



Solution combustion synthesis of calcium zirconate, CaZrO_3 , powders

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ABSTRACT

Single-phase CaZrO_3 powder was prepared by heating at 300 °C an aqueous solution of $\text{Ca}(\text{NO}_3)_2$, $\text{ZrO}(\text{NO}_3)_2$ and $\beta\text{-C}_3\text{H}_7\text{NO}_2$ (molar ratio=3:3:4). TG-DTA analysis indicated that an intense exothermic reaction occurred at 255 °C, which led to the formation of a voluminous white powder. No additional annealing was required, as pure crystalline CaZrO_3 resulted directly from the combustion reaction. Although no advanced milling was performed, the specific surface area of the powder was 21.5 m²/g. The average crystallite size of CaZrO_3 was 23.9 nm. After sintering in air at 1400 °C for 2 h, the pellets – shaped by uniaxial pressing at 200 MPa – reached 95% of the theoretical density, had no open pores and were slightly translucent.

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1. Introduction

CaO-ZrO_2 system is one of the main research topics material scientists are focused on. However, most of these investigations are aimed at the synthesis and characterization of CaO stabilized ZrO_2 solid solutions and little attention has been paid to the study of the CaZrO_3 phase. Although the existence of CaZrO_3 in the CaO-ZrO_2 equilibrium diagram is known for several decades, it was only in 2008 this mineral has been identified in nature in the North Caucasus, Kabardino-Balkaria region, Russia [1].

Calcium zirconate, CaZrO_3 , also known as lakargiite is a refractory compound, which congruently melts at 2340 °C [1]. In terms of crystalline structure, CaZrO_3 is an orthorhombic perovskite consisting of slightly deformed $[\text{ZrO}_6]$ octahedra and $[\text{CaO}_8]$ [2,3]. At 1750 °C CaZrO_3 undergoes polymorph transformation where orthorhombic $\text{CaZrO}_3 \rightarrow$ cubic CaZrO_3 .

Due to its valuable properties, CaZrO_3 is a ceramic material that is currently being used in a wide range of applications: multilayer ceramic capacitors [4], solid electrolyte [5], crystalline host for phosphor materials [6], moderate temperature thermal barrier [7], catalyst [8], etc.

According to Azimov et al. [9], in many aspects CaZrO_3 shows better properties than the solid solutions of CaO stabilized ZrO_2 . The same authors emphasized that the sintering process, as well as mechanical, electrical and chemical properties of CaZrO_3

products are negatively affected by the presence of traces of free CaO and ZrO_2 [9].

The preparation of CaZrO_3 powders via ceramic route involves annealing a mixture of CaCO_3 and ZrO_2 at elevated temperature for several hours, followed by an intensive milling operation to reduce the grain size. For instance, Wang et al. [10] reported the preparation of single-phase CaZrO_3 powders by annealing stoichiometric mixtures of CaCO_3 and ZrO_2 in the temperature range 1000–1400 °C for 12 h. Similar results were presented by Hwang and Choi [11], who prepared CaZrO_3 from CaCO_3 and ZrO_2 after a heat treatment of 4 h at 1350 °C.

The CaZrO_3 powders obtained by the ceramic method present several major drawbacks (large particle size, wide grain size distribution, low surface area, high agglomeration degree, lack of chemical homogeneity, etc.), which are detrimental to the sintering process. Róg et al. [2] prepared dense CaZrO_3 with a relative density higher than 95% after annealing at 1600 °C for 12 h. Wang et al. [10] managed to obtain 95% of the theoretical density of CaZrO_3 after sintering the cold-pressed specimens at 1550 °C for 48 h.

In order to overcome the disadvantages of the ceramic method, new chemical preparation methods have been tested. Zhang et al. [6] synthesized $\text{CaZrO}_3\text{:Eu}$ red phosphor at 1000 °C by the polymerization complex method based on the Pechini-type reaction. Gonenli and Tas [12] reported the preparation of pure CaZrO_3 powders by annealing at 1200 °C for 17 h the amorphous precursor obtained from the combustion reaction of corresponding metal chlorides with urea. Prasanth et al. [13] synthesized pure CaZrO_3 powders of crystallite size 33 nm by annealing at 700 °C the amorphous powder resulting from the reaction of

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calcium nitrate, zirconil oxy-chloride, citric acid and urea. Yu et al. [14] applied the sol-gel method for the preparation of thin films and concluded that pure CaZrO_3 films could be obtained after a heat treatment at 1000°C for 10 h.

