

Characteristics of zirconia nanoparticles prepared by molten salts and microwave synthesis

J Grabis, Dz Jankovica, E Sokolova, I Steins

Institute of Inorganic Chemistry RTU, Miera 34, Salaspils, LV-2169, Latvia

E-mail: grabis@nki.lv

Abstract. Zirconia and yttria stabilized zirconia (3YSZ) nanoparticles were prepared from zirconia and yttria salts using molten salts (MS) and microwave (MW) synthesis. The crystalline ZrO_2 and 3YSZ nanoparticles with crystallite size in the range of 3–27 nm were obtained by MS synthesis in NaCl – NaNO_3 salts. The zirconia and 3YSZ powders with close characteristics were obtained by combining MW synthesis with calcination of products at 400–800 °C. The crystallite size depends upon synthesis or calcination temperature, and the precursors used. The powders prepared by MS and MW synthesis ensured manufacturing of bulk materials with relative density of 98.6% and 97.2% respectively by using spark plasma sintering at 1300 °C.

Introduction

Stabilized zirconia nanoparticles due to their unique physical, chemical and mechanical properties find application as solid electrolytes, gas sensors, catalysts, high-temperature and bio- materials [1]. Owing to the wide application of zirconia, several preparation methods with different particle size and phase composition have been elaborated [1, 2, 3]. At room temperature the high-temperature phases of ZrO_2 have been stabilized by introducing trivalent oxides as solid solution in the ZrO_2 lattice [4]. These synthesis methods allow to prepare nanoparticles containing t-, m- ZrO_2 or pure monoclinic, tetragonal as well as cubic phase depending on the precursors used, calcination temperature and conditions of synthesis. Each method has its characteristic advantages and disadvantages which mainly relate to complexity of the process, expensive precursors, production rate, cost, and use of several solvents.

The present trends in technology are directed to development of highly effective, economic and environment friendly preparation methods of nanoparticles. From this point of view, fast microwave (MW) [1] and solvent free molten salts (MS) [2, 3] synthesis could be very perspective preparation methods. These methods can be used together with the fast spark plasma sintering (SPS) method for processing the powders produced. However, influence of different salts, precipitation agents, and synthesis temperature on characteristics of zirconia nanoparticles prepared by MS and MW synthesis and their sinterability by using the SPS method is not fully known.

In the present paper the characteristics and sinterability of the zirconia nanoparticles prepared by MS and MW synthesis are studied and compared.

2. Experimental

Experiments were performed by using following reagent grade chemicals $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{Y}_2(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, NaCl , NaNO_3 , NH_4OH , urea. For MS synthesis the Zr and Y salts were mixed with definite amounts of NaCl and NaNO_3 (ratio of Zr and sodium salts was varying in the



range of 0.1–0.5). The melting temperature of the salts and therefore also synthesis temperature in the range of 400–800 °C was changed by varying the ratio of sodium salts. The ZrO₂ nanoparticles were extracted from the products by dissolving sodium salts in distilled water and washing with ethanol.

The MW synthesis of the zirconia nanoparticles was conducted using a commercial reactor Masterwave BTR (Anton Paar). The Zr salts or their mixture with Y₂(NO₃)₃·6H₂O (3 mol%) were dissolved in distilled water, stirred and then NH₄OH or urea was added. The synthesis of the zirconia was performed at 180 °C during 20 min at pressure about 26 bar with continuous stirring. The obtained particles were extracted by filtration and washing with distilled water and ethanol followed by drying at 100 °C for 20 h. ZrO₂ was calcinated at 400–800 °C.

The samples prepared by both methods were densified in vacuum at temperature 1200–1400 °C and a pressure of 30 MPa using the spark plasma sintering technique (SPS-825.CE).

The phase composition of powders and bulk materials was determined by X-ray diffraction (XRD) analysis at the room temperature (AdvanceD8, Bruker AXS). Presence of c-ZrO₂ phase was detected by splitting maxima of c-ZrO₂ and t-ZrO₂ at 2 θ in the range of 73–75 °C. The crystallite size was calculated using X-ray diffractometer software EVA12 based on the Scherrer formula. The specific surface area (SSA) of powders was determined by the argon absorption-desorption method. Density of bulk samples was determined by using the Archimede's method

3. Results and discussion

Typical parameters of the molten salts and microwave synthesis and characteristics of the prepared pure zirconia and stabilized with 3 mol% yttria (3YSZ) are shown in Table 1.

