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

R. Fazli [a,*], M. Fazli [b], 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

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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.

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

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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

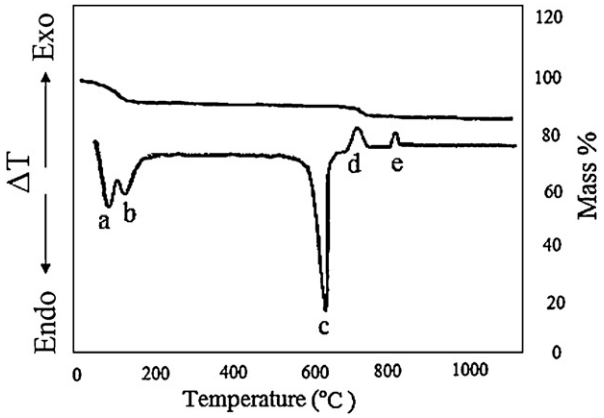

Fig. 1. DTA/TG curve of Na_2CO_3, $CaCl_2$ and nano-ZrO_2 mixture.

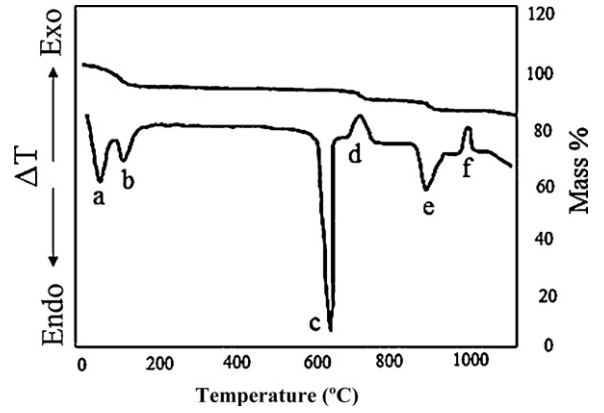

Fig. 2. DTA/TG curve of Na_2CO_3, $CaCl_2$ and micro-ZrO_2 mixture.

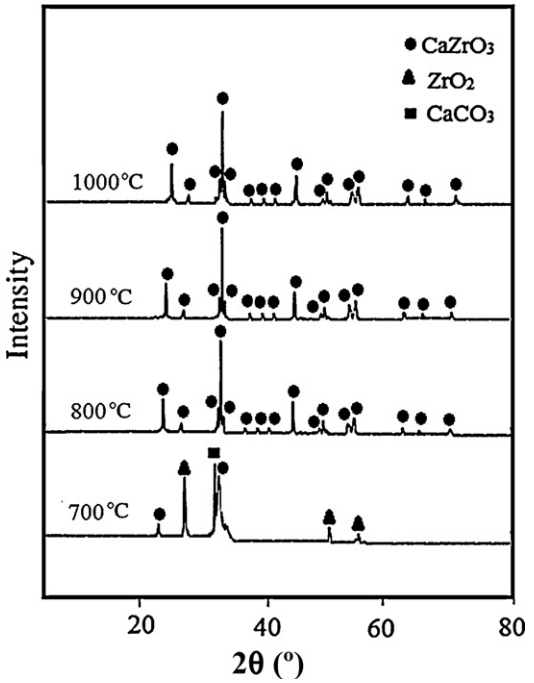

Fig. 3. XRD patterns of nano-ZrO_2 inclusive samples heated for 3 h at different temperatures.

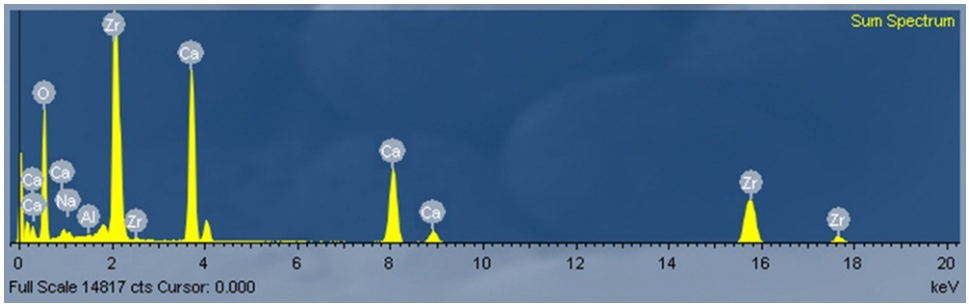

Fig. 4. EDS micrograph of nano-ZrO_2 inclusive samples heated at 800 °C for 3 h.

