Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 5363–5368

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

The effects of temperature, holding time and salt amount on formation of nano $CaZrO_3$ via molten salt method

R. Fazli [a,*], M. Fazli [b], Y. Safaei-Naeini [a], F. Golestani-fard [a], A. Mirhabibi [a]

[a] School of Metallurgy and Materials Engineering, Iran University of Science and Technology, Tehran, Iran
[b] Department of Materials Science and Engineering, University of Malek Ashtar, Tehran, Iran

Received 28 January 2012; received in revised form 5 March 2012; accepted 18 March 2012
Available online 28 March 2012

Abstract

Nano-particles of $CaZrO_3$ were successfully synthesized at 800 °C using the molten-salt method, and the effects of processing parameters, such as temperature, holding time and amount of salt on the crystallization of $CaZrO_3$ were investigated. Na_2CO_3, $CaCl_2$ and nano-ZrO_2 were used as starting materials. On heating, Na_2CO_3 reacted with $CaCl_2$ to form NaCl and in situ $CaCO_3$. Na_2CO_3–NaCl molten eutectic salt provided a liquid medium for reaction of $CaCO_3$ and ZrO_2 to form $CaZrO_3$. The results demonstrated that $CaZrO_3$ started to form at about 700 °C and that, after the temperature was increased to 1000 °C, the amounts of $CaZrO_3$ in the resultant powders increased with a concomitant decrease in $CaCO_3$ and ZrO_2 contents. After washing with hot-distilled water, the samples heated for 3 h at 800 °C were single-phase $CaZrO_3$ with 70–90 nm particle size. Furthermore, the synthesized $CaZrO_3$ particles retained the size and morphology of the ZrO_2 powders, which indicated that a template formation mechanism dominated the formation of $CaZrO_3$ by molten-salt synthesis.

Keywords: Molten salt method; Nano materials; Calcium zirconate; Template growth

1. Introduction

Calcium zirconate ($CaZrO_3$) due to its valuable properties such as high melting point (2340 °C), high dielectric permittivity and low dissipation factor, is a ceramic material that is currently being used in a wide range of applications: multilayer ceramic capacitors, solid electrolyte, crystalline host for phosphor materials, moderate temperature thermal barrier catalyst, etc. [1–3]. There are several methods for the synthesis of this material. $CaZrO_3$ powders is conventionally synthesized via a high temperature (1500 °C) solid state reaction of powdered CaO (or $CaCO_3$) and zirconia (ZrO_2) (conventional mixed oxide synthesis (CMOS)). As the reactions are generally controlled by slow diffusion mechanisms, highly reactive raw materials, high temperatures and long times have to be used for the reactions to achieve completion. The resultant product is a hard mass, which often needs to be crushed and ground to achieve the desired particle size [4]. Other methods such as electro-fusion [5], wet chemical [6–8], combustion [9] and mechanical alloying (MA) [10] have been reported for synthesis of calcium zirconate. Almost all above methods are not commodious, because their synthesis temperatures are high in solid state and electro-fusion methods and thus need so much thermal energy and time. Therefore, it is necessary to follow methods decreasing synthesis temperature and time. Besides the above techniques, a low temperature synthesis technique, molten salt synthesis (MSS), is beginning to attract interest. In this method, a salt is used as liquid medium, the reactions are faster and synthesis is complete in significantly lower temperature and time [4,11–13]. Zushu Li et al. investigation is perhaps the most important research on the synthesis of $CaZrO_3$ via molten salt method that prepared $CaZrO_3$ powder at 1050 °C for 5 h [4]. In this work, $CaZrO_3$ has been synthesized by heating of Na_2CO_3, $CaCl_2$ and nano-ZrO_2 mixture and the effect of temperature, holding time and salt to oxide ratio on synthesis process has been investigated. Also, synthesis mechanism has been analyzed.

* Corresponding author. Tel.: +98 937 2139453.
E-mail address: rhmnfazli@yahoo.com (R. Fazli).