Table 1. Parameters of synthesis and characteristics of as-prepared zirconia particles

Sam- ple	Precursors	SSA, m ² /g	Crystallite size, nm	Phase composition, %
Molten salts synthesis, temperature 400 °C, time 120 min				
M1	ZrO(NO ₃) ₂ ·2H ₂ O, NaNO ₃ , NaCl	104.0	8	m-ZrO ₂ 20%; t-ZrO ₂ 80%
M2	ZrOCl ₂ ·8H ₂ O, NaNO ₃ , NaCl	116.2	7	m-ZrO ₂ 15%; t-ZrO ₂ 85%
M3	ZrO(NO ₃) ₂ ·2H ₂ O, Y ₂ (NO ₃) ₃ ·6H ₂ O, NaNO ₃ , NaCl	107.1	5	t-, c-ZrO ₂ 100%
M4	ZrOCl ₂ ·8H ₂ O, Y ₂ (NO ₃) ₃ ·6H ₂ O, NaNO ₃ , NaCl	120.9	3	t-, c-ZrO ₂ 100%
Microwave synthesis, temperature 180 °C, time 20 min				
MW1	ZrOCl ₂ ·8H ₂ O, NH ₄ OH	140.2	...	X-ray amorphous
MW2	ZrOCl ₂ ·8H ₂ O, CH ₄ N ₂ O	140.5	...	X-ray amorphous

All as-prepared powders had the high SSA. Data showed small increase of SSA and decrease of crystallite size in the samples prepared by MS synthesis using ZrOCl₂·8H₂O or Zr salts with yttria additives as precursors, possibly, due to the change of phase composition of powders.

The higher SSA of the samples prepared by MW synthesis can be explained by lower synthesis temperature and formation X-ray amorphous products. Besides this, the SSA is determined by concentration of zirconium in reaction medium. The increase of the ratio Zr/Na salts from 0.1 up to 0.5 decreased the SSA of powders prepared by MS synthesis from 142 m²/g to 102 m²/g.

The pure ZrO_2 powders prepared by MS synthesis contained t- ZrO_2 and some amount of m- ZrO_2 despite very small crystallite size. The MS synthesis of 3YSZ powders resulted in obtaining fully stabilized zirconia containing t-, c- ZrO_2 phases. The similar phase composition was detected for yttria stabilized zirconia samples prepared by MS synthesis using NaNO_3 – KNO_3 , ZrOCl_2 , YCl_3 salts [2].

The XRD patterns of as-prepared ZrO_2 by MW synthesis showed very broad weak maxima indicating formation of hydrous-zirconia particles due to low synthesis temperature compared to the MS process. Such hydrous-zirconia has been prepared by hydrolysis of $\text{ZrO}(\text{NO}_3)_2$ in a reverse microemulsion at 60–75 °C for 72 h [5]. Additional calcination of powders at the temperature in the range of 400–800 °C led to formation of crystalline particles and mass loss up to 15.2% at 600 °C.