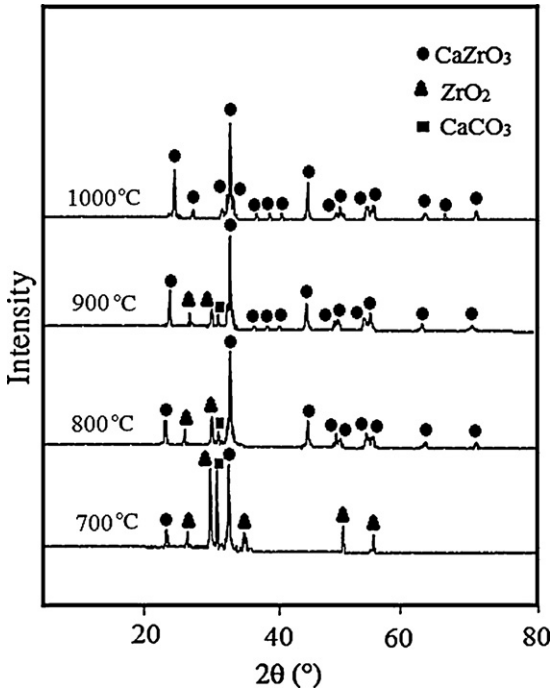

Fig. 5. XRD patterns of micro-ZrO_2 inclusive samples heated for 3 h at different temperatures.

are related to dehydration of the precursors, the reaction between Na_2CO_3 and $CaCl_2$, melting of eutectic salt, formation and crystallization of the $CaZrO_3$ phase, respectively. The endothermic peak at about 900 °C (peak e) which was not observed in nanozirconia inclusive mixture, can be attributed to the decomposition of $CaCO_3$ to CO_2 and CaO. In nano-ZrO_2 inclusive mixture, the synthesis process was completed before acceding decomposition temperature of $CaCO_3$ (910 °C). In other words, $CaCO_3$ was completely transformed to $CaZrO_3$. Therefore, this peak was not observed.

Fig. 3 shows XRD patterns of nano-ZrO_2 inclusive 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 $CaCO_3$ were completely transformed to $CaZrO_3$. At temperatures above 800 °C, the samples were likewise single-phase $CaZrO_3$ and just their crystallinity has increased that was confirmed by means of increasing in peaks intensity. At 1000 °C, the peak intensity has insignificantly decreased and peaks have partly become wider that can be attributed to acceding decomposition temperature of $CaZrO_3$.

Energy dispersive X-ray spectroscopy (EDS) micrograph of nano-ZrO_2 inclusive samples heated at 800 °C for 3 h shown in Fig. 4 confirms that optimum temperature for these samples is 800 °C. As seen, almost only [Ca], [Zr] and [O] elements are observed and another elements have been eliminated.

XRD patterns of micro-ZrO_2 inclusive samples heated 3 h at different temperatures have been shown in Fig. 5. It is seen that optimum temperature for these samples is 1000 °C that is confirmed by EDS micrograph of samples heated for 3 h at 1000 °C which is shown in Fig. 6. As seen, almost only [Ca], [Zr] and [O] elements are observed and another elements have been eliminated. At this temperature, synthesis was completed and ZrO_2 and $CaCO_3$ were completely transformed to $CaZrO_3$. Thus, in both mixtures, increasing in temperature was an effective factor for completion of the synthesis process.