Considering that the synthesis of CaZrO_3 powders is a subject of wide interest, this paper reports a fast and efficient procedure for obtaining large surface area CaZrO_3 powders, which does not require any annealing step.

2. Experimental

2.1. Preparation of CaZrO_3 powders

CaZrO_3 powders were prepared using two different synthesis methods: the solution combustion synthesis and the ceramic method, which was used for comparison. Table 1 shows the starting raw materials as well as the molar ratio of the investigated samples. In both synthesis routes, recipes were designed in order to obtain 0.06 mol of CaZrO_3 .

Since the general procedure for the synthesis of CaZrO_3 via ceramic route is widely known (Fig. 1), only the solution combustion synthesis of CaZrO_3 is described in detail below.

According to the thermo-chemical concepts from propellants chemistry the energy released by a combustion reaction is maximum when the total oxidizing and reducing valencies of metal nitrates and fuel reach unity, which corresponds to a $\text{Ca}(\text{NO}_3)_2:\text{ZrO}(\text{NO}_3)_2:\text{C}_3\text{H}_7\text{NO}_2$ molar ratio of 3:3:4.

An aqueous solution of β -alanine was initially prepared by dissolving 0.24 mol of $\beta\text{-C}_3\text{H}_7\text{NO}_2$ in 30.0 mL of distilled water (Fig. 2); 0.18 mol of $\text{ZrO}(\text{NO}_3)_2$ and 0.18 mol of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were subsequently added to the solution of β -alanine under continuous stirring. The porcelain evaporating dish containing the clear solution was then placed in a heating mantle preheated at 300°C . In the beginning the solution boils, foams and undergoes intense flaming combustion, yielding a very voluminous white powder. The resulting powder was uniaxially pressed at 200 MPa into pellets of 2 mm height and 25 mm diameter in order to investigate the sintering behavior of CaZrO_3 , and 2 wt% polyethylene glycol (PEG 200) was added as a plasticizer. In order to achieve a better distribution of the plasticizer, the necessary amount of PEG 200 was initially dissolved in acetone and the acetone was subsequently removed by evaporation (Fig. 2). The resulting green pellets were annealed at 1400°C for 2 h. Water absorption, open porosity and apparent density of the sintered pellets were determined using the Archimedes principle.

Small portions of the powders prepared using the two synthesis routes were annealed at $800\text{--}1000^\circ\text{C}$ for 1 h in a muffle furnace.

2.2. Characterization methods

Heating behavior of the precursor mixture containing $\text{Ca}(\text{NO}_3)_2$, $\text{ZrO}(\text{NO}_3)_2$ and $\beta\text{-C}_3\text{H}_7\text{NO}_2$ (sample 2) was investigated by thermal analysis using a Netzsch STA 449 C instrument equipped with alumina crucibles. The TG and DTA curves were recorded under N_2 atmosphere over the interval $25\text{--}700^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$.

The phase composition of the powders was determined by XRD using a Bruker D8 Advance System (monochromatic $\text{CuK}\alpha$ radiation) operating at 40 kV and 40 mA. The average crystallite size was calculated based on the XRD patterns using the Sherrer's

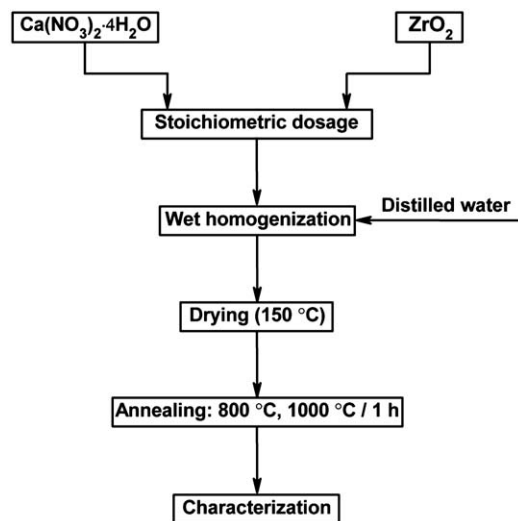


Fig. 1. Preparation of CaZrO_3 powder via ceramic route (sample 1).

