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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*

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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).

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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) 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 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.

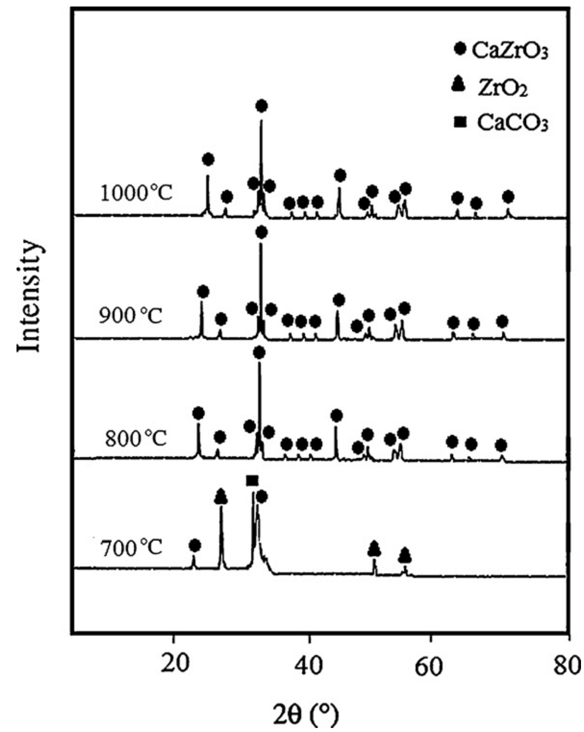

Fig. 1. XRD patterns of samples (water washed) heated for 3 h at different temperatures.

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

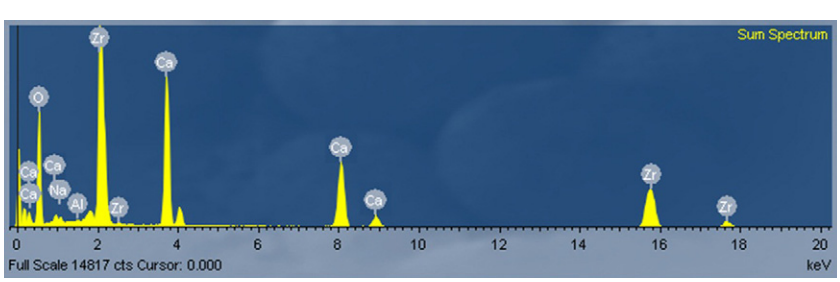

Fig. 2. EDS micrograph of samples heated at 800 °C for 3 h.

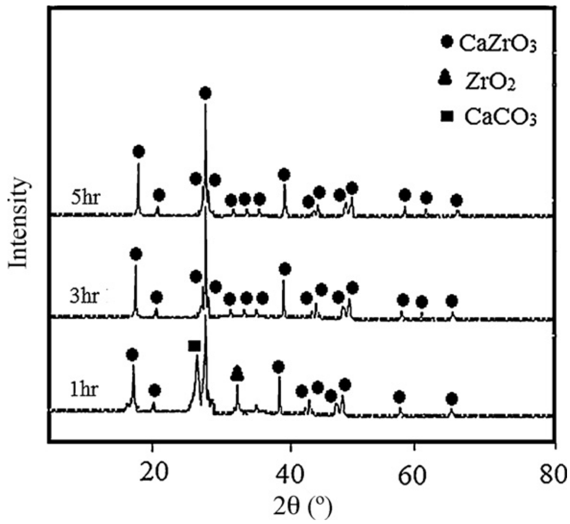

Fig. 3. XRD patterns of samples (water washed) heated at 800 °C with different holding times.

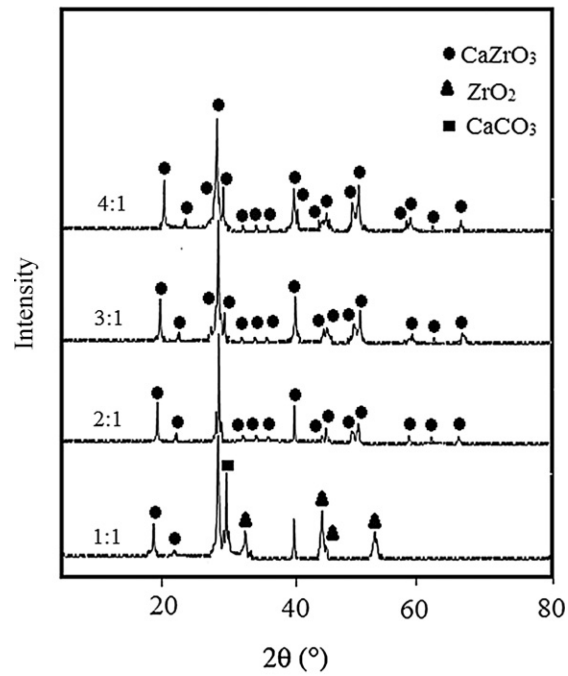

Fig. 4. XRD patterns of samples (water washed) heated at 800 °C with different salt to oxide ratios.