Fig. 7 shows the SEM micrograph of nano-ZrO_2 inclusive samples heated 3 h at 800 °C. In this condition, just single-phase $CaZrO_3$ was observed and another phases have been eliminated. Particle size of synthesized $CaZrO_3$ was in the

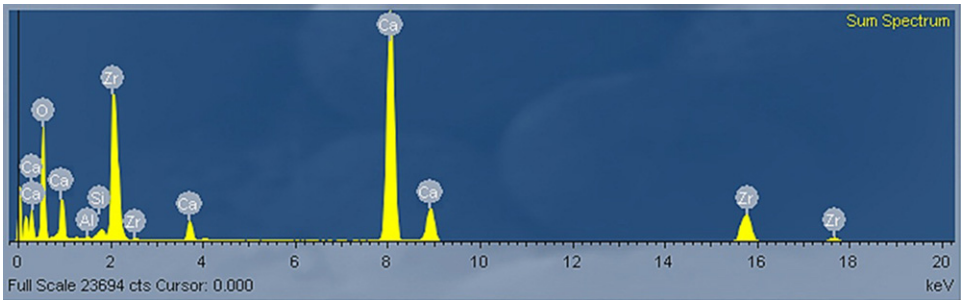

Fig. 6. EDS micrograph of micro-ZrO_2 inclusive samples heated at 1000 °C for 3 h.

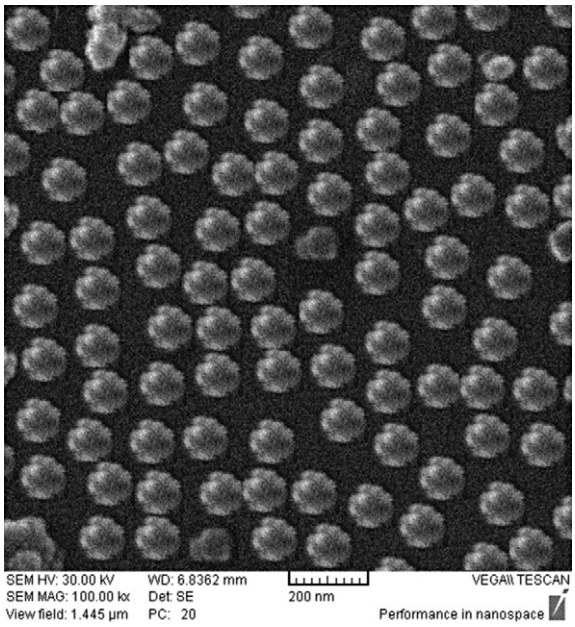

Fig. 7. SEM micrograph of nano-ZrO_2 inclusive samples heated 3 h at 800 °C.

range of 70–80 nm that was confirmed by TEM micrograph of these samples shown in Fig. 8. SEM micrograph of micro-ZrO_2 inclusive samples heated for 3 h at 10,000 °C has been shown in Fig. 9. According to the previous results, this temperature is the optimum temperature for these samples and just single-phase $CaZrO_3$ has been seen. Particle size of synthesized $CaZrO_3$ was in the range of 250–400 nm.

For investigation of salt type effect on the synthesis process, both mixtures were heated in the presence of eutectic (Na_2CO_3–NaCl) and singular (NaCl) salts. Melting points of these salts are 632 °C and 801 °C, respectively [14].

XRD patterns of nano-ZrO_2 inclusive samples heated for 3 h at 800 °C in the presence of two types of salts have been shown in Fig. 10. As observed, the synthesis process was completed using eutectic salt, but in the presence of singular salt, the

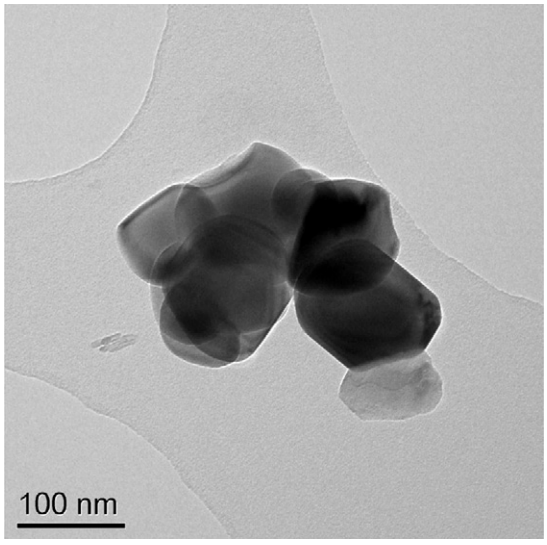

Fig. 8. TEM micrograph of nano-ZrO_2 inclusive samples heated for 3 h at 800 °C.

