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Short communication

# $Ca_{0.15}Zr_{0.85}O_{1.85}$ powder from oxalate precursor: Microwave aided synthesis and thermal characterization

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ABSTRACT

Calcia stabilized zirconia ($Ca_{0.15}Zr_{0.85}O_{1.85}$) (CSZ) an oxygen ion conducting electrolyte was synthesized from mixed oxalate precursor, namely calcium zirconyl oxalate (CZO). CZO heated in microwave heating system for 1 h yielded the stabilized zirconia in the cubic form at 400 °C. Same precursor (CZO) heated in resistance heated furnace for 1 h yielded pure CSZ at 800 °C. Thermogravimetry, differential thermal analysis and X-ray diffraction techniques were used to characterize the precursor and optimize the conditions for microwave processing. BET surface areas of CSZ powders prepared by conventional and microwave heating method at 800 and 400 °C are 3.28 and 4.46 $m^2\ g^{-1}$, respectively.

## 1. Introduction

Zirconium dioxide ($ZrO_2$) has a M.P. ~2700 °C. It transforms from monoclinic to tetragonal form at about 1100 °C. This undesirable phase transformation can be eliminated by stabilization of zirconium dioxide ($ZrO_2$) in cubic phase. $ZrO_2$ could be stabilized in the cubic phase by the addition of both alkaline earth as well as rare earth oxides in appropriate proportion [1]. Stabilized zirconia is technologically important material and has been widely used in various high temperature refractory applications [2]. It acts as an oxygen ion conducting electrolyte and is used for the construction of galvanic cells [3,4]. It is also used in the development of oxygen sensors [5], solid state batteries and the solid oxide fuel cells [6].

Different methods of preparation of stabilized zirconia (in cubic phase) are reported in literature. These includes (1) conventional method [7,8], (2) hydroxide co-precipitation [3], (3) EDTA-precipitation [9] and (4) alkoxide method [10]. Synthesis of CSZ by all these methods requires heating of reactants at high temperature (800–1300 °C) for long periods (12–24 h).

The tetravalent zirconium (Zr) atom in CSZ replaced by divalent calcium (Ca) produces oxygen ion vacancies in the CSZ lattice. These vacancies have been reported to interact strongly with the microwave field [11]. In our previous work [12–15] we have shown that microwave technique can be effectively used to synthesize the mixed oxide powders ($BaTiO_3$, $LaCoO_3$, $LaCrO_3$, $NaZr_2P_3O_{12}$, etc.) at much lower temperatures than by normal ceramic technique [16]. The strong microwave interaction of oxygen vacancies in doped $ZrO_2$, could possibly facilitate the synthesis of CSZ at fairly low temperature. In this paper we report the synthesis of CSZ from CZO precursor. No literature data is available on the synthesis of CSZ from CZO precursor. Thermal techniques, TG and DTA were used to arrive at the optimum temperature of synthesis of CSZ from its precursor in microwave system.

## 2. Experimental

### 2.1. Preparation of CZO precursor

Zirconyl chloride ($ZrOCl_2{\cdot}8H_2O$) and calcium carbonate ($CaCO_3$) used for the synthesis were procured from Central Drug House (P) Ltd., New Delhi. Oxalic acid ($C_2H_2O_4{\cdot}2H_2O$) was procured from E. Merck (India) Ltd. Mixed oxalate precursor was prepared from aqueous solutions of zirconyl chloride, calcium carbonate and oxalic acid. Aqueous solution of zirconyl chloride was prepared by dissolving 27.391 g $ZrOCl_2{\cdot}8H_2O$ in 100 mL distilled water. In this solution 1.502 g $CaCO_3$ was added slowly with a constant stirring. Aqueous solution of oxalic acid was prepared by dissolving 12.607 g $C_2H_2O_4{\cdot}2H_2O$ in distilled water. Cation solution was added to the oxalic acid solution slowly with constant stirring. Precipitate formed was separated, washed first with distilled water,

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then with acetone and dried in the oven at 40 °C for 12 h. The white compound formed was analyzed and assigned the formula $Ca_{0.15}Zr_{0.85}O(C_2O_4)\cdot 6H_2O$ (CZO).

### 2.2. Thermogravimetry (TG) and differential thermal analysis (DTA)

Simultaneous TG/DTG and DTA curves of CZO were recorded on 3.118 mg of sample in flowing nitrogen at the heating rate of 10 °C $min^{-1}$ using the thermogravimetric (Diamond TG/DTA) system. In addition DTA plot of the decomposition of CZO was recorded in static air at the heating rate of 10 °C $min^{-1}$, using the instrument supplied by Universal Thermal Analysis Instruments, Mumbai, built to our specifications. Calcined alumina was used as a reference material for recording the DTA curve.

### 2.3. Synthesis of calcia stabilized zirconia ($Ca_{0.15}Zr_{0.85}O_{1.85}$)

CSZ was prepared by heating CZO in a resistance heated furnace as well as in microwave heating system. CZO was heated in resistance heated furnace in temperature range 400–800 °C with an interval of 100 °C for 1 h. In separate experiments it was heated in microwave heating system in the temperature range 400–600 °C at an interval of 100 °C for the same period.

