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Ceramics International 38 (2012) 5775–5781

CERAMICS INTERNATIONAL

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The effects of raw materials particle size and salt type on formation of nano-$CaZrO_3$ from molten salts

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Received 18 March 2012; received in revised form 7 April 2012; accepted 8 April 2012
Available online 15 April 2012

Abstract

Nano-$CaZrO_3$ was successfully synthesized at 800 °C using the molten-salt method, and the effects of salt type and raw materials particle size on the formation of $CaZrO_3$ were investigated. Na_2CO_3, $CaCl_2$, nano-ZrO_2 and micro-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 in both nano- and micro-ZrO_2 inclusive samples, $CaZrO_3$ 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 containing nano- and micro-ZrO_2 heated for 3 h at 800 °C and 1000 °C, were single-phase $CaZrO_3$ with 70–90 nm and 400–450 nm particle size, respectively. Also, the synthesis process was completed in lower temperatures using eutectic salts. 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; Nanomaterials; Calcium zirconate

1. Introduction

Calcium zirconate ($CaZrO_3$) is an important raw material for refractories and advanced ceramics due to its excellent thermal and electrical properties such as high melting point (2340 °C), high dielectric permittivity, and low dissipation factor [1–3]. There are several methods for the synthesis of this material. $CaZrO_3$ powder is conventionally synthesized via a high temperature (1500 °C) solid–solid 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 precursor powders, 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]. Another methods such as electro fusion [5], wet chemical [6–8], combustion [9] and mechanical alloying (MA) [10] have been reported for the synthesis of calcium zirconate. Almost all above methods are not commodious, because their synthesis temperatures are high 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, as a salt is used as liquid medium, the reactions are faster and synthesis is complete in significantly lower temperature and time [4,11–13]. Li et al. investigation is perhaps the most important investigation on the synthesis of $CaZrO_3$ via molten salt method that prepared $CaZrO_3$ powder in 1050 °C and 5 h [4]. In this work, nanoparticles of $CaZrO_3$ have been synthesized by heating of Na_2CO_3, $CaCl_2$ and ZrO_2 mixture and the effects of ZrO_2 particle size and salt type on microstructure and synthesis temperature have been investigated. Also, synthesis mechanism has been analysed.

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0272-8842/$36.00
http://dx.doi.org/10.1016/j.ceramint.2012.04.024

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), nano-ZrO_2 (Neutrino, Germany, $D_{50} = 60$ nm, >99% pure) and micro-ZrO_2 (Merck, Germany, $D_{50} = 250$ nm, 99.5% pure) were used as starting materials. Two mixtures were prepared from starting materials. The first was a mixture of Na_2CO_3, $CaCl_2$ and nano-ZrO_2, and the second was a mixture of Na_2CO_3, $CaCl_2$ and micro-ZrO_2. Firstly, Na_2CO_3 and $CaCl_2$ were mixed and then heated 12 h at 150 °C to dry completely. Agglomerated nano-ZrO_2 was dispersed in distilled water that its pH was controlled to 4 using hydrochloric acid. For more dispersion, the suspension was placed 1 h in ultrasonic probe. Then, Na_2CO_3–$CaCl_2$ mixture was added to completely disperse nano-ZrO_2 and the obtained mixture was 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). Dry mixing was used for preparation of micro-ZrO_2 inclusive mixture. For this purpose, Na_2CO_3, $CaCl_2$ and micro-ZrO_2 were completely mixed and ground at above molar ratio using an agate mortar to pass through a 100 mesh screen. Finally, both mixtures (20 g) were placed in an alumina crucible covered with an alumina lid, heated to 700, 800, 900 and 1000 °C and held for 3 h. 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

DTA/TG analysis was performed to determine the proper reaction temperature range as well as the reaction order in the molten-salt method. DTA/TG curve of Na_2CO_3, $CaCl_2$ and nano-ZrO_2 mixture has been shown in Fig. 1. The DTA curve exhibits an endothermic peak (peak a), which is associated with a slow weight loss (10%) in the TG curve at 100 °C. This weight loss is attributed to dehydration of the precursors. The small endothermic peak at approximately 150 °C (peak b) is related to the reaction between Na_2CO_3 and $CaCl_2$. The big endothermic peak at about 600 °C (peak c) is attributed to melting of Na_2CO_3–NaCl eutectic salt. The exothermic peak at approximately 700 °C (peak d) which is associated with a slow weight loss in the TG curve is related to formation of $CaZrO_3$. The small exothermic peak at 800 °C (peak e) is interpreted as the crystallization of the $CaZrO_3$ phase.