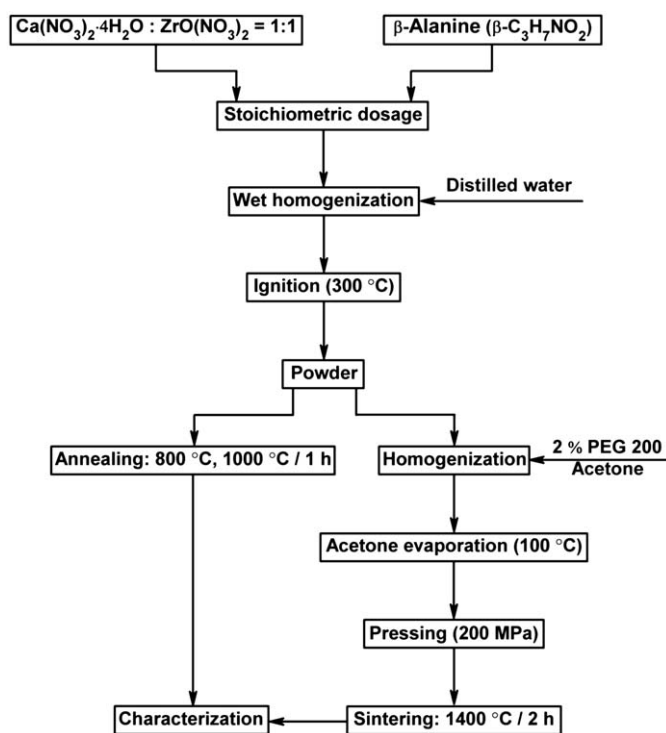


Fig. 2. Preparation of CaZrO_3 powder via solution combustion synthesis (sample 2).

Table 1
Molar composition of the designed samples.

Sample	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ Merck, pro analysi	ZrO_2 Carlo Erba, pro analysi	$\text{ZrO}(\text{NO}_3)_2$ Fluka, purum	$\beta\text{-C}_3\text{H}_7\text{NO}_2$ Merck, pro analysi
1 (ceramic method)	1	1	–	–
2 (combustion synthesis)	3	–	3	4

equation (1). The peaks used for the crystallite size calculation were the ones corresponding to 101 and 202 *hkl* planes.

$$D_{\text{XRD}} = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where D_{XRD} is the crystallite size (nm), λ the radiation wavelength (CuK α , 0.15406 nm), β the full width at half of the maximum (radians) and θ the Bragg angle.

BET (Brunauer, Emmett and Teller) surface area measurements were performed using a Micromeritics ASAP 2020 instrument and nitrogen as adsorption gas. The grain size, D_{BET} , was calculated using equation (2).

$$D_{\text{BET}} = \frac{6000}{\rho S_{\text{BET}}} \quad (2)$$

where D_{BET} is the grain size (nm), ρ the theoretical density of CaZrO₃ (4.78 g/cm³) and S_{BET} the BET surface area (m²/g).

The morphology of the powders was investigated by SEM using a FEI Inspect S scanning electron microscope. The SEM images were acquired after the powder was fixed to the aluminum support using a double-faced carbon tape. Elemental analysis was performed by Energy Dispersive X-ray Analysis (EDAX) using the same instrument. The EDAX measurements were conducted on pellets mounted with double-sided adhesive carbon tape on the aluminum support.

Using the thermodynamic data available in [15–17] and assuming that combustion reaction is complete (that is to say that the reaction by-products are N₂, CO₂ and H₂O), the standard enthalpy of reaction as well as and the adiabatic temperature (equation (3)) were calculated:

$$T_{\text{ad}} = T_0 + \frac{\Delta H_{\text{f,r}}^0 - \Delta H_{\text{f,p}}^0}{C_p} \quad (3)$$

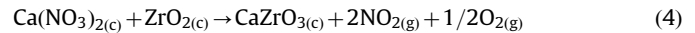
where T_{ad} is the adiabatic temperature (K); T_0 is 298 K; $\Delta H_{\text{f,r}}^0$ and $\Delta H_{\text{f,p}}^0$ are the standard enthalpies of formation of reactants and

reaction products (kJ/mol), respectively; C_p is the heat capacity of reaction products at constant pressure in (kJ/mol K).

3. Results and discussion

3.1. Ceramic method

In the case of the ceramic method the formation of CaZrO₃ could be described by reaction (4). The standard enthalpy of reaction (4) is 142 kJ/mol, which indicates that under standard conditions reaction (4) is an endothermic process:



Experimental results revealed that during the annealing of an equimolecular mixture of Ca(NO₃)₂ and ZrO₂ (sample 1) the formation of CaZrO₃ begins at a relatively low temperature, below 800 °C (Fig. 3). However, in order to achieve CaZrO₃ as a single phase a much higher temperature is required.