The details of microwave system used in the present study are described elsewhere [12,17]. The microwave oven used could supply maximum 750 W input power. The power to the unit could be maintained to a constant set value to fix the desired temperature needed for the experiments, employing the proportional type (PID) temperature controller coupled to a solid state relay (SSR). A shielded chromel-alumel thermocouple was used as a sensor for controlling the input power to the microwave oven at the set temperature. The thermocouple shield had to be grounded to avoid sparking between the thermocouple tip and magnetron. The temperature of the sample could be maintained constant to ±1 °C and measured by a separate calibrated chromel-alumel thermocouple. The influence of microwave field on the measured temperature, if any, was checked by momentarily putting off the microwave oven. No difference was observed in the temperature displayed on the indicator. The sample contained in a cylindrical zirconia crucible was surrounded symmetrically by four silicon carbide rods, which act as preheaters for the samples poorly interacting with the microwaves at ambient temperature. The system was calibrated for temperature by measuring the temperature in steps and physically observing the melting of inorganic compounds such as $KNO_3$, NaCl, etc. contained in silica crucible. The multimode microwave system used in the present study is identical to that described by Roy et al. [18].

The products obtained after the heat treatment at different temperatures were analyzed using X-ray diffractometer (Philips) using monochromatised X-ray beam of wavelength 0.15405 nm.

Surface area of CSZ powder was measured using BET gas adsorption technique.

## 3. Results and discussion

### 3.1. Thermogravimetry (TG) and differential thermal analysis (DTA) of CZO

The simultaneous TG/DTG and DTA curves recorded for the CZO are represented in Fig. 1. The TG curve shows that the CZO decomposes in three steps involving dehydration and decarboxylation.

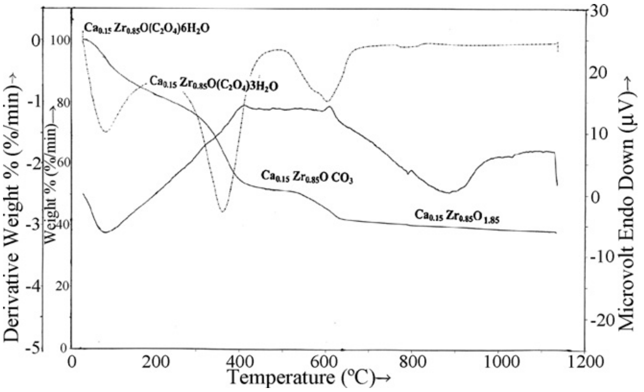

**Fig. 1.** TG, DTG and DTA curve of CZO recorded in flowing nitrogen.

**Table 1**
TGA data on as dried CZO precursor

| Steps | Temperature range (°C) | Expected weight loss (%) | Observed weight loss (%) |
|---|---|---|---|
| I | RT–300 | 18.28 | 18.50 |
| II | 300–500 | 27.75 | 28.32 |
| III | 500–650 | 15.70 | 15.35 |
| Total weight loss | | 61.73 | 62.17 |

The sequence of the steps could be expressed as

$$Ca_{0.15}Zr_{0.85}O(C_2O_4)6H_2O \rightarrow Ca_{0.15}Zr_{0.85}O(C_2O_4)3H_2O + 3H_2O \tag{1}$$

$$Ca_{0.15}Zr_{0.85}O(C_2O_4)3H_2O \rightarrow Ca_{0.15}Zr_{0.85}OCO_3 + 3H_2O + CO \tag{2}$$

$$Ca_{0.15}Zr_{0.85}O(CO_3) \rightarrow Ca_{0.15}Zr_{0.85}O_{1.85} + CO_2 + 0.075O_2 \tag{3}$$

The mass losses expected in each of the above decomposition steps were in good agreement with those calculated from the TG curve (Table 1).

DTA curve recorded in static air atmosphere is presented in Fig. 2. The first two endothermic peaks in DTA located around 110 and 330 °C are due to dehydration. Second endothermic peak was followed by two exothermic peaks in the temperature range 370–600 °C indicating the decomposition of carboxylate with the evolution of CO and its subsequent oxidation to $CO_2$. Finally, a small