for these samples is 3 h. In this holding time, synthesis process is complete and the samples are single-phase $CaZrO_3$ and $CaCO_3$ and ZrO_2 peaks are not observed.

In holding time 1 h, $CaCO_3$ and ZrO_2 peaks have been seen in addition of $CaZrO_3$ peaks. On the other words, synthesis process has not been completed. In holding time 5 h, the samples are likewise single-phase $CaZrO_3$ and just intensity of their peaks has insignificantly increased compared with holding time 3 h which means that their crystallinity has venially increased. Thus, increasing in holding time before optimum holding time is an effective factor for completion of synthesis process and after this holding time does not have a significant effect.

3.3. Effect of salt amount

XRD patterns of samples heated with different salt to oxide ratios at 800 °C have been shown in Fig. 4 It can be resulted that optimum salt to oxide ratio is 2:1 and synthesis process is complete in this salt to oxide ratio. In salt to oxide ratio 1:1, the samples still do not become single-phase $CaZrO_3$ and it is necessary to increase salt to oxide ratio for completion of synthesis. With increasing salt to oxide ratio 2:1 to higher values, the samples remain single-phase and more increasing in salt to oxide ratio, more increasing in peaks intensity and more increasing in crystallinity property. Thus, increasing in salt to oxide ratio is a very effective factor for completion of synthesis process.

3.4. Particle size

Fig. 5 shows SEM micrographs of samples synthesized at different temperatures. As seen, the particle size of $CaZrO_3$ synthesized at 700, 800 and 900 °C was in the range of 70–90 nm. Whereas, the particle size of $CaZrO_3$ synthesized at 1000 °C was in the range of 140–150 nm which can be attributable to grain growth phenomenon that starts at above 1000 °C.

3.5. Salt assembly and molten salt synthesis of $CaZrO_3$

NaCl or NaCl–Na_2CO_3 salts could be used as molten salts media. As melting point of eutectic salts is lower than both singular salts, NaCl–Na_2CO_3 eutectic salt were more suitable. Na_2CO_3, $CaCl_2$ and ZrO_2, as starting materials, were mixed with specific molar ratio and then were heated. On heating mixture, the first reaction was between Na_2CO_3 and $CaCl_2$ (Reaction 1).

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

This is consistent with the thermodynamic prediction that reaction (1) could occur at as low as room temperature, because the ΔG° is negative in the whole temperature range between 25 and 600 °C [14]. Once reaction (1) was complete, $CaCl_2$ would disappear, and the salt assembly would become one essentially composed of NaCl and excess Na_2CO_3. The molar ratio between NaCl and the excess Na_2CO_3 is 2:0.2 and the NaCl–Na_2CO_3 phase diagram indicates that salt with such a composition will start to melt at 632 °C (eutectic temperature) in the areas where the eutectic exists and become completely liquid at about 780 °C (liquidus temperature), while melting point of NaCl and Na_2CO_3 is 801 °C and 858 °C, respectively [15]. This molten

