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Facile, scalable synthesis of nanocrystalline calcium zirconate by the solution combustion method

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Abstract

Single phasic nanocrystalline $CaZrO_3$ powder has been synthesized by glycine nitrate solution combustion method around 300 °C using nitrate as oxidant and glycine as fuel. The as prepared product obtained as a result of combustion itself is crystalline and nearly single phasic $CaZrO_3$ confirmed by X-ray diffraction (XRD). The product calcined at 600 °C reveals carbonate free single phasic orthorhombic structured $CaZrO_3$. To study the impact of oxidant to fuel ratio (O/F) and ignition temperature, a systematic variation of O/F and ignition temperature of combustion reaction has been investigated by analyzing the products through XRD in each case. These products have been characterized by XRD, Fourier Transform Raman spectroscopy, Thermal Analysis (TGA/DTA), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Raman Spectrum reveals single phasic nanocrystalline perovskite $CaZrO_3$. Spherical shaped particles were observed through SEM. TEM results also confirm the particles to be in nano regime (30–90 nm).

Keywords: Solution combustion method; Calcium zirconate; XRD; TEM

1. Introduction

Perovskite structured $CaZrO_3$ is an attractive material for a wide variety of applications in various fields due to its excellent electrical, mechanical, catalytic, luminescence properties and their chemical stability. It is a ceramic material that is currently being used as multilayer ceramic capacitors [1], solid electrolyte [2], crystalline host for phosphor materials [3], moderate temperature thermal barrier [4], catalyst [5], it exhibits excellent corrosion resistance against alkali, earth alkali oxides, and basic slags [6]. Calcium zirconate, $CaZrO_3$, is a refractory compound, which congruently melts at 2340 °C [7]. $CaZrO_3$ crystallites as an orthorhombic perovskite structure at room temperature. At 1750 °C and above $CaZrO_3$ undergoes polymorph transformation from orthorhombic to cubic phase.

$CaZrO_3$ can be prepared either by the solid state method or by wet chemical methods. Although, the solid state method is easily performed, obviously, it has major drawbacks such as longer reaction duration, large particle size, wide grain size distribution, low surface area, high agglomeration degree, lack of chemical homogeneity, etc., which affect the sintering process and also the functional properties of the products. In order to overcome these disadvantages, wet chemical methods have been preferred. Wet chemical methods like Modified Pechini sol–gel method, combustion method have been used to prepare $CaZrO_3$ powder. Some important literatures are cited below. Prasanth et al. [8] prepared pure $CaZrO_3$ powders via the combustion method using citric acid as complexing agent and urea as fuel by calcining the product at 700 °C. Gonenli and Tas [9] adopted the single fuel method using urea as fuel to prepare $CaZrO_3$ by the combustion method. Pure phase was obtained by calcining the product at 1200 °C for 17 h.

Combustion method with appropriate fuels has been proved to be an efficient and the cost effective method for the preparation of nanocrystalline multi-component metal oxides [10–12]. It has the advantages of applying inexpensive, maintaining a relatively simple and fast preparation process,

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and achieving fine powders with high homogeneity. It is also a scalable batch process, if process parameters are optimized. The process is due to a redox exothermic reaction between nitrate ions and the fuel. The fast expulsion of gases disintegrates the precursor thus yielding nanoparticles. The oxidizer and the fuel are mixed in a fixed proportion, which provides plenty of heat thereby promoting an exothermic reaction. The onset temperature for a rapid reaction between oxidizer and fuel is termed as the ignition temperature.

An auto-ignition combustion process was first used by Zhang et al., [13] to synthesize $CaZr_{0.9}In_{0.1}O_{3-\delta}$ powders. In this process glycine was used as fuel along with nitrates as oxidant. Ignition temperature of 147 °C followed by calcination at 1000 °C was employed to prepare the product. This product has the impurity of calcia stabilized zirconia, another functional material, as a competing phase for $CaZrO_3$. We report here synthesis of $CaZrO_3$ by the simple single fuel approach (glycine) to obtain nearly single phasic $CaZrO_3$ (impurity $CaCO_3$, 7%) just after combustion. $CaCO_3$ is a reactant only and is not a competing functional material to $CaZrO_3$ as contrast to earlier report [13]. It is expected not to influence the properties of $CaZrO_3$. However, at 600 °C the unreacted $CaCO_3$ is made to react with remaining ZrO_2 (not observed by XRD) to form $CaZrO_3$. In this paper we demonstrate that the glycine/nitrate solution combustion method can be conveniently employed to prepare single phasic nanocrystalline $CaZrO_3$ at lower temperature (300 °C).

