spectrum for a crystalline ZrO_2 , i.e., is an amorphous ZrO_2 . However, in Fig. 2(a), the ZrO_2 samples subjected to the microwave annealing at 300 °C, 500 °C and 700 °C, display Raman spectra with vibrational modes characteristic of the ZrO_2 crystalline. The ZrO_2 sample processed at 300 °C (Fig. 2(a)) presented weak peaks indicating very low degree of crystallinity at short-range. All vibrational modes observed in the Raman spectra (Fig. 2(a-d)) are localized at 147, 178, 190, 267, 223, 317, 333, 346, 381, 475, 502, 539, 562, 618 and 647 cm^{-1} . According to group theory [39,40], the Raman-active modes localized at 147 (E_g), 267 (E_g), 317 (B_{1g}), 475 (B_{1g}) and 647 cm^{-1} (A_{1g}) are associated to the tetragonal phase, while the presence of the monoclinic phase is assigned to Raman-active modes located at 178 cm^{-1} ($A_g + B_g$), 190 (B_g), 223 (A_g), 333 (A_g), 346 (B_g), 381 (B_g), 475 (B_g), 539 (B_g), 502 (A_g), 539 (B_g), 562 (B_g) and 618 (A_g) cm^{-1} [41,42]. The increasing of dopant concentration into the ZrO_2 lattice tends to enhance the structural stabilization, at short-range, in the tetragonal phase (see Fig. 2(c)–(d)). However, with doping concentration of 2.5 mol%, a very weak shoulder close to the band localized at 600 cm^{-1} was detected

which is assigned to the monoclinic phase (Fig. 2(c)). Thereby, it is not clear, only with Raman results, that ZrO_2 with 2.5 mol% of Gd^{3+} is a fully stabilized zirconia, at short-range, in tetragonal phase. On the other hand, for 5 mol% of Gd^{3+} only the Raman-active modes assigned to the tetragonal phase are observed (see Fig. 2(d)).

From the analysis of the structural ordering at long-range, the XRD pattern (Fig. 3) revealed that when the xerogel is not processed by microwave heating (Fig. 1b), the ZrO_2 structure exhibits high structural disorder at long-range, compatible to XRD pattern of amorphous ZrO_2 , in good according Raman result (Fig. 2a). However, when the xerogels are annealing through microwave heating (Fig. 1b), the Rietveld refinement (TOPAS Academic v. 5.0 [43]) data (Table 1) and the XRD patterns (Fig. 4) shown that crystalline ZrO_2 were obtained. The reliability factors, R_{wp} and Gof (goodness-of-fit), shown in Table 1, confirm the good refinement quality [44]. The incorporation of Gd^{3+} ions into the ZrO_2 lattice caused a decreasing in the diffraction intensities, so that the degree of crystallinity of the Gd-doped ZrO_2 is lower than pristine ZrO_2 . Despite the microwave annealing to promote the crystallization of the ZrO_2 xerogels, the pristine ZrO_2 (Fig. 4a-c) and Gd-doped ZrO_2 with 0.5 mol% of Gd^{3+} (Fig. 4d) exhibited two crystallographic structures assigned to the tetragonal (ICSD#85322) and monoclinic (ICSD#18190) phases, independent of the processing temperature (see Table 1), i.e., partially stabilized zirconia, at long-range, were obtained. On the other hand, the fully stabilized zirconia, at long-range, in the tetragonal phase (ICSD#85322) were obtained when the Gd^{3+} ions are incorporated into the ZrO_2 lattice for doping concentration of 2.5 and 5 mol% (Fig. 4(e, f)). The choice of the Gd doped- ZrO_2 samples processed at 300 °C for XRD analysis occurred because the most deviation in the phase content (see Table 1) was observed for these samples. Thereby, the structural stabilization for these samples would be the most difficult to achieve. Rietveld refinement revealed that at doping concentration of 2.5 and 5 mol%, the zirconia is fully

