

EFFECT OF ZrO_2 PARTICLE SIZE ON MORPHOLOGY and SYNTHESIS OF NANO $CaZrO_3$ Via MOLTEN SALT METHOD

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Received: December 2013

Accepted: May 2014

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Abstract: Well crystallized pure calcium zirconate ($CaZrO_3$) nanopowder was successfully synthesized using the molten-salt method. $CaCl_2$, Na_2CO_3 , micro- ZrO_2 and nano- ZrO_2 were used as starting materials. On heating, Na_2CO_3 reacted with $CaCl_2$ to form $NaCl$ and $CaCO_3$. Nano $CaZrO_3$ was formed by reacting equimolar amounts of in situ-formed $CaCO_3$ (or CaO) and ZrO_2 in molten Na_2CO_3 - $NaCl$ eutectic mixture. $CaZrO_3$ particle size and synthesis temperature was tailored as a function of ZrO_2 particle size. Due to the usage of nano- ZrO_2 , the molten salt synthesis (MSS) temperature was decreased and possible impurity phases in the final product were suppressed. The synthesis temperature was lowered to 800°C and soaking time of the optimal synthesis condition was reduced to 3h. After washing with hot-distilled water; the n- ZrO_2 sample heated at 800°C for 3h, was single phase $CaZrO_3$ with 70-90 nm in particle size, while the m- ZrO_2 sample heated at 1000°C for 3h, was single phase $CaZrO_3$ with 250-400 nm in particle size. Based on the TEM observation and thermodynamic analysis, the synthesized $CaZrO_3$ grains retained the morphology of the ZrO_2 nanopowders, which indicated that a template formation mechanism play a dominant role in synthesis process.

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

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]. In general, $CaZrO_3$ powders have been prepared from compositions in the CaO - ZrO_2 system by a high temperature (1500°C) reaction sintering. This process present several drawbacks such as hard agglomerates of as-synthesized powders and consequently a postsynthesis grinding step is needed to pulverize the reaction products to fine powders, which increase production cost and also deteriorate the $CaZrO_3$ structure [4]. So far, other methods such as electro-fusion, wet chemical [5-7], combustion [8] and mechanical alloying [9] have been reported for synthesis of calcium zirconate powders. Besides the above techniques, Molten salt synthesis (abbreviated as MSS) as a low temperature synthesis technique, has received a lot of attention in recent years. Several complex oxides such as niobate [10], lead zirconate titanate (PZT)

[11], lead ferroniobate [11], $BaZrO_3$ [11] and low-melting electroceramic powder [4] have been synthesized by this method.

In the molten salt method, a molten salt is used as liquid medium, the reactions are faster and synthesis is complete in significantly lower temperature and time [4, 12-18]. In our previous research, nano spinel was synthesized in KCl molten salt [19-20]. In addition Zushu Li et al [4] synthesized the $CaZrO_3$ compound with the molten salt method at the temperature of 1050°C for 5 h. To synthesize $CaZrO_3$ nanopowder, in this work, a mixture of Na_2CO_3 , $CaCl_2$ and ZrO_2 was used with molten salt synthesis (MSS) method. In situ-formed CaO and nano- ZrO_2 are helpful to lower the synthesis temperature and time. Also synthesis mechanism has been discussed based on the experimental results and thermodynamic analysis.

2. EXPERIMENTAL PROCEDURE

Na_2CO_3 (Merck, Germany, D50= 1mm, 99.5% pure), $CaCl_2$ (Merck, Germany, D50= 4mm,