XRD analysis indicated that the powder obtained after annealing the mixture of Ca(NO₃)₂ and ZrO₂ (sample 1) at 800 °C for 1 h is a mixture of three crystalline phases: CaZrO₃, unreacted ZrO₂ and free CaO, which originates from the thermal decomposition of Ca(NO₃)₂ (Fig. 3). In addition, the resulting powder has a very low specific surface area (1.5 m²/g; Table 2).

Since it is generally known that low surface area powders exhibit a poor sintering behavior, the solution of increasing furthermore the annealing temperature – in order to obtain pure CaZrO₃ – is a futile alternative. Indeed, raising the annealing temperature to 1000 °C has no positive effect on the phase composition of the powder, since alongside CaZrO₃, CaO and ZrO₂ – which still persists – a new crystalline phase appears, i.e. CaO stabilized ZrO₂ solid solution (Fig. 3).

The presence of cubic CaO stabilized ZrO₂ solid solution is also confirmed by the SEM images of powder 1 annealed at 1000 °C (Fig. 4). At the same time, there is a slight increase of the CaZrO₃ crystallite size from 28.4 to 28.7 nm, whereas the specific surface area decreases to 1.4 m²/g (Table 2).

The huge difference between D_{BET} and D_{XRD} in the case of powder 1 annealed at 800–1000 °C indicates that each grain contains a very large number of crystallites and the crystallites are highly agglomerated (Table 2).

To summarize, synthesis of pure CaZrO₃ via the ceramic method takes place at very difficult conditions and at temperatures exceeding 1000 °C. Under these circumstances the obtained powders are highly agglomerated and have very low specific surface areas. These features point out that CaZrO₃ powders prepared by the ceramic method are very difficult to sinter, which is also confirmed by other papers [2,10].

3.2. Solution combustion synthesis

Reaction (5) describes in a simplified manner the formation of CaZrO₃ via solution combustion synthesis—also known as low-temperature combustion synthesis. One should consider that the terminology “low-temperature combustion synthesis” does not

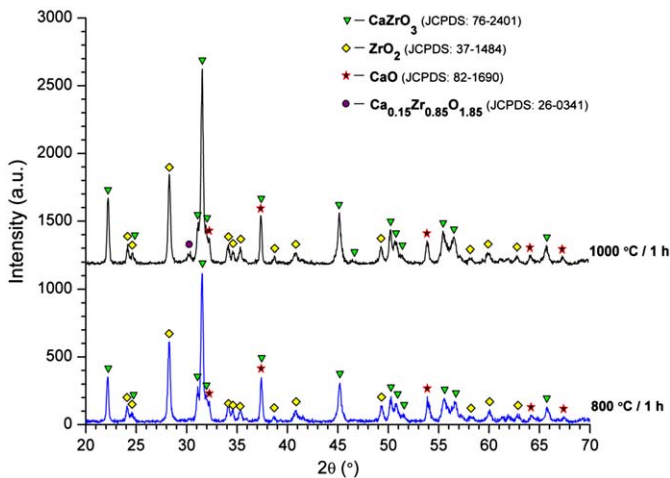


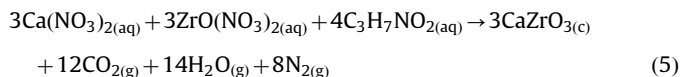
Fig. 3. XRD patterns of the powders prepared via ceramic method (sample 1), after annealing for 1 h at 800 and 1000 °C.

Table 2

Average crystallite size (D_{XRD}), specific surface area (S_{BET}) and grain size (D_{BET}) of the powders.

Sample	Before annealing			800 °C/1 h			1000 °C/1 h		
	D_{XRD} (nm)	S_{BET} (m ² /g)	D_{BET} (nm)	D_{XRD} (nm)	S_{BET} (m ² /g)	D_{BET} (nm)	D_{XRD} (nm)	S_{BET} (m ² /g)	D_{BET} (nm)
1	–	–	–	28.4	1.5	836.8	28.7	1.4	896.6
2	23.9	21.5	58.4	25.3	20.1	62.4	28.1	13.5	93.0

refer to the maximum combustion temperature – which can easily exceed 1000 °C – but rather to the ignition temperature, which is at relatively low temperature (below 300 °C).