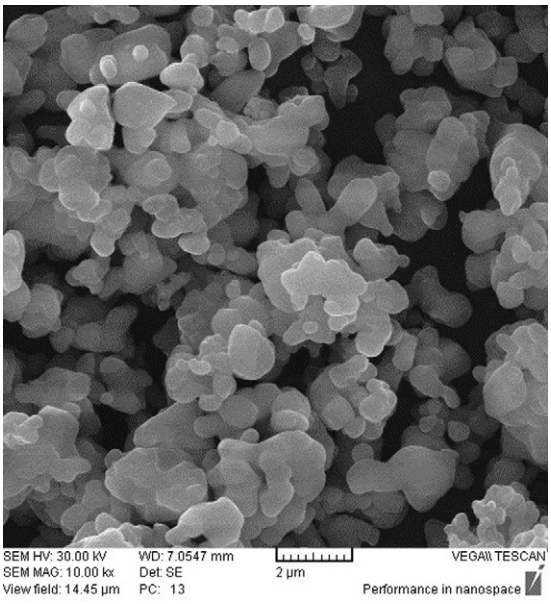

Fig. 9. SEM micrograph of micro-ZrO_2 inclusive samples heated for 3 h at 1000 °C.

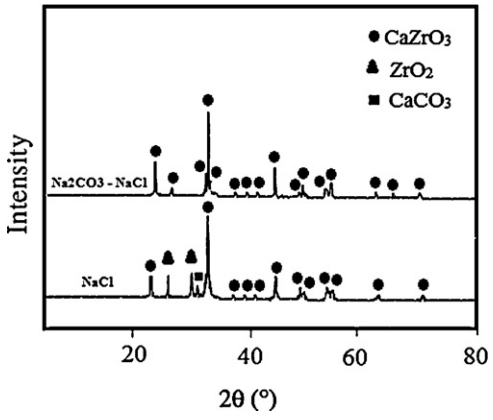

Fig. 10. XRD patterns of nano-ZrO_2 inclusive samples heated for 3 h at 800 °C in the presence of two types of salts.

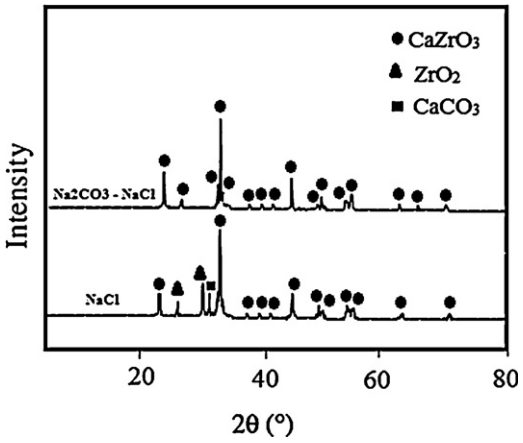

Fig. 11. XRD patterns of micro-ZrO_2 inclusive samples heated for 3 h at 1000 °C in the presence of two types of salts.