99.5% pure) nano-ZrO₂ (Neutrino, Germany, D50= 60 nm, >99% pure) and micro-ZrO₂ (Neutrino, Germany, D50= 200 nm, >99% pure) were used as starting materials. First, Na₂CO₃ (1 mol) and CaCl₂ (1.2 mol) powders were completely mixed and then heated at 150°C for 12 h to dry. Agglomerated nano-scale ZrO₂ powders were dispersed in distilled water that its pH was controlled in 4 using hydrochloric acid. To more dispersion, the resulting suspension was sonicated for 1 h. Then, Na₂CO₃-CaCl₂ powder mixture was added to the aforementioned suspension and obtained mixture was stirred 1h to homogenize extremely. Molar ratio of obtained mixture is ZrO₂:CaCl₂:Na₂CO₃=1:1:1.2. Water was first evaporated by continuous stirring during heating at 120 °C for 12h on a hot plate. The resulted precursor were grounded by an agate mortar and then sieved to pass through a 325 mesh screen (45 μm) and named as n-ZrO₂. The micro-ZrO₂, Na₂CO₃ and CaCl₂ eutectic salts also dry mixed at the same molar ratio and named as m-ZrO₂. Finally, 20 g of each mixture was placed in an alumina crucible covered with an alumina lid, fired at various temperatures between 700, 800, 900 and 1000 °C and held for 3h. The heating and cooling rates were 3 °C/min and 5 °C/min, respectively. After cooling to room temperature, the reacted mass was washed and filtered in hot-distilled water five times to remove the salts. The resultant powder was dried at 120°C for 4h before further characterizations. The phase formation and morphology of the as-prepared nanopowders were characterized via X-ray diffraction (XRD, Philips and pw3710), scanning electron microscopy (SEM, Tescan, Vega II) and transmission electron microscopy

(TEM, CM 200, Philips).

3. RESULTS AND DISCUSSION

3. 1. Optimal Synthesis Temperature

Figure 1 provides XRD patterns of n-ZrO₂ samples heated for 3h at different temperatures (after water washing). After heating for 3 h at 700°C, CaCO₃ and n-ZrO₂ are identified as the dominant phases, but CaZrO₃ was not detected.

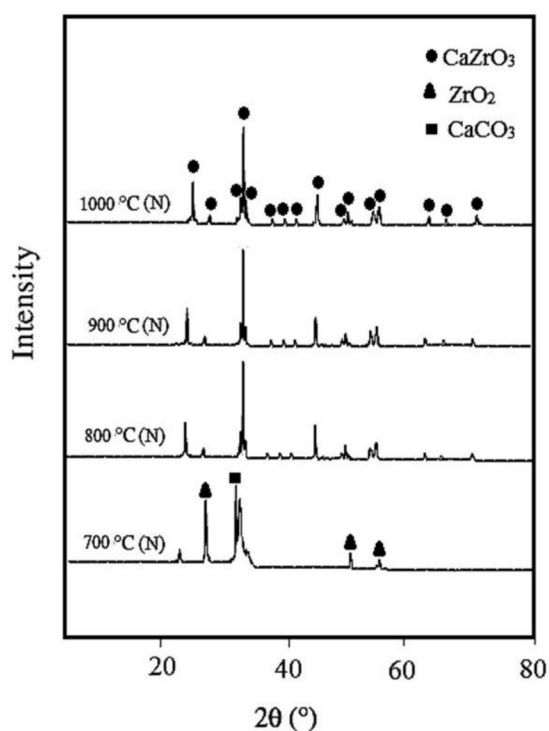


Fig. 1. XRD patterns of water-washed n-ZrO₂ samples heated at different temperatures for 3 h.

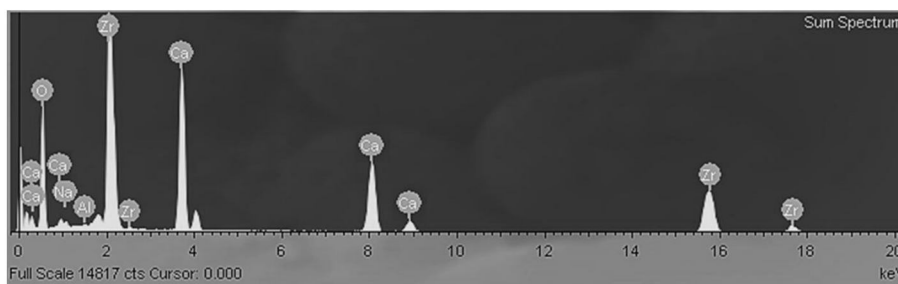


Fig. 2. EDS micrograph of n-ZrO₂ samples heated at 800°C for 3 h.