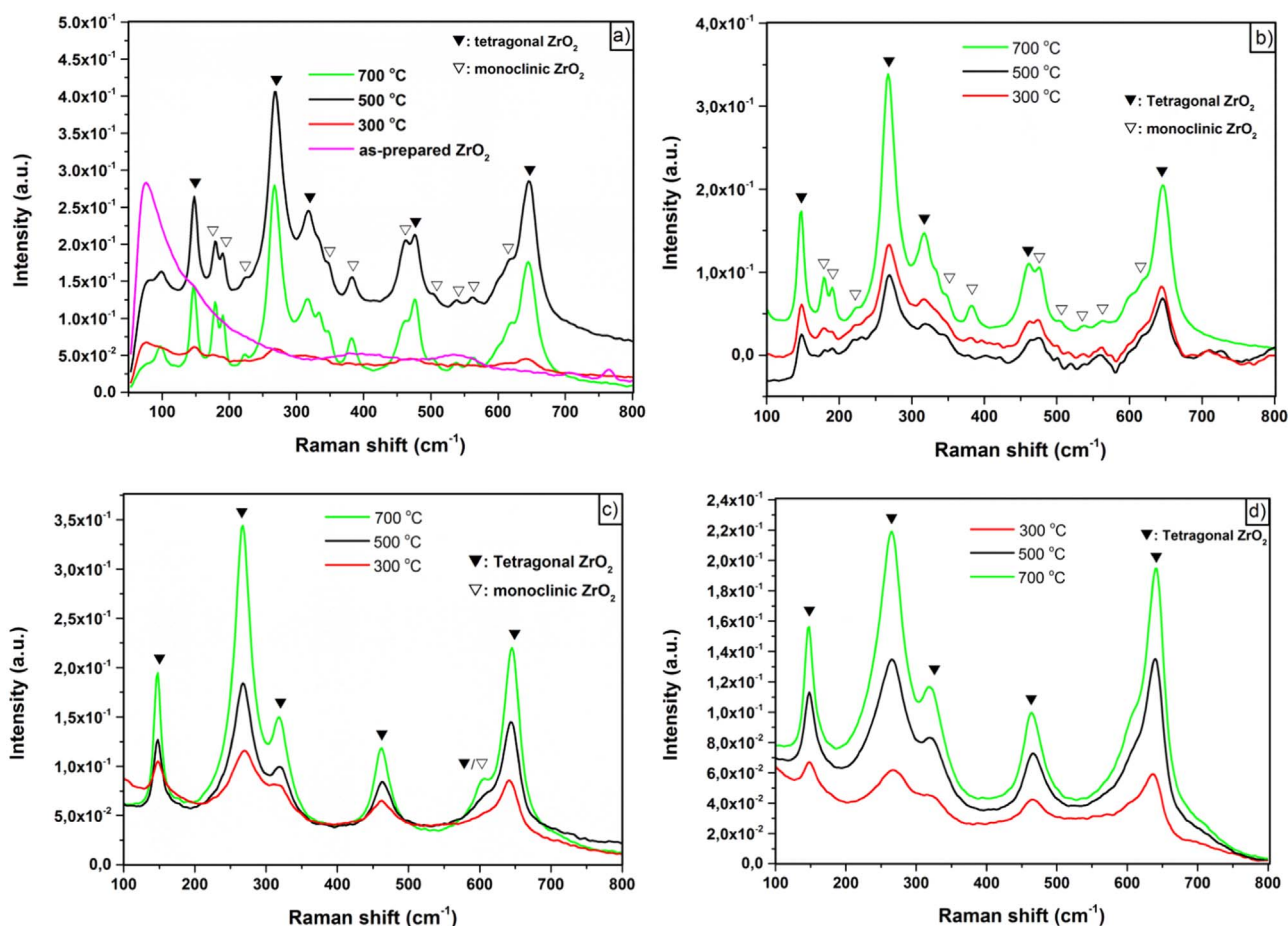


Fig. 2. Raman spectra of the as-prepared ZrO_2 and pristine ZrO_2 obtained by the proposed method in different temperatures of processing (a). Raman spectra of the Gd-doped ZrO_2 obtained by the proposed method in different temperatures of processing with Gd^{3+} doping concentration of 0.5 mol% (b); 2.5 mol% (c); 5 mol% (d).