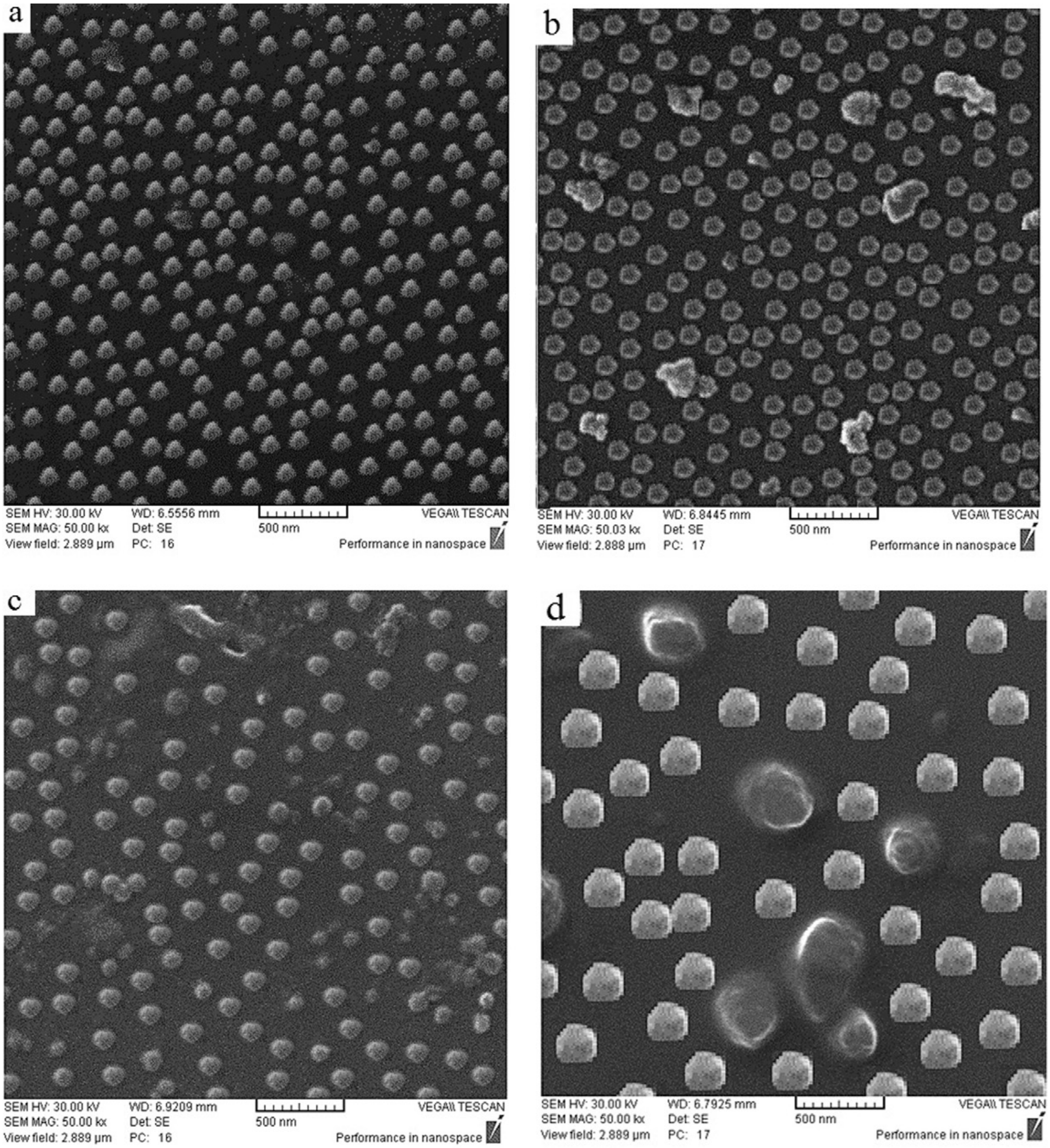

Fig. 5. SEM micrographs of samples synthesized at (a) 700 °C, (b) 800 °C, (c) 900 °C, (d) 1000 °C.

$NaCl–Na_2CO_3$ salt provided a reaction medium for the $CaZrO_3$ synthesis. Thus, selection of $NaCl–Na_2CO_3$ eutectic salt is scientifically justified.

According to the thermodynamic prediction, reaction (1) is completed at 600 °C. At above this temperature, stoichiometry Na_2CO_3 and $CaCl_2$ are eliminated and remain NaCl salt, excess Na_2CO_3 and in situ formed $CaCO_3$. With increasing temperature to 632 °C, $NaCl–Na_2CO_3$ eutectic salt is formed and provide a liquid medium for reaction (2) that thermodynamically starts at about 670 °C. With increasing temperature to 670 °C, $CaCO_3$ reacts with ZrO_2 and some $CaZrO_3$ is formed. With increasing temperature to 780 °C, $NaCl–Na_2CO_3$ salt completely melts and rate of reaction 2 becomes maximum. Due to very high reactivity of nano size ZrO_2, synthesis of $CaZrO_3$ was completed at 800 °C.

$$CaCO_3 + ZrO_2 = CaZrO_3 + CO_2$$
$$\Delta G^\circ = 193,400 - 289T \qquad (2)$$

To understand the reaction mechanisms, the whole synthesis process of $CaZrO_3$ discussed above is schematically illustrated in Fig. 6.