Basically, in the case of this method, the heat required for the CaZrO_3 formation is not supplied by an external source – as in the case of the ceramic method – but is self-generated by the exothermic reaction between $\text{Ca}(\text{NO}_3)_2$, $\text{ZrO}(\text{NO}_3)_2$ and β -alanine. The highly exothermic nature of this process is confirmed by the thermodynamic calculations, which indicate that the standard enthalpy of reaction (5) is -947 kJ/mol .

Fig. 5 depicts a series of successive digital images recorded during different stages of the combustion reaction (5). The numbers on each image represent the time (in seconds) when that frame was recorded. Time stamps are relative to the first frame in the series. Fig. 5 clearly indicates the ignition and the propagation of the reaction front evidenced as a highly incandescent area. The presence of glowing flames and the absence of reddish-brown gases (NO_x) could have also been noticed.

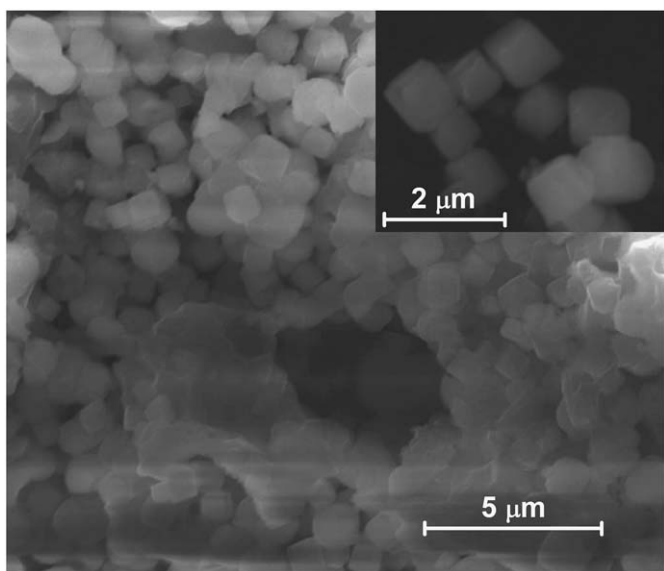


Fig. 4. SEM image of sample 1 after annealing at 1000 °C for 1 h.

During the combustion process – which takes 17 s – the sample undergoes huge expansion, generating a very fluffy white reaction product (Fig. 5), which was easily crumbled using a pestle and a mortar. Although no advanced milling operation was performed, the specific surface area of this powder was $21.5 \text{ m}^2/\text{g}$ (Table 2).

The DTA curve of precursor mixture 2 (Fig. 6) indicates that an endothermic process takes place at 111 °C, which could be assigned to water removal. The total mass loss assigned to this process is about 50%, as seen on the TG curve.

The ignition of the combustion process occurs at 245–255 °C. The exothermic peak is accompanied by a mass loss of about 40% on the TG curve. Both, the exothermic peak on the DTA curve and the rapid and significant mass loss on the TG curve are typical for combustion reactions. After the combustion process reached an end, the sample underwent no more transformations.

The lack of other phenomena accompanied by mass loss is in agreement with the negligible loss on ignition (1.6%) of powder 2. Actually, the elemental composition of combustion-synthesized powder (Fig. 7) – which contains no C or N – leads to the conclusion that the adsorbed moisture, H_2O , is solely responsible for this loss on ignition.

It is also noteworthy that the elemental composition of powder 2 expressed in atomic % (Fig. 7) is very close to the theoretical composition of pure CaZrO_3 : 20% Ca, 20% Zr and 60% O.

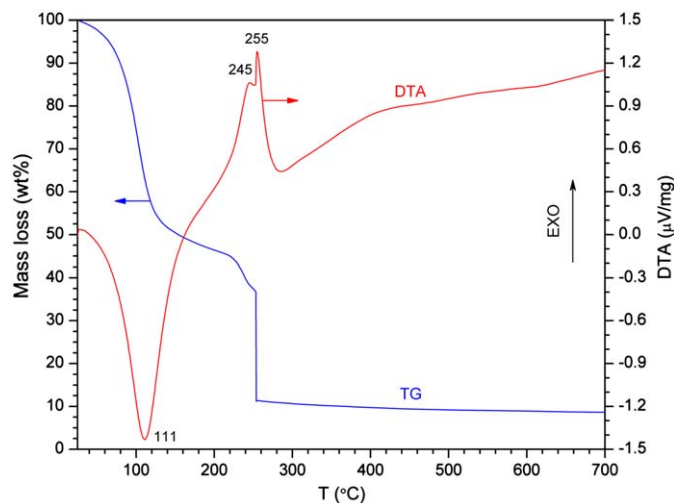


Fig. 6. TG and DTA curves of the precursor mixture 2 (solution combustion synthesis).