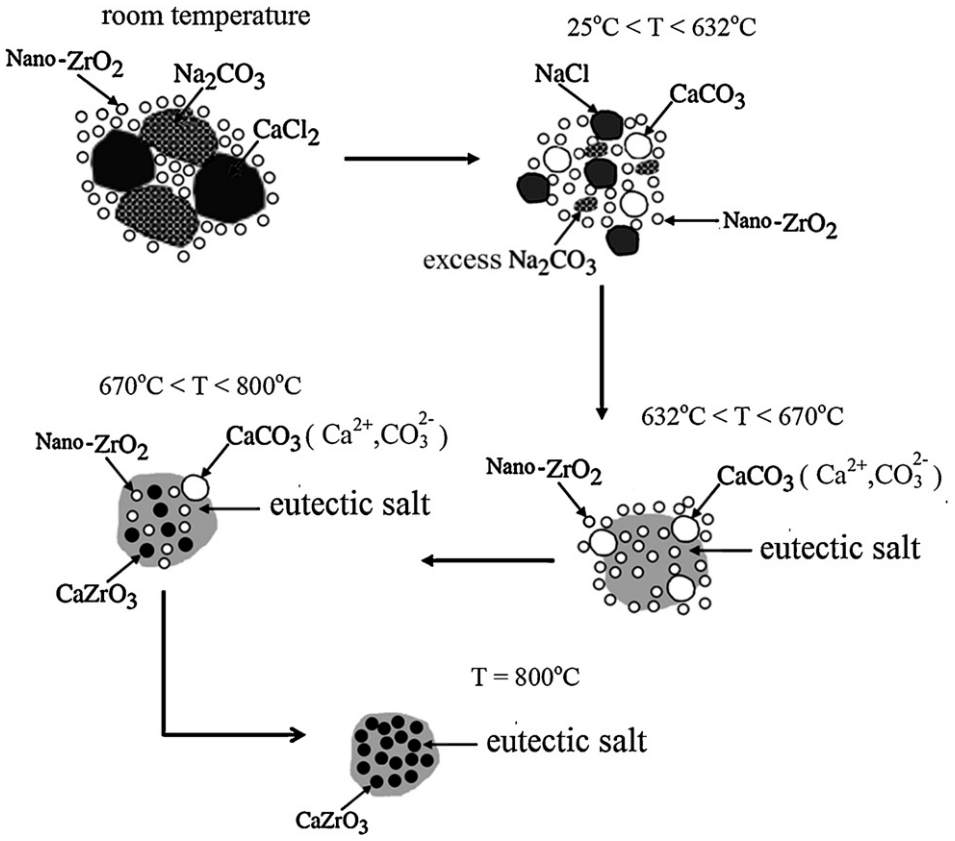

Fig. 12. Schematic diagram illustrating the synthesis of $CaZrO_3$ powder by heating nano-ZrO_2, $CaCl_2$ and Na_2CO_3.