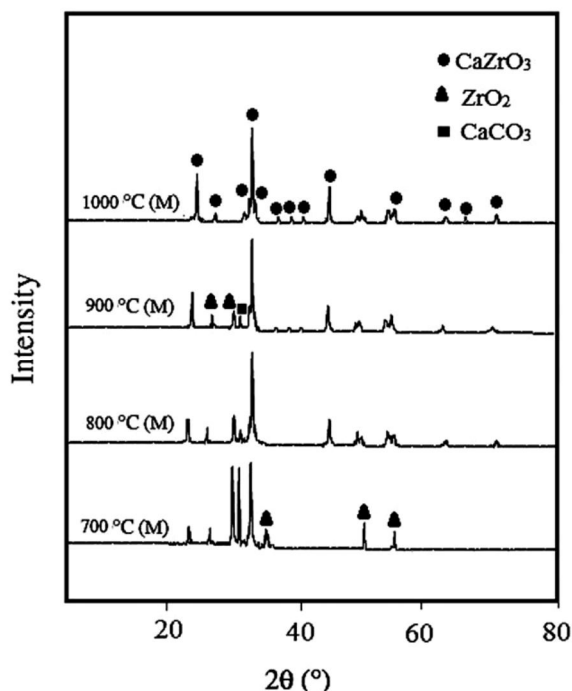


Fig. 3. XRD patterns of water-washed m-ZrO₂ samples heated at different temperatures for 3 h.

CaZrO₃ peaks began to appear at 800°C and aforementioned impurity phases were suppressed. At 900 °C, the sample was single-phase CaZrO₃ and higher degree of crystallinity was obtained that was confirmed by means of increasing in peak intensity. At 1000°C, the peak intensities were insignificantly decreased and peaks partly became broader that can be attributed to acceding temperature of CaZrO₃. Energy dispersive X-ray spectroscopy (EDS) micrograph of n-ZrO₂ sample heated at 800°C for 3h are shown in Figure 2. Only [Ca], [Zr] and [O] elements are observed and other elements have been diminished. Based on the above results, optimal synthesis temperature and soaking time for n-ZrO₂ sample are 800°C and 3h respectively.

Figure 3 shows XRD patterns of m-ZrO₂ samples heated for 3 h at different temperatures (after water washing). Using the micron size ZrO₂ powders delay the CaZrO₃ phase formation. The complete CaZrO₃ phase formation was achieved in the m-ZrO₂ samples that heated at 1000°C for 3h.

3. 2. Particle Size

SEM micrograph of n-ZrO₂ sample (800°C/3h) has been shown in Figure 4. As seen, particle size of the synthesized CaZrO₃ is about 70-90 nm and almost mono-sized particles is prepared. SEM micrograph of m-ZrO₂ sample (1000°C/3h) has been shown in Figure 5. For this sample, particle size of synthesized CaZrO₃ is about 250-400 nm.

3. 3. Salt Assembly and MSS of CaZrO₃

NaCl or NaCl–Na₂CO₃ salts can be used as molten salts media. As melting point of NaCl–Na₂CO₃ eutectic mixture is lower than both singular salts, eutectic mixture is more suitable. On heating starting raw materials, Na₂CO₃ and CaCl₂ can react with each other to form in-situ CaCO₃ and NaCl (Reaction 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 25-600°C [21]. Once reaction (1) was complete, CaCl₂ would disappear, and the salt assembly would become one essentially composed of NaCl and

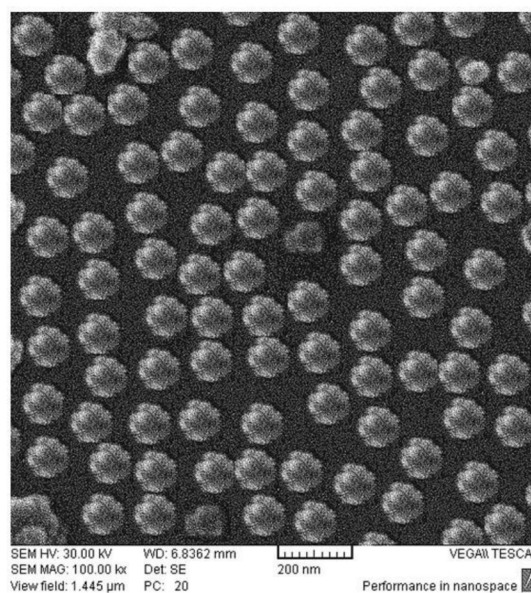


Fig. 4. Scanning electron microscopy micrograph of n-ZrO₂ samples heated at 800°C for 3 h.