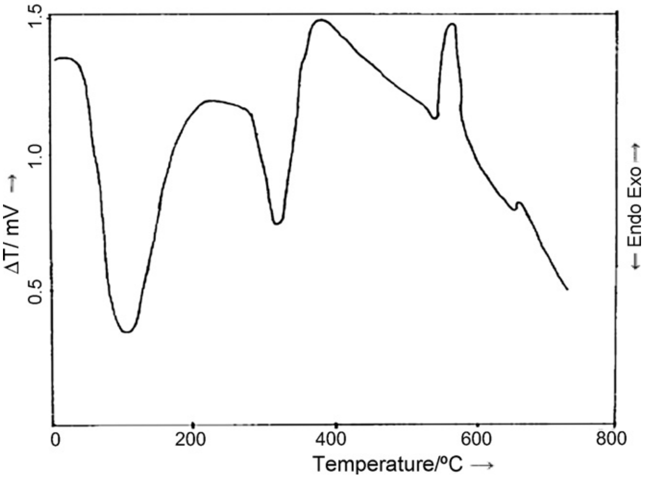

**Fig. 2.** DTA curve of CZO recorded in static air.

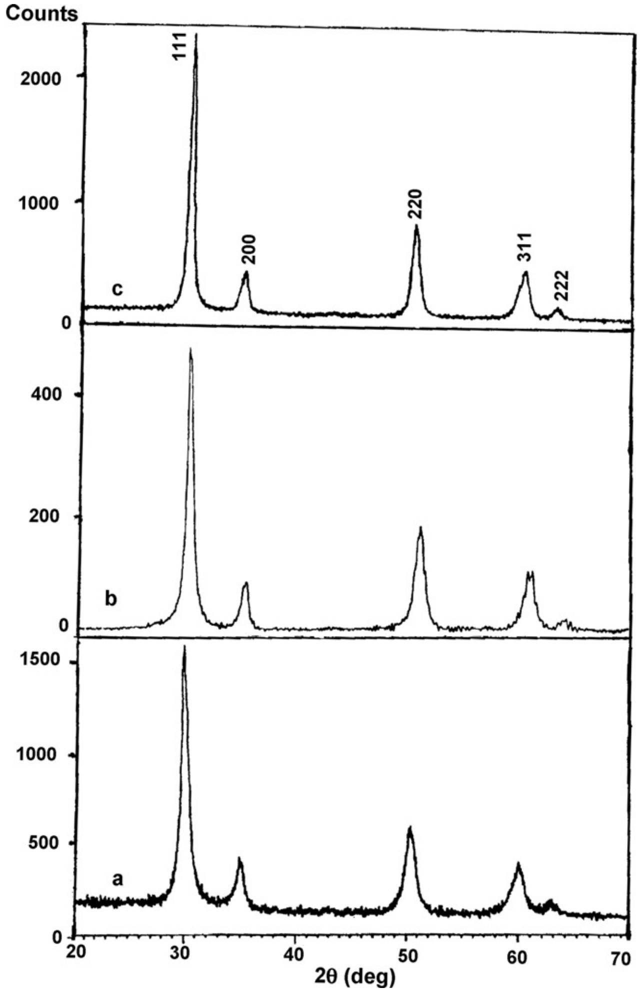

**Fig. 3.** XRD patterns of CZO calcined in microwave heating system at (a) 400 °C and resistance heated furnace at (b) 600 °C and (c) 800 °C for 1 h.

endotherm is observed ∼650 °C indicating the formation of CSZ phase according to reaction (3).

TG and DTA curves show that CZO decomposes through three steps giving final product CSZ above 600 °C. This information was used to choose the calcinations temperature for CZO to yield final product CSZ.

### 3.2. *X-ray diffraction patterns*

The X-ray diffraction pattern of CZO calcined in microwave heating system at 400 °C for 1 h is presented in Fig. 3a. The XRD pattern shows that CZO heated in microwave heating system at 400 °C for 1 h yields stable CSZ cubic phase. The XRD pattern recorded is in good agreement with that reported for cubic CSZ by earlier workers [9,19,20]. CZO precursor heated in microwave heating system at higher temperatures (500 and 600 °C) yields the same product but is more crystalline as concluded from its line width. XRD pattern of the CZO heated in resistance heated furnace at 400 °C for 1 h indicates that the product formed at this temperature is amorphous in nature. XRD patterns of the CZO heated in resistance heated furnace at 600 and 800 °C for the same period are presented in Fig. 3b and c, respectively. The XRD pattern of the product obtained at 600 °C in resistance heated furnace (Fig. 3b) indicates the formation of CSZ but is relatively less crystalline compared to the product obtained at 800 °C under identical conditions. Also, the peaks $\sim 2\theta = 60$ and 62.5 are not well resolved. Fig. 3c shows that CZO heated in resistance heated furnace gives pure crystalline CSZ at 800 °C.

Surface areas of CSZ powders prepared by conventional and microwave heating technique measured using BET gas adsorption technique are 3.28 and 4.46 $m^2\,g^{-1}$, respectively.

## 4. Conclusion

CSZ is technologically important compound. Various methods of synthesis of CSZ are reported in literature [7–10]. Synthesis of CSZ by all these methods requires high temperature and long heating period. Present paper reports the microwave assisted low temperature synthesis of CSZ powder from the oxalate precursor. Mixed oxalate precursor in combination with microwave technique yielded pure cubic CSZ at temperature as low as 400 °C within 1 h. In situ generated oxides formed by thermal decomposition of mixed oxalates are expected to be much more reactive [21] and would react much faster to produce the product layer at the interface of the two oxide particles. Since this layer contain oxygen vacancies caused by the partial substitution of $Zr^{4+}$ by $Ca^{2+}$, these vacancies could interact strongly with microwave and produce sharp local heating. This will result in the propagation of the reaction in the bulk and increase the overall reaction rate. The results presented in this paper suggest that the microwave heating technique is superior compared to the conventional resistance heating technique and yields the products at the lowest temperature within the short time, if suitable precursor is selected in the synthesis.

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