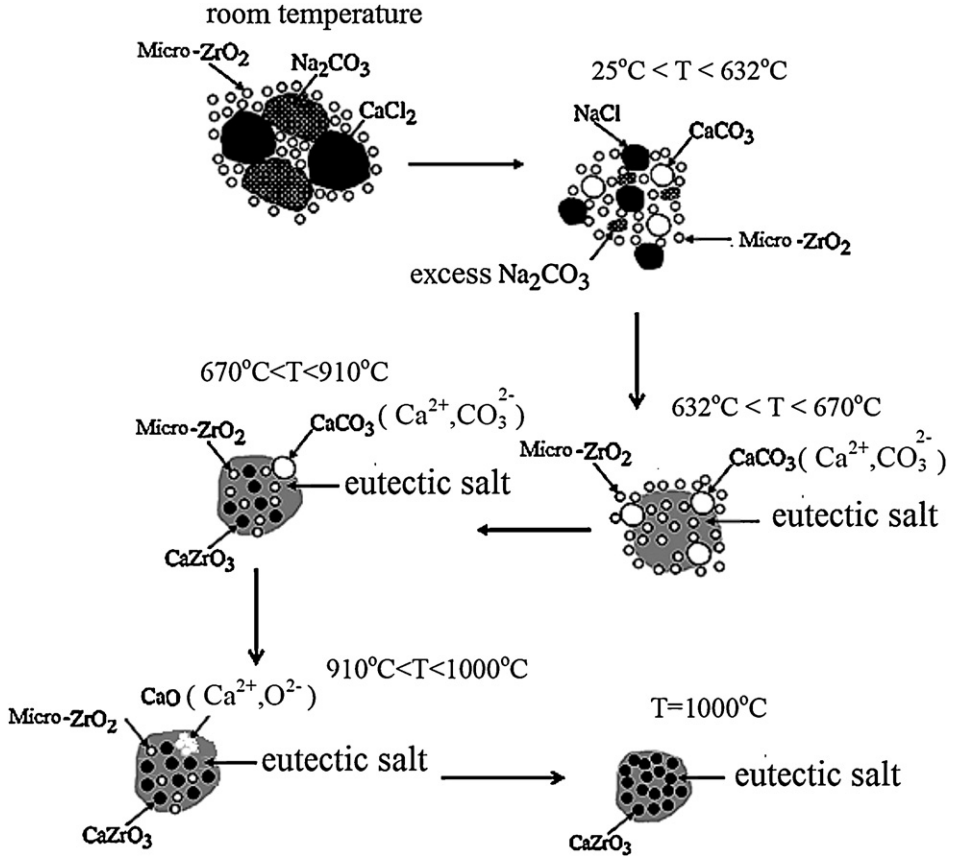

Fig. 13. Schematic diagram illustrating the synthesis of $CaZrO_3$ powder by heating micro-ZrO_2, $CaCl_2$ and Na_2CO_3.

samples still have not become single-phase $CaZrO_3$ and in addition of this phase, $CaCO_3$ and ZrO_2 were observed which can be attributed to lower melting point of eutectic salt that causes faster diffusion and more complete reactions. XRD patterns of micro-ZrO_2 inclusive samples heated for 3 h at 1000 °C in the presence of two types of salts have been shown in Fig. 11. According to above, in the presence of eutectic salt, the synthesis process has been completed.

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl \quad (\Delta G^0 = -118,123 + 198T) \tag{1}$$

According to the thermodynamic prediction, Reaction (1) is complete in 600 °C [15]. After this temperature, stoichiometry Na_2CO_3 and $CaCl_2$ are eliminated and NaCl salt, excess Na_2CO_3 and in situ formed $CaCO_3$ remain. By increasing the temperature to 632 °C, NaCl–Na_2CO_3 eutectic salt is formed and provides a liquid medium for Reaction (2) that thermodynamically starts at about 670 °C. By increasing the temperature to 670 °C, $CaCO_3$ reacts with ZrO_2 and some $CaZrO_3$ is formed. By increasing the temperature to 780 °C, NaCl–Na_2CO_3 salt completely melts and the rate of Reaction (2) becomes maximum.

$$CaCO_3 + ZrO_2 = CaZrO_3 + CO_2 \quad (\Delta G^0 = 193,400 - 289T) \tag{2}$$

Due to very high reactivity of nano-ZrO_2, the synthesis process of nano-ZrO_2 inclusive samples was completed at 800 °C. At 910 °C that is decomposition temperature of $CaCO_3$, Reaction (2) is stopped and Reaction (3) is done and $CaCO_3$ decomposes to CaO and CO_2. After 910 °C, $CaZrO_3$ is formed from Reaction (4) that thermodynamically starts at about 670 °C. Thus, before 910 °C, $CaCO_3$ and after this temperature, CaO involve in the synthesis reactions of $CaZrO_3$.

$$CaCO_3 = CaO + CO_2 \quad (\Delta G^0 = 168,400 - 18T) \tag{3}$$

$$CaO + ZrO_2 = CaZrO_3 \quad (\Delta G^0 = 193,400 - 289T) \tag{4}$$

To understand the reaction mechanisms, the whole synthesis process of $CaZrO_3$ discussed above for both mixtures have schematically been illustrated in Figs. 12 and 13, respectively.

Two main mechanisms, ''template-growth'' and ''dissolution-precipitation'', were involved in MSS. Reactant solubilities in the molten salt plays an important role in MSS. They not only affect the reaction rate but also the morphologies of the synthesized grains. If both of the reactants are soluble in the molten salt, then the product phase will be readily synthesized via precipitation from the salt containing the dissolved reactants (''dissolution–precipitation'' mechanism). In this case, the morphologies of the product grains will generally be different from those of the reactants. On the other hand, if one reactant is much more soluble than another, the more soluble reactant will dissolve into the salt first and then diffuse onto surfaces of the less soluble reactant and react in situ to form the product phase. In this case, the morphology of the synthesized grain will, to a large extent, retain that of the less soluble reactant (''template growth'' mechanism) [16,17].