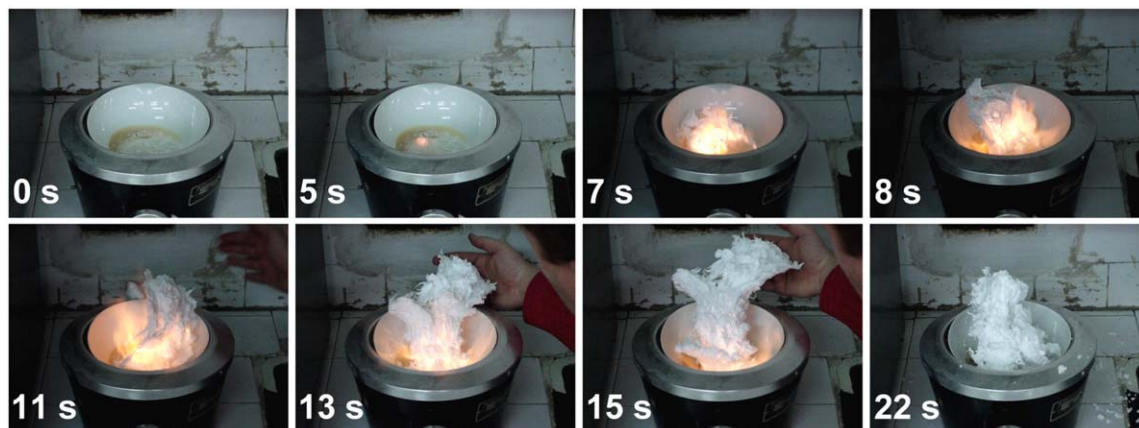


Fig. 5. Different stages of the combustion reaction between $\text{Ca}(\text{NO}_3)_2$, $\text{ZrO}(\text{NO}_3)_2$ and $\beta\text{-C}_3\text{H}_7\text{NO}_2$.

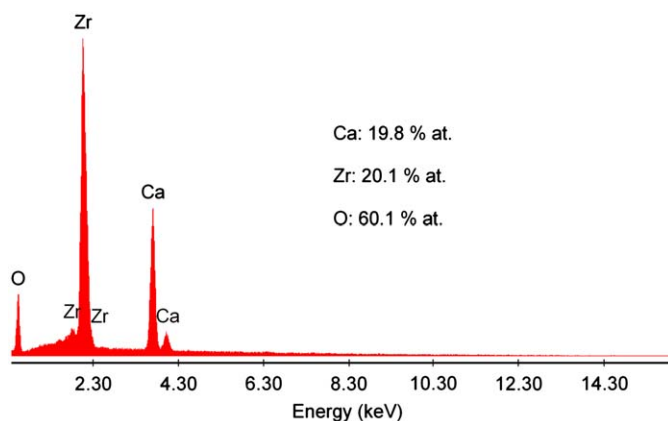


Fig. 7. X-ray emission spectra of powder 2, resulting from the combustion reaction.

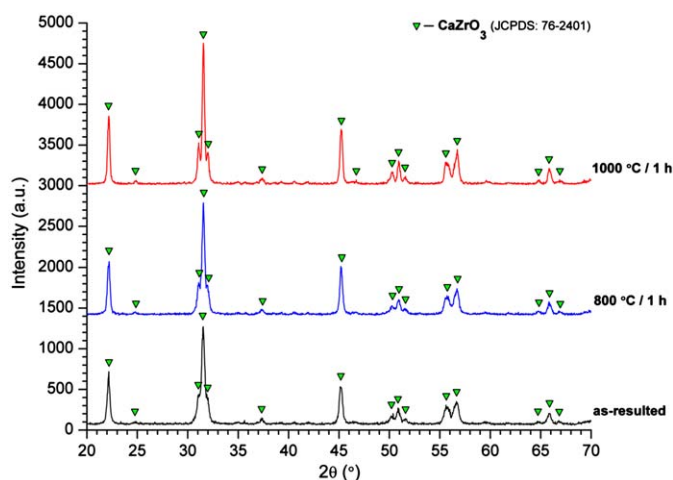


Fig. 8. XRD patterns of the powders prepared via solution combustion synthesis (sample 2), before and after annealing at 800 and 1000 °C for 1 h.