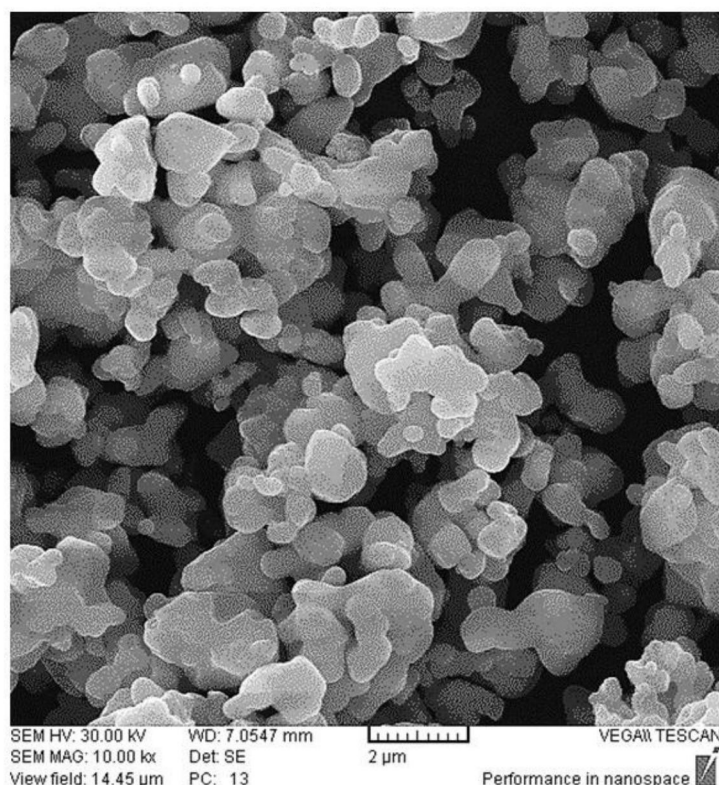


Fig. 5. Scanning electron microscopy micrograph of m-ZrO₂ samples heated at 1000°C for 3 h.

excess Na₂CO₃. The molar ratio between NaCl and the excess Na₂CO₃ is 2:0.2 and the NaCl–Na₂CO₃ 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 Na₂CO₃ is 801 °C and 858°C, respectively [22]. This molten NaCl–Na₂CO₃ salt provided a reaction medium for the CaZrO₃ synthesis. Thus, selection of NaCl–Na₂CO₃ eutectic salt is scientifically justified.

According to the thermodynamic prediction, reaction 1 is completed at 600°C. At above this temperature point, stoichiometry Na₂CO₃ and CaCl₂ reagent are eliminated and reaction products become composed of NaCl salt and in situ formed CaCO₃. Moreover excess amount of Na₂CO₃ also be remained in the reaction products. With increasing temperature to 632°C, NaCl–Na₂CO₃ eutectic mixture is formed and provides a liquid medium for reaction (2) that thermodynamically starts at about 670°C. CaCO₃

reacts with ZrO₂ and some CaZrO₃ is formed by a slight increase of temperature to 670 °C, With increasing temperature to 780°C, NaCl–Na₂CO₃ salts completely melts and the reaction target resulting in maximum rate.