According to Refs. [18,19], both $CaCO_3$ and CaO are soluble in a chloride molten salt. Their solubilities in a NaCl-based salt at 700–1000 °C are in the order of 10^{-3} (molar fraction), which is 1000 times higher than those of ZrO_2 (in the order of 10^{-6}). Therefore, during the MSS process, $CaCO_3$/CaO would be dissolved more in the NaCl–Na_2CO_3 molten salt and react with ZrO_2 ''templates'' to form in situ $CaZrO_3$. This explains the similarity between the grain shapes of the synthesized $CaZrO_3$ and those of the as-received ZrO_2. The morphology and particle size of the synthesized $CaZrO_3$ grains are similar to ZrO_2 grains, therefore, ''template-growth''

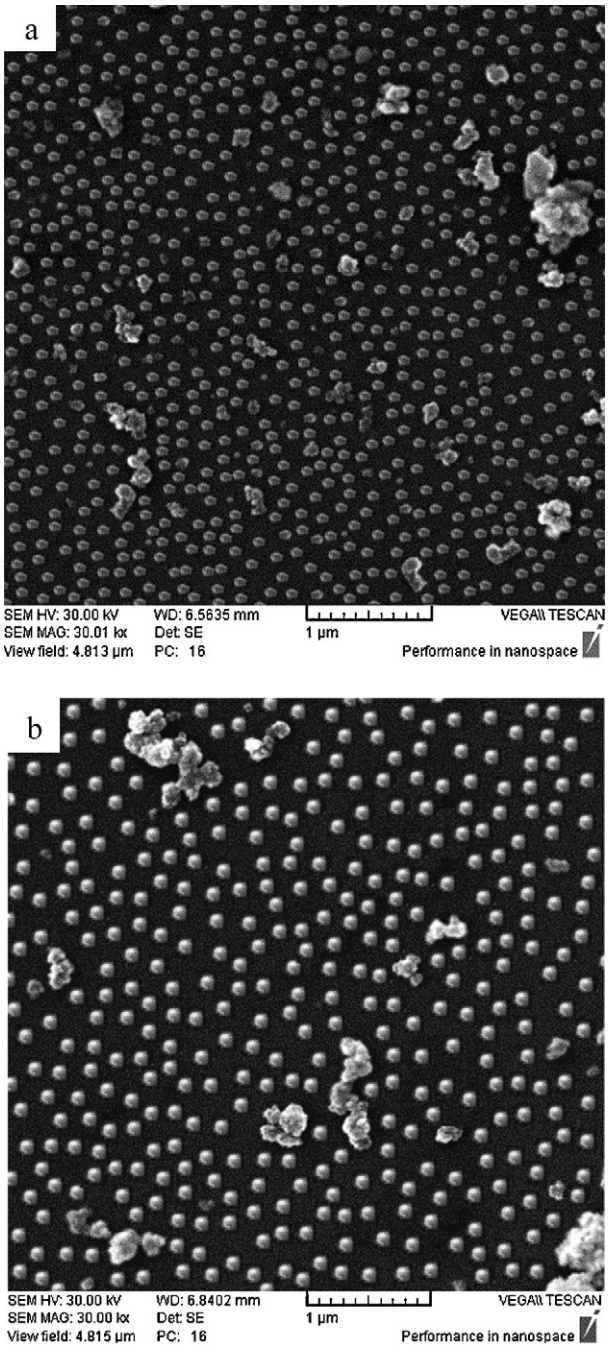

Fig. 14. SEM micrographs of (a) nano-ZrO_2 and (b) synthesized $CaZrO_3$.

mechanism has played a dominant role in the low temperature molten salt synthesis of $CaZrO_3$ particles (Fig. 14).

4. Conclusion

1. Calcium zirconate particles were synthesized via molten salt method. Two mixtures were used as 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.
2. Optimum temperatures for nano- and micro-zirconia inclusive samples were 800 °C and 1000 °C, respectively.
3. Particle size of $CaZrO_3$ synthesized from the first and the second mixtures was in the range of 70–80 nm and 300–400 nm, respectively.
4. Eutectic salt due to its lower melting point which causes faster diffusion and more complete reactions, was very more effective than singular salt in lowering synthesis temperature.
5. Similarity of morphology and particle size of synthesized $CaZrO_3$ to ZrO_2 grains showed that ''template-growth'' was the dominant mechanism in the synthesis process.

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