The adiabatic temperature (the maximum theoretical temperature reached during the combustion process, assuming that reaction is conducted under adiabatic conditions) of combustion reaction (5) is 2262 K. Although in reality the combustion temperature is lower than the adiabatic temperature due to various factors (heat loss, incomplete combustion, etc.) it seems that the CaZrO_3 formation requirements are met.

XRD analysis revealed that the powder resulting from the combustion reaction consists of single-phase CaZrO_3 (Fig. 8) and has an average crystallite size of 23.9 nm (Table 2). Unlike the powder prepared by the ceramic method, where the $D_{\text{BET}}/D_{\text{XRD}}$ ratio is about 30, in the case of the combustion synthesized powder, the grain size, D_{BET} , is only 2.4 times larger than the crystallite size, D_{XRD} , which reflects much smaller grains and lower agglomeration tendency (Table 2).

Despite other reports that indicate that an amorphous product results from the combustion reaction [12], it seems that under right circumstances, the combustion method is able to ensure the formation of CaZrO_3 directly from the combustion reaction and no additional heat treatment is required. It is quite obvious that the reason for the difficult formation of CaZrO_3 – as Gonenli and Tas [12] have reported – is the lack of the combustion reaction caused by the inadequate choice of the starting raw materials (metal chlorides and urea). Given the fact that metal chlorides do not act as oxidizers, metal nitrates should have been used instead of

metal chlorides. Moreover, since urea induces the precipitation of ZrO_2 , which alters both the homogeneity of the raw material mixture and the redox balance of the combustion process, another fuel should have been used.

The heat treatment at 800 or 1000 °C for 1 h does not change the phase composition of powder 2 (Fig. 8), but leads to an increase of the CaZrO_3 crystallites. At the same time, a significant decrease of the specific surface area occurs due to pore closure within CaZrO_3 grains (Table 2).

The SEM image of powder 2 indicates that CaZrO_3 grains resulting from the combustion reaction have a scaly appearance similar to that of thin foils, which form a veil-like three-dimensional structure (Fig. 9). This microstructure is the result of the combustion reaction development, which involved the expansion of the sample (Fig. 5).

After the preparation of CaZrO_3 by solution combustion synthesis, the next step was to investigate the sintering behavior of this powder. In this case, the main objective was to achieve a relative density close to the unit by sintering the CaZrO_3 green pellets below the melting temperature of Ni (1453 °C). This condition is imposed by the ceramic capacitor manufacturing technology, which involves the simultaneous sintering of CaZrO_3 and Ni [4].

The CaZrO_3 green pellets were uniaxially pressed at 200 MPa and then annealed at 1400 °C for 2 h (Fig. 2), reaching 95% of the theoretical density. Table 3 shows a comparison between the results of the sintering process reported hereby and the results reported by other authors [2,10].

According to the literature data summarized in Table 3, CaZrO_3 powders prepared by the ceramic method are able to reach 95% of the theoretical density only by performing the sintering stage at higher temperature (above 1550 °C) and using a much longer soaking time, more than 10 h (Table 3). One should also consider that in the case of the ceramic method the preparation of CaZrO_3 powder requires additional heat treatments, whilst in the case of the combustion synthesis single-phase CaZrO_3 results directly from the combustion reaction.

A more detailed analysis of sintered pellets revealed that the apparent porosity and water absorption are null, which indicates the absence of open pores. The visual inspection of the pellets showed they were slightly translucent, suggesting an advanced sintering stage. The microstructure of sample 2 after sintering at