3.6. $CaZrO_3$ synthesis mechanism

Two main mechanisms, ''template-growth'' and ''dissolution–precipitation'', were involved in MSS. Solubility of

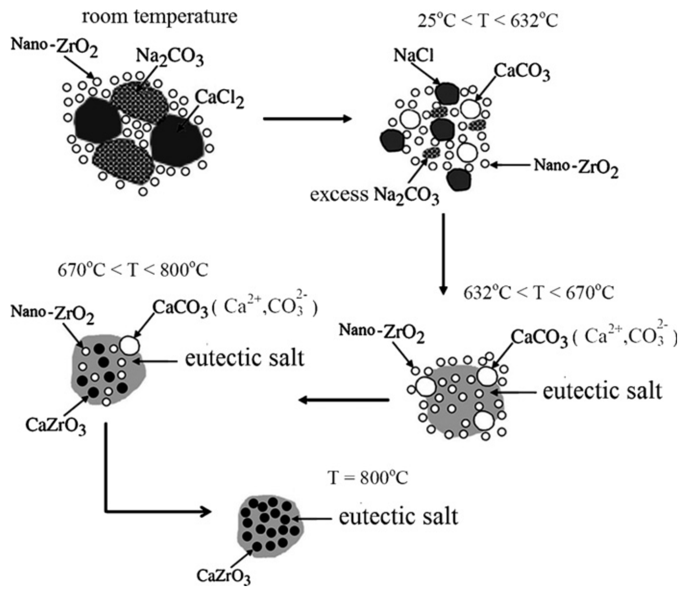

Fig. 6. Schematic diagram illustrating the synthesis of $CaZrO_3$ powder by heating nano-ZrO_2, $CaCl_2$ and Na_2CO_3.

reactants in the molten salt plays an important role in MSS. This not only affects the reaction rate but also the morphologies of the synthesized particles. 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 of reactants 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 retain the less soluble reactant (template-growth mechanism) [16,17].

According to Refs. [18,19], $CaCO_3$ is soluble in a chloride molten salt. Its solubility in a NaCl-based salt at 700–1000 °C are on the order of 10^{-3} (molar fraction), which is 1000 times higher than that of ZrO_2 (on the order of 10^{-6}). Therefore, during the MSS process, $CaCO_3$ 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 original ZrO_2 powder. The morphology and particle size of the synthesized $CaZrO_3$ grains was similar to ZrO_2 grains which means that the ''template-growth'' mechanism has played a dominant role in the low temperature molten salt synthesis of $CaZrO_3$ particles (Figs. 7 and 8).

4. Conclusions

1. Nano-size calcium zirconate powders were synthesized via molten salt method. Na_2CO_3, $CaCl_2$ and nano-ZrO_2 were used as starting materials.
2. Optimum temperature for samples was 800 °C that was significantly lower than that required by solid state method. Increasing in temperature is a very effective factor for completion of synthesis process.
3. Optimum holding time for samples was 3 h. Increasing in holding time significantly does not affect synthesis process.
4. Optimum salt to oxide ratio for samples was 2:1 (stoichiometry ratio). Increasing in salt to oxide ratio resulted in an increase in the crystallinity. Also, increasing in salt to oxide ratio was an effective factor for completion of synthesis process.