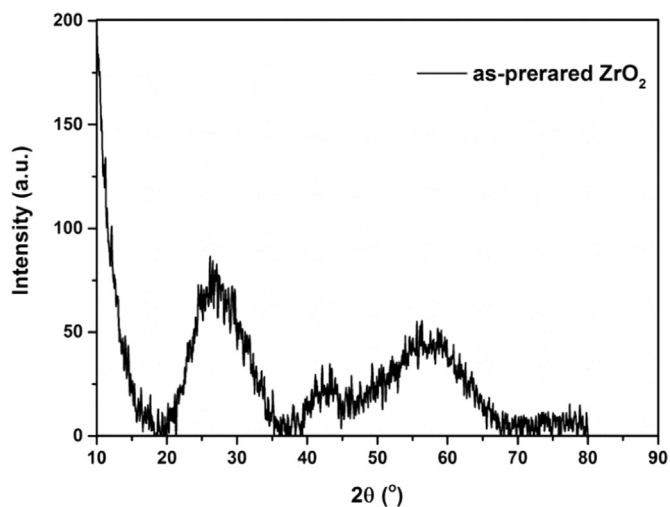


Fig. 3. XRD pattern of the pristine ZrO_2 obtained without microwave heating (as-prepared ZrO_2).

stabilized in the tetragonal phase at long-range, whereas at short-range, Raman results shown that only for 5 mol% the stabilization is obtained. Low valence cations, such as trivalent lanthanide ions, tend to increase the oxygen vacancy concentration to ensure the charge balance of the ZrO_2 crystal, which in turn induces extrinsic defects on the ZrO_2 lattice such as, internal stress, strain and distortions changing the crystal field surrounding [45–47]. Therefore, the fully stabilized ZrO_2 in the tetragonal phase, in accordance with DRX, Rietveld refinement and Raman

Table 1
Rietveld refinement parameters of the pristine and Gd-doped ZrO_2 .

Pristine ZrO_2						
Temp. ^a proc.	300 °C		500 °C		700 °C	
R_{wp}	8.1		8.7		8.0	
Gof	1.7		1.9		1.6	
phases %	<i>t</i> - ZrO_2	<i>m</i> - ZrO_2	<i>t</i> - ZrO_2	<i>m</i> - ZrO_2	<i>t</i> - ZrO_2	<i>m</i> - ZrO_2
	68.1 (3)	31.9(3)	85.0(2)	15.0(2)	77.1(2)	22.9(2)
Gd-doped ZrO_2 (300 °C)						
Doping cont. ^b	0.5% Gd^{3+}		2.5% Gd^{3+}		5% Gd^{3+}	
R_{wp}	6.7		8.7		7.7	
Gof	1.5		1.6		1.6	
phase %	<i>t</i> - ZrO_2	<i>m</i> - ZrO_2	<i>t</i> - ZrO_2	<i>m</i> - ZrO_2	<i>t</i> - ZrO_2	<i>m</i> - ZrO_2
	86.4(8)	13.6(8)	100	–	100	–

^a Temperature of processing.

^b Doping content (% mol). *t*- ZrO_2 = tetragonal. *m*- ZrO_2 = monoclinic.

scattering results, can be attributed to the oxygen vacancies generated due to the mismatch ionic radius between Gd^{3+} ($r_{ion} \sim 1.07 \text{ \AA}$) and Zr^{4+} ($r_{ion} \sim 0.86 \text{ \AA}$) entailing the substitution of the cations Zr^{4+} by Gd^{3+} [20–22].