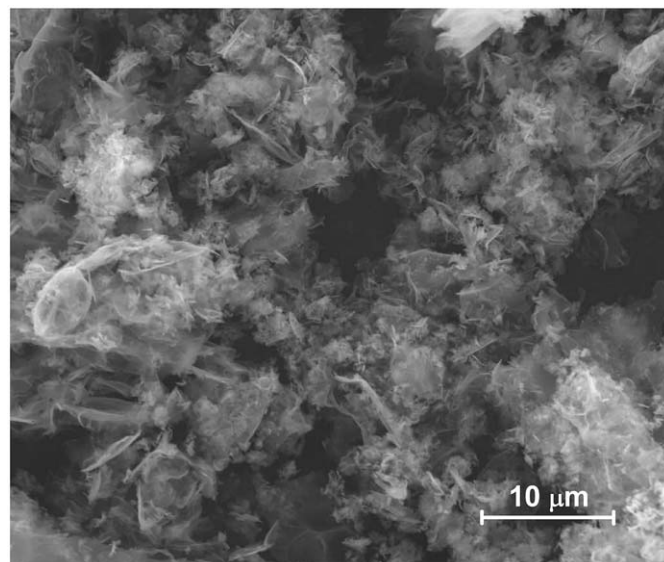
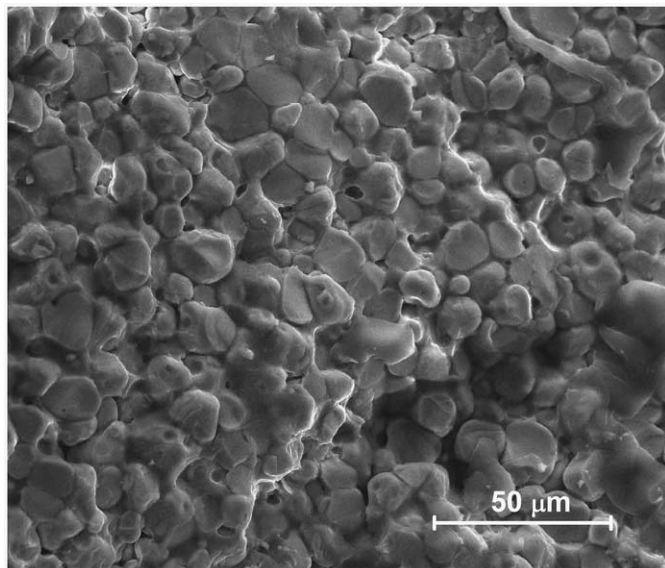


Fig. 9. SEM image of the powder prepared by solution combustion synthesis (sample 2).

Table 3

Comparison of the results reported here with the results presented by other authors.

Reference	Synthesis method	Sintering temperature (°C)	Soaking time (h)	Relative density (%)
This paper	Combustion synthesis	1400	2	95
[2]	Ceramic method	1600	12	> 95
[10]	Ceramic method	1550	48	95

**Fig. 10.** SEM image of sample 2 after sintering at 1400 °C for 2 h.

1400 °C for 2 h (Fig. 10) indicates that few closed pores exist and the size of the grains is less than 15 μm.

4. Conclusions

The formation of CaZrO₃ was investigated using two different methods: solution combustion synthesis and the traditional ceramic method.

In the case of the ceramic method – starting from a stoichiometric mixture of Ca(NO₃)₂ and ZrO₂ – a heat treatment of 1 h at 1000 °C leads to the formation of several crystalline phases: CaZrO₃, CaO, ZrO₂ and CaO stabilized ZrO₂ solid solution. Therefore, the formation of single-phase CaZrO₃ requires temperatures exceeding 1000 °C. Unfortunately, due to the elevated annealing temperature, the resulting powder is highly agglomerated and has low surface area (1.4 m²/g).

On the other hand, solution combustion synthesis enables the formation of pure crystalline CaZrO₃ powder directly from the

combustion reaction between Ca(NO₃)₂, ZrO(NO₃)₂ and β-C₃H₇NO₂. In this case no additional heat treatment is required. Although no advanced milling was performed, the as-prepared CaZrO₃ powder had large surface area (21.5 m²/g) and small crystallite size (23.9 nm). The subsequent annealing of combustion synthesized CaZrO₃ powder is a detrimental operation since it leads to an increase of the crystallite size and a decrease of the specific surface area.

The CaZrO₃ powder resulting from the combustion reaction was pressed into pellets (200 MPa) and then sintered at 1400 °C for 2 h, reaching 95% of theoretical density.

Experimental observations regarding the formation of single-phase CaZrO₃ directly from the combustion reaction – without any annealing step – are an undeniable advantage of the combustion method. In addition, the excellent sintering behavior of CaZrO₃ powder prepared by solution combustion synthesis suggests that this method represents a rapid, cheap and economical solution for CaZrO₃ powder preparation.

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