Fig. 2 shows the DTA/TG curve of Na_2CO_3, $CaCl_2$ and micro-ZrO_2 mixture. According to above, peaks a, b, c, d and f

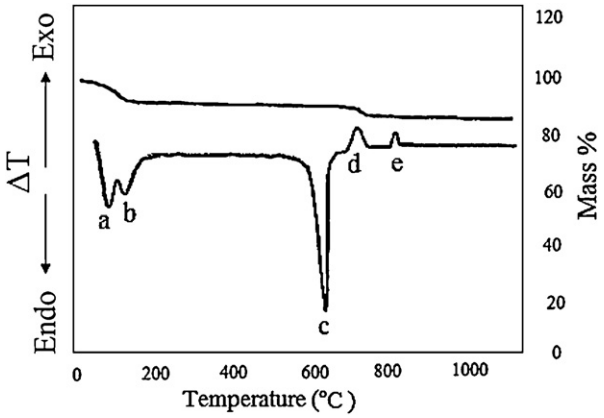

Fig. 1. DTA/TG curve of Na_2CO_3, $CaCl_2$ and nano-ZrO_2 mixture.

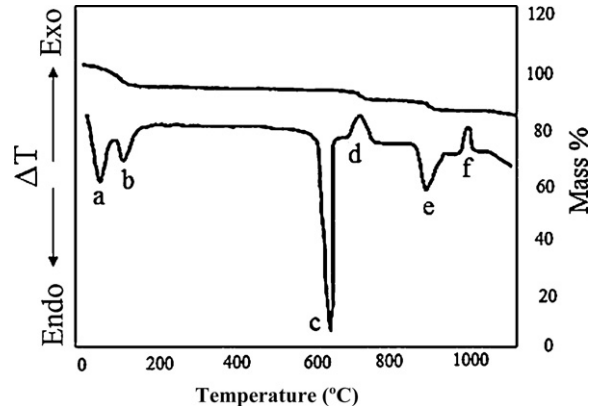

Fig. 2. DTA/TG curve of Na_2CO_3, $CaCl_2$ and micro-ZrO_2 mixture.

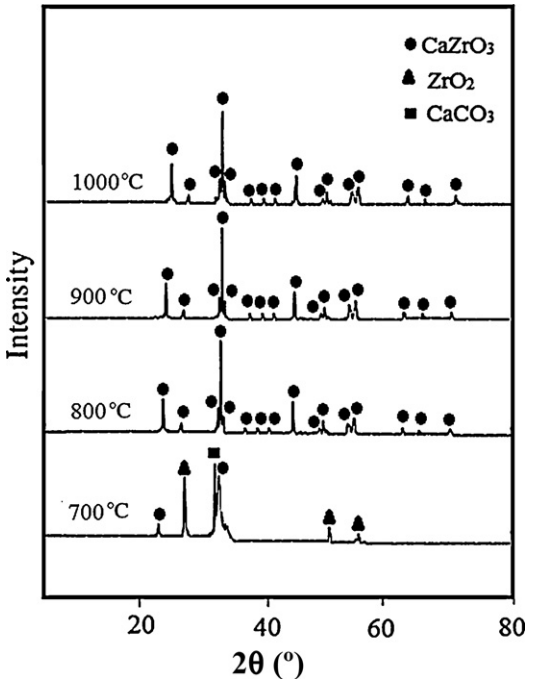

Fig. 3. XRD patterns of nano-ZrO_2 inclusive samples heated for 3 h at different temperatures.