0272-8842/$36.00
doi:10.1016/j.ceramint.2012.03.043

2. Experimental procedure

Na_2CO_3 (Merck, Germany, D_{50} = 1 mm, 99.5% pure), $CaCl_2$ (Merck, Germany, D_{50} = 4 mm, 99.5% pure) and nano-ZrO_2 (Neutrino, Germany, D_{50} = 60 nm, >99% pure) were used as starting materials. Firstly, stoichiometric compositions of Na_2CO_3 and $CaCl_2$ were completely mixed and then heated at 150 °C for 12 h to dry. Agglomerated nano-ZrO_2 were dispersed in distilled water that its pH was controlled in 4 using hydrochloric acid. To more dispersion, the suspension was placed 1 h in ultrasonic probe. Then, Na_2CO_3–$CaCl_2$ mixture were added to completely dispersed nano-ZrO_2 and obtained mixture were stirred 1 h to homogenize extremely. The mixture was fully dried at 120 °C for 12 h. Molar ratio of mixture is ZrO_2:$CaCl_2$:Na_2CO_3 = 1:1:1.2. Agglomerations of obtained powder that is a completely homogenous mixture, were broken using an agate mortar and then sifted to pass through a 325 mesh screen (45 μm). Finally, the mixture (20 g) was placed in an alumina crucible covered with an alumina lid, heated to 700, 800, 900 and 1000 °C and held for 1,3 and 5 h. For investigation of the effect of salt to oxide ratio on the synthesis process, the samples were heated in optimum temperature with 1:1, 2:1, 3:1 and 4:1 salt to oxide ratios. The heating and cooling rates were 3 °C/min and 5 °C/min, respectively. After cooling to room temperature, the solidified mass was washed and filtered in hot-distilled water five times to remove the salts. The obtained powder was then dried at 120 °C for 4 h. The phase formation and morphology of the synthesized powders were characterized via X-ray diffraction (XRD, Philips pw3710), scanning electron microscopy (SEM, Tescan Vega II) and transition electron microscopy (TEM, CM 200, Philips), respectively.

3. Results and discussion

3.1. Effect of temperature

Fig. 1 shows XRD patterns of samples heated for 3 h at different temperatures. It is obvious that optimum temperature for these samples is 800 °C. At this temperature, the samples are single-phase $CaZrO_3$ and $CaCO_3$ and ZrO_2 peaks are not observed. On the other words, ZrO_2 and $CaCO_3$ was completely transformed to $CaZrO_3$. At temperatures above 800 °C, the samples were likewise single-phase $CaZrO_3$ and

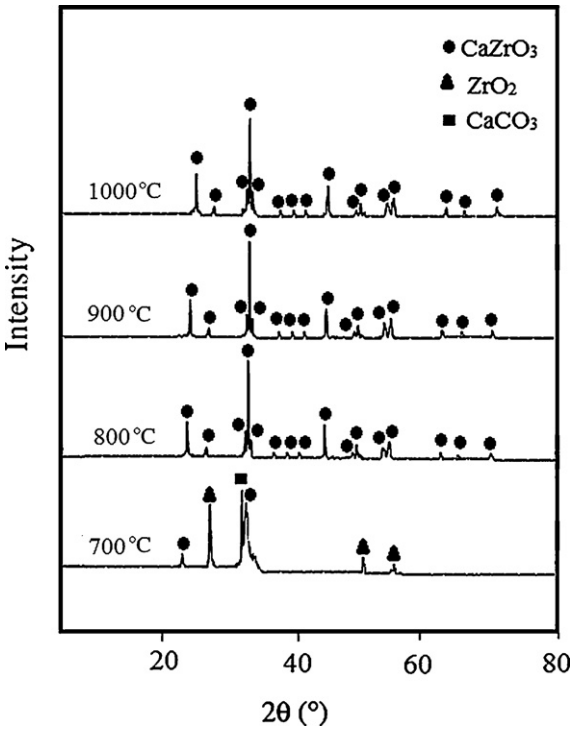

Fig. 1. XRD patterns of samples (water washed) heated for 3 h at different temperatures.

just their crystallinity has increased that was confirmed by means of increasing in peaks intensity. At 1000 °C, the peaks intensity has insignificantly decreased and peaks have partly become wider that can be attributed to acceding decomposition temperature of $CaZrO_3$. Thus, increasing in temperature is a very effective factor for completion of synthesis process.

Energy dispersive X-ray spectroscopy (EDS) micrograph of samples heated at 800 °C for 3 h shown in Fig. 2 confirms that optimum temperature for synthesized samples is 800 °C. As seen, almost only [Ca], [Zr] and [O] elements are observed and other elements have been eliminated.

3.2. Effect of holding time

Fig. 3 shows XRD patterns of samples heated for different holding times at 800 °C. It is seen that optimum holding time

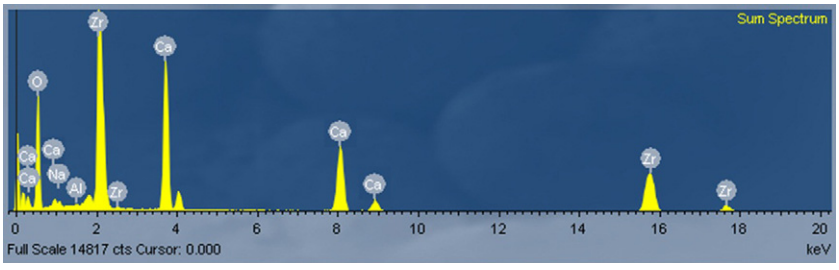

Fig. 2. EDS micrograph of samples heated at 800 °C for 3 h.