The classical sol-gel method usually requires a heat treatment in order to obtain a crystalline material at the end of the process [48]. In this sense, Montoya and co-workers [30] prepared by annealing dried gels of $Gd_xZr_{1-x}O_2$ ($0 \leq x \leq 0.2$) at temperatures between 450 and 1300 °C for 3 h under conventional heating. The authors observed that for low Gd doping content ($x < 0.05$), *t*- ZrO_2 were obtained up to 1100 °C, whereas the *m*- ZrO_2 were detected up to 1300 °C. Behera et al. [31] reported stabilization of the *t*- ZrO_2 at concentration range

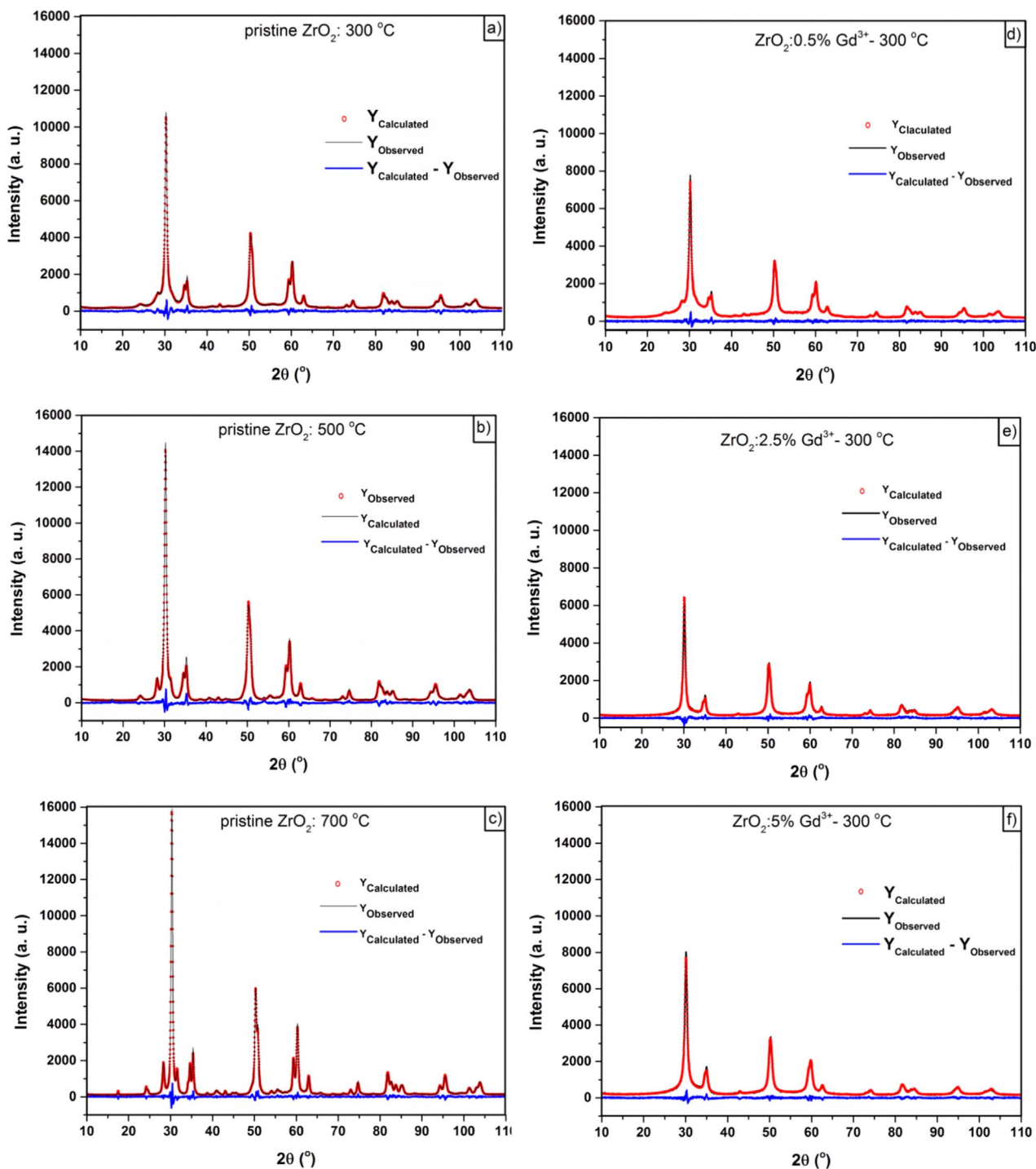


Fig. 4. XRD patterns from Rietveld refinements data of the pristine ZrO_2 (a-c) and Gd-doped ZrO_2 (d-f) obtained from proposed method and processed at 300 °C.

(5–10 mol%) of Gd^{3+} under heat treated at different temperatures (300–1100 °C) for 4 h, whereas higher dopants contents (> 10 mol%) led to the formation of cubic ZrO_2 (*c*- ZrO_2). Manjunatha and Dharmaprakash [33] managed to get FSZ (*c*- ZrO_2) by co-doping with 2.5 mol% of Gd^{3+} and 2.5 mol% of Eu^{3+} using a microwave assisted solution combustion method during 30 s of time processing. Therefore, the chemical and structural evolutions taking place in the ZrO_2 depend strongly of the type of heat treat employed in the sol-gel process (combustion method, microwave power, conventional heating, etc.) as well as of the processing time.

Fig. 5 illustrates TEM/HRTEM/SAED images of the pristine ZrO_2 and Gd-doped ZrO_2 (5 mol% of Gd^{3+}), both processed at 700 °C. TEM

(Fig. 5(a, d)) and HRTEM images (Fig. 5(b, e)) revealed that ZrO_2 particles tend to agglomerate like nanoparticles with heterogeneous size distribution. Thereby, the TEM/HRTEM images implies that the nucleation and growth mechanisms are governed by the coalescence process, whose attachment mechanism occurs randomly between grain boundaries with crystallographic misorientation to form the ZrO_2 nanoparticles [49,50]. Fig. 5(c, f) exhibit the SAED patterns with well-defined rings, characteristic of the polycrystalline materials, produced by the diffraction from the various families of planes (*t*- ZrO_2 and *m*- ZrO_2) within the randomly oriented crystals [51]. For pristine ZrO_2 sample (Fig. 5c), the indexing SAED pattern revealed that *t*- ZrO_2 was well indexed by the appearance of the characteristic planes T(011),