Due to very high reactivity of ZrO₂ nanoparticles, synthesis of CaZrO₃ in n-ZrO₂ sample is completed at lower temperature (800°C) compared with m-ZrO₂ sample (1000°C). A point that has to be stressed out is that on heating (> 910 °C), CaCO₃ formed from reaction (1) would decompose and produce CaO according to the reaction (3). As a result for the m-ZrO₂, CaO also have been involved in the synthesis reaction of CaZrO₃ according to reaction (4). Several factors such as amount of liquid salt at specified temperature, solubility of the reactions in salt medium and activity of less soluble reactant (ZrO₂) to react with Ca²⁺ and O²⁻ ions have kinetic effect for the formation of CaZrO₃ nanoparticles. Finally it should be stated that highly active ZrO₂ nanoparticle promote its reaction with Ca²⁺ and O²⁻ ions and formation of

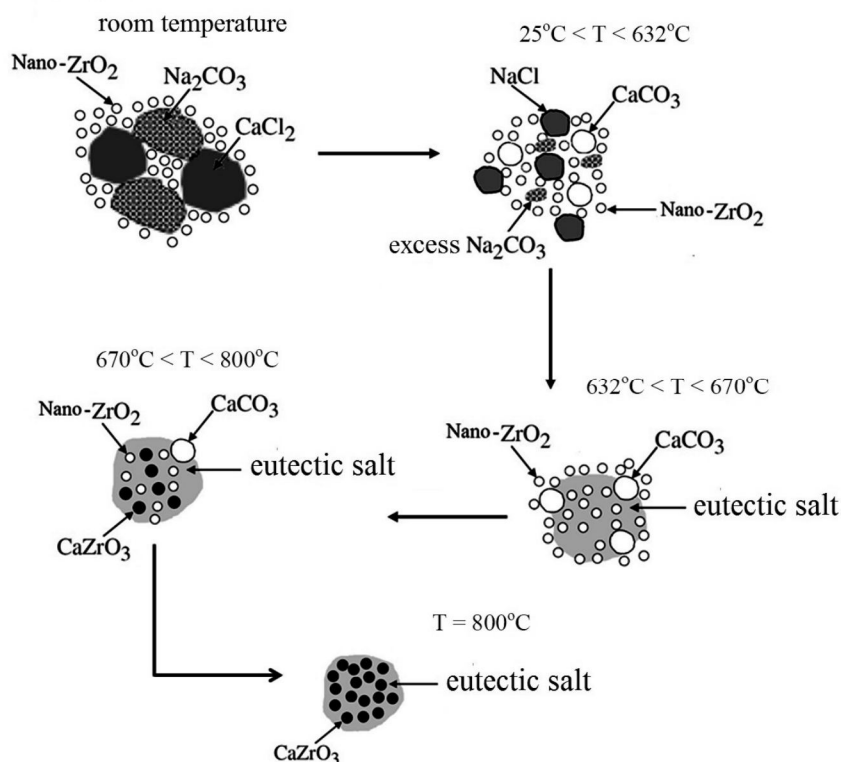


Fig. 6. Schematic diagram illustrating the synthesis of CaZrO_3 powder by heating nano- ZrO_2 , CaCl_2 and Na_2CO_3 .

nano CaZrO_3 was accelerated in lower temperature (800°C).

To understand the reaction mechanisms, the whole synthesis process of CaZrO_3 synthesized from n- ZrO_2 sample is schematically illustrated in Figure 6. As seen, in these samples, synthesis completes before decomposition of CaCO_3 . Therefore, only CaCO_3 involves in the synthesis reactions of CaZrO_3 . Figure 7 shows schematically synthesis process of CaZrO_3 synthesized from m- ZrO_2 sample. In this sample, synthesis reaction did not complete before decomposition of CaCO_3 , consequently, both CaCO_3 and CaO have been involved in the synthesis reactions of CaZrO_3 .

3. 4. CaZrO_3 Synthesis Mechanism

Two main mechanisms, “template-growth” and “dissolution-precipitation”, are involved in MSS. Solubilities of the reactants in the molten salt method play an important role. 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 morphology 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 retain the less soluble reactant (Template growth mechanism) [24-25].

According to references [26-27], both CaCO_3 and CaO are soluble in a chloride molten salt. Their solubility's in a NaCl -based salt at $700\text{--}1000^\circ\text{C}$ 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 or CaO would dissolve more in the $\text{NaCl}\text{--}\text{Na}_2\text{CO}_3$ molten salt and react with ZrO_2 templates to form in situ CaZrO_3 . This explains the similarity between the grain shapes