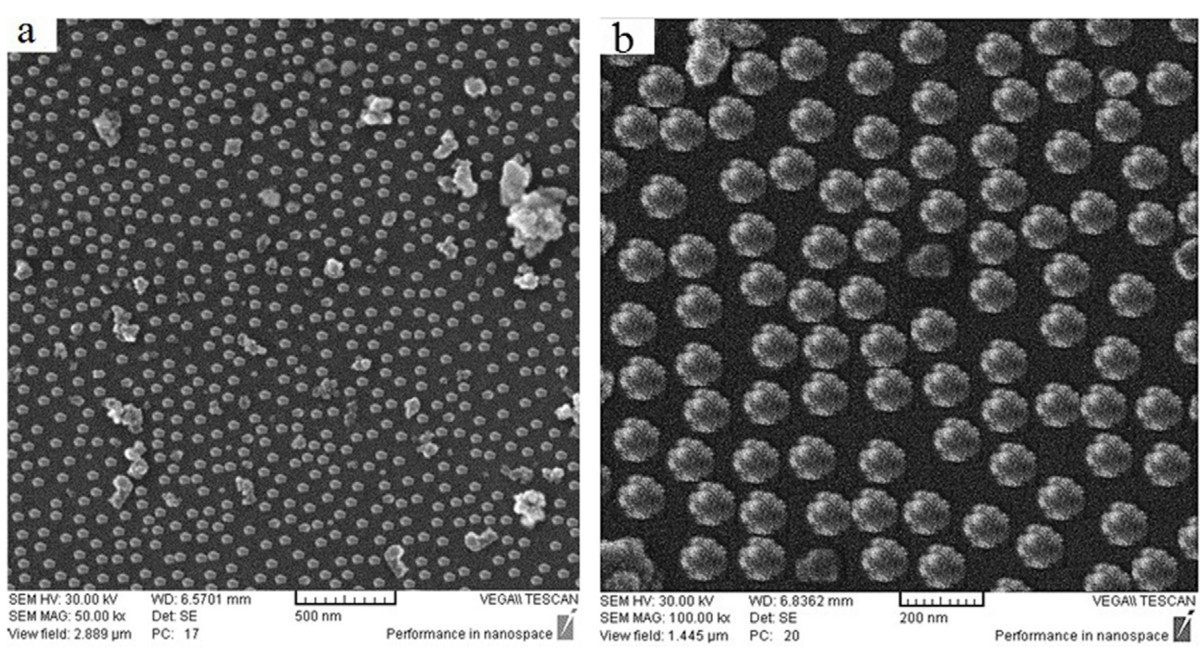

Fig. 7. SEM micrographs of (a) nano-ZrO_2 and (b) synthesized $CaZrO_3$.

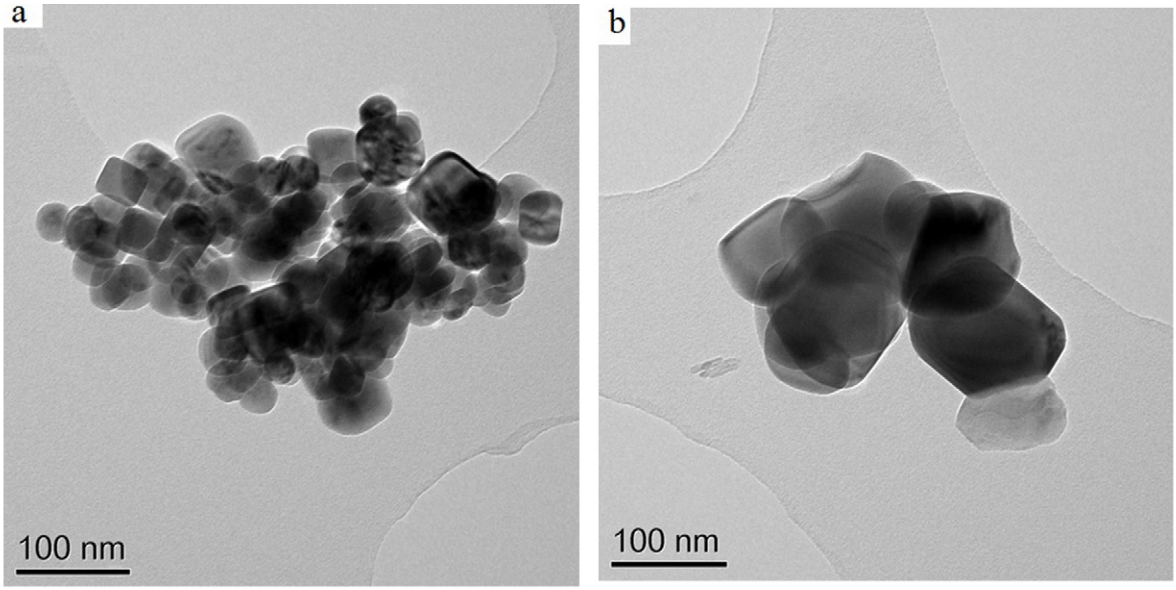

Fig. 8. TEM micrographs of (a) nano-ZrO_2 and (b) synthesized $CaZrO_3$.

5. Particle size of synthesized $CaZrO_3$ was 70–80 nm. At above 1000 °C, grain growth phenomenon causes increasing particle size.
6. Similarity of morphology and particle size of synthesized $CaZrO_3$ to ZrO_2 grains showed that ''template-growth'' was dominant mechanism in synthesis process.

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