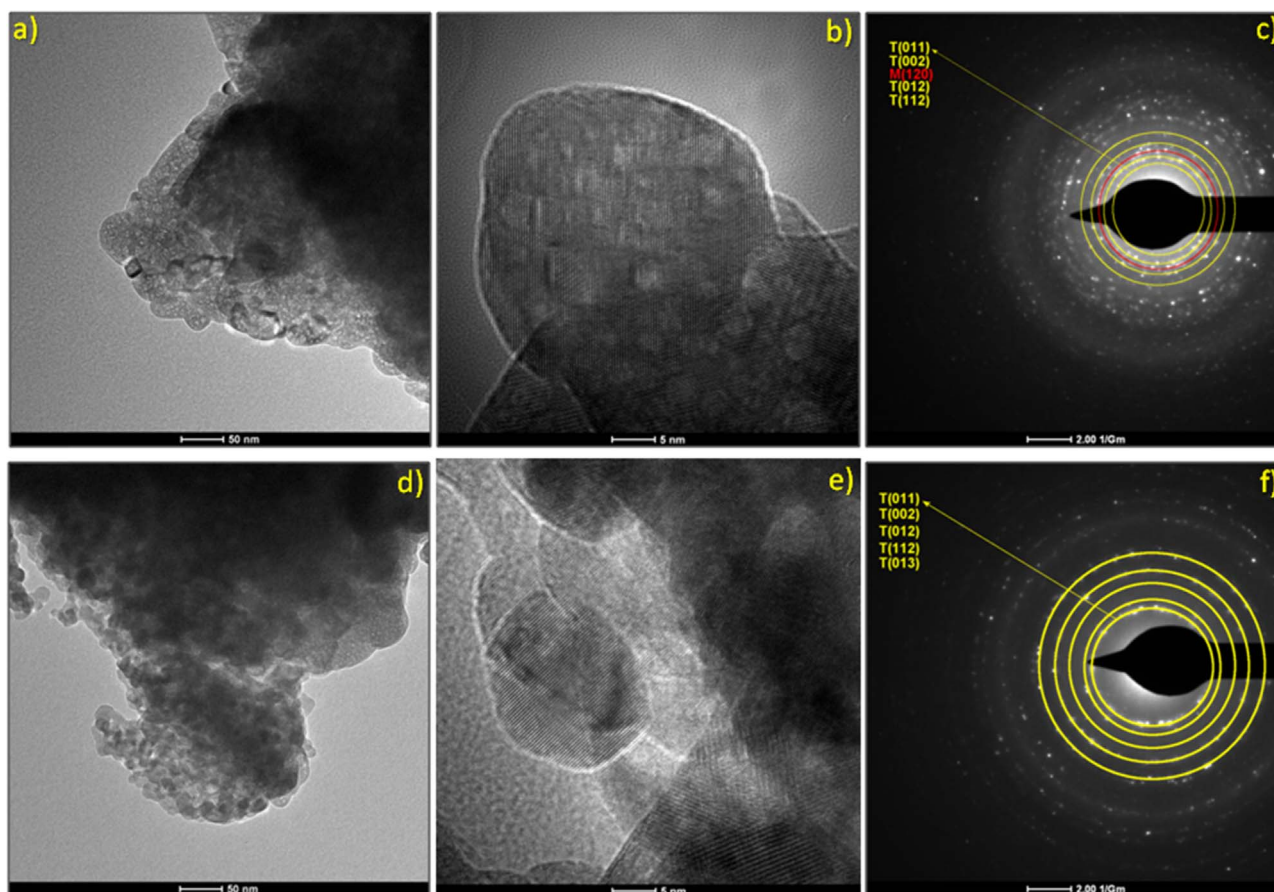


Fig. 5. TEM, HRTEM and SAED of the pristine ZrO_2 and Gd-doped ZrO_2 (5 mol% of Gd^{3+}) both processed at 700 °C. Pristine ZrO_2 = TEM (a), HRTEM (b) and SAED (c). Gd-doped ZrO_2 = TEM (d), HRTEM (e) and SAED (f).

T(002), T(012), T(112) and T(013). However, the plane M(120), ascribed to the *m*- ZrO_2 , also was indexed. On the other hand, the SAED pattern (Fig. 5f) shown that for doping concentration at 5 mol% of Gd^{3+} FSZ (*t*- ZrO_2) was obtained, once only the planes T(011), T(002), T(012), T(112) and T(013), ascribed to the *t*- ZrO_2 were well indexed.

4. Conclusion

Partially and fully stabilized zirconia powders were successfully synthesized from route aided by microwave power, using simpler and faster processing steps as compared to the conventional methods reported in literature. The microwave heating mechanism provided a particular energy transfer which promoted a fast crystallization of the ZrO_2 samples, besides to antecede the gel point. The FSZ can be attributed to the oxygen vacancies created entailing the enough substitution of Zr^{4+} by Gd^{3+} ions (5 mol%) which induce extrinsic defects on the ZrO_2 lattice such as, internal stress, strain and distortions thereby stabilizes in the tetragonal phase. Therefore, considering its viability, the method proposed here showed to be a very promising to obtain rare-earth doped zirconia powders highly stabilized, at both long- and short-range.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.ceramint.2017.11.145>.

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