2. Experimental

2.1. Method

Zirconium oxynitrate and calcium nitrate were used as oxidant and glycine was used as fuel. A typical procedure is described below. Different oxidant to fuel (fuel rich, stoichiometry and fuel lean) ratios were used to prepare single phase nanocrystalline $CaZrO_3$. O/F ratio of 1 was used for preparing nanocrystalline $CaZrO_3$ powders and this ratio was arrived at by optimizing experimental conditions, subsequent observations during combustion and analysis of products. Optimized quantities of metal nitrates and fuel were dissolved in minimum amount of distilled water. This solution was stirred for an half an hour for complete dissolution and for complex formation of metal ions with organic ligands. The transparent clear solution was directly introduced into the preheated furnace kept at 300 °C. In the beginning the solution boils, foams and undergoes flaming combustion, yielding a very voluminous white powder within 10 min. The schematic representation of preparation of nanocrystalline $CaZrO_3$ is given in Fig. 1. The as prepared powder obtained at O/F ratio of 1 was calcined at different temperatures of 500 °C/3 h, 600 °C/3 h, 700 °C/3 h, 900 °C/2 h to study the phase evolution of the product with temperature. Impact of oxidant to fuel ratio and ignition temperature (300 °C, 400 °C and 500 °C) was also studied on the phase formation of $CaZrO_3$.

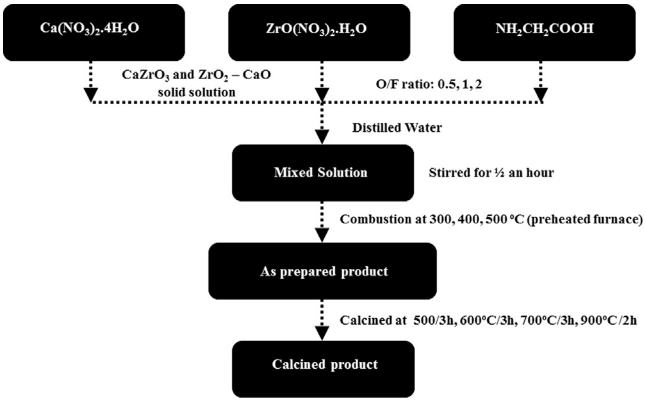

Fig. 1. Schematic representation of preparation of nanocrystalline $CaZrO_3$.

2.2. Characterization

Phase identification and the crystallite sizes of the products were obtained by a Bruker D8 Advance (Bruker AXS GmbH, Karlsruhe, Germany) powder X-ray diffractometer with Cu Kα source. The operation voltage and current were 40 kV and 30 mA respectively. Raman spectra were collected using a BRUKER RFS 27 (Bruker, Germany) stand alone Fourier transform – Raman spectrometer. The excitation wavelength used was 1064 nm from Nd:YAG laser source. The spectra were collected in the frequency range of 100–600 cm^{-1}. The precursor was subjected to Thermal Analysis (DTA and TGA) with thermal analyzer (Q600, TA Instruments, USA). This experiment was conducted up to 1200 °C with a heating rate of 10 °C min^{-1} in nitrogen. Morphology of the product was studied with well dispersed, gold sputtered powder over carbon tape using Scanning Electron Microscope (Inspect F equipment, FEI, USA) at an accelerating voltage of 30 kV. Transmission electron micrographs have been recorded using a copper grid dipped in a suspension containing $CaZrO_3$ particles dispersed in acetone by ultrasonication using a Tecnai T20 electron microscope (FEI, USA) at an accelerating voltage of 200 kV.

3. Results and discussion

3.1. Impact of process parameters

3.1.1. Oxidant to fuel ratio

The oxidant to fuel ratio is one of the important parameter that plays a major role on the combustion process and product formation [14]. In our present study, three different oxidant to fuel ratios (O/F = 0.5, 1 and 2) are attempted and the corresponding XRD patterns of the as synthesized products just after combustion are shown in Fig. 2. It (Fig. 2b) clearly shows the formation of $CaZrO_3$ in near single phase at O/F ratio = 1. At fuel lean region (O/F = 2) the product is amorphous, probably, indicating the heat liberated during combustion is not sufficient for the formation of crystalline product. At fuel rich (O/F = 0.5) region $CaZrO_3$ is formed with more $CaCO_3$ as an impurity (34%). The observed results may be