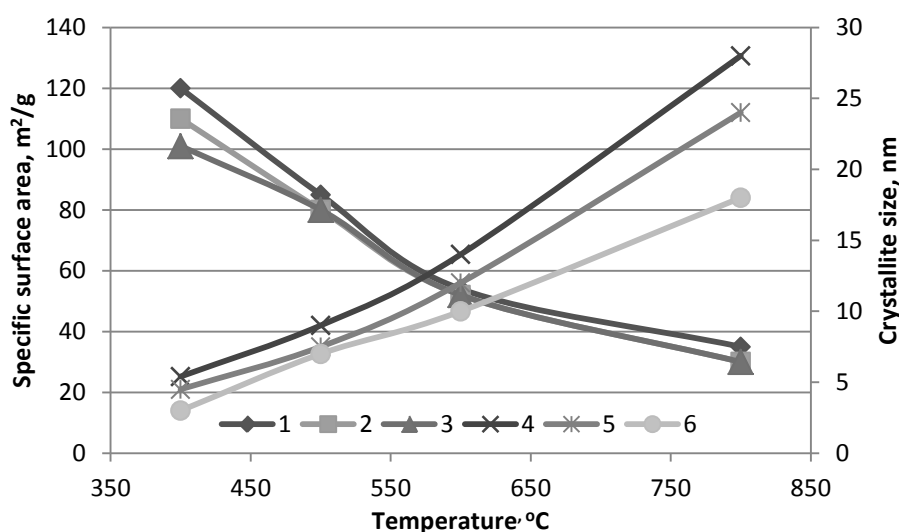


Figure 1. SSA (1, 2, 3) and crystallite size (4, 5, 6) of 3YSZ nanoparticles prepared by MS synthesis using $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (1, 6) or $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (3, 4) and by MW synthesis (2, 5) in dependence on synthesis or calcination temperature

The additional calcination of MW synthesis powders had significant impact on SSA and crystallite size (Figure 1). The SSA and crystallite size of the calcinated MW synthesis powders were very close to that of MS synthesis powders prepared at the same temperature. This indicated the important role of temperature in formation of zirconia nanoparticles.

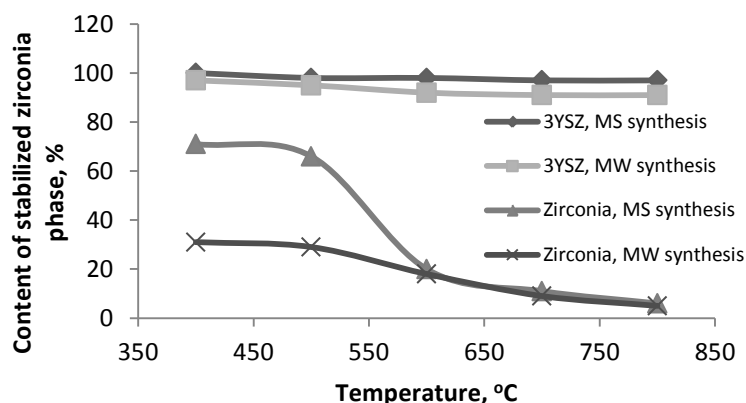


Figure 2. Content of stabilized zirconia phase in 3YSZ and zirconia powders prepared by MS and MW synthesis in dependence on synthesis or calcination temperature

The phase transition of powders depends upon the methods used in their preparation and preparation temperature (Figure 2). For unstabilized zirconia, calcination at 500–600 °C promoted

formation of m-ZrO₂ phase although the crystallite size was below a critical size for tetragonal phase stabilization. The XRD patterns of 3YSZ powders prepared by MS synthesis at temperature higher as 500 °C showed only traces of m-ZrO₂ but MW synthesis powders calcinated at 400 °C and 800 °C contained about 3% and 9% of m-ZrO₂ respectively.

The densification of MS and MW synthesis powders during SPS process started at 820–840 °C depending on the SSA of the samples (Table 2) and was connected with their compacting as well as with release of absorbed gases. The final density was reached during 2 min at 1225–1250 °C.

Table 2. Spark plasma sintering process of powders.

Synthesis; temperature, °C	SSA, m ² /g	Temperature of shrinkage, °C		Relative density, %
		starting	final	
MS; 600	50.1	820	1225	98.3
MS; 800	33.4	850	1250	98.6
MW; 600	52.1	820	1220	97.0
MW; 800	36.9	840	1240	97.2

The different relative density of the bulk samples sintered from MS and MW synthesis powders could be explained by the higher content of monoclinic phase in MW powders. The increase of the sintering temperature up to 1400 °C did not improve relative density of the samples. The phase composition of the sintered bulk materials corresponded to that of the used powders.

4. Conclusions

1. Molten salts synthesis ensured preparation of crystalline zirconia and fully stabilized 3YSZ nanoparticles at temperature 400–800 °C with crystallite size in the range of 5–28 nm.
2. Microwave synthesis resulted in formation of hydrous zirconia which additional calcination at temperature 400–800 °C led to formation of crystalline zirconia nanoparticles with crystallite size close to that of molten salts process but increased content of monoclinic phase.
3. The 3YSZ nanoparticles prepared by simple one-stage molten salts process showed higher content of stabilized phase of zirconia and better sinterability with respect to microwave synthesis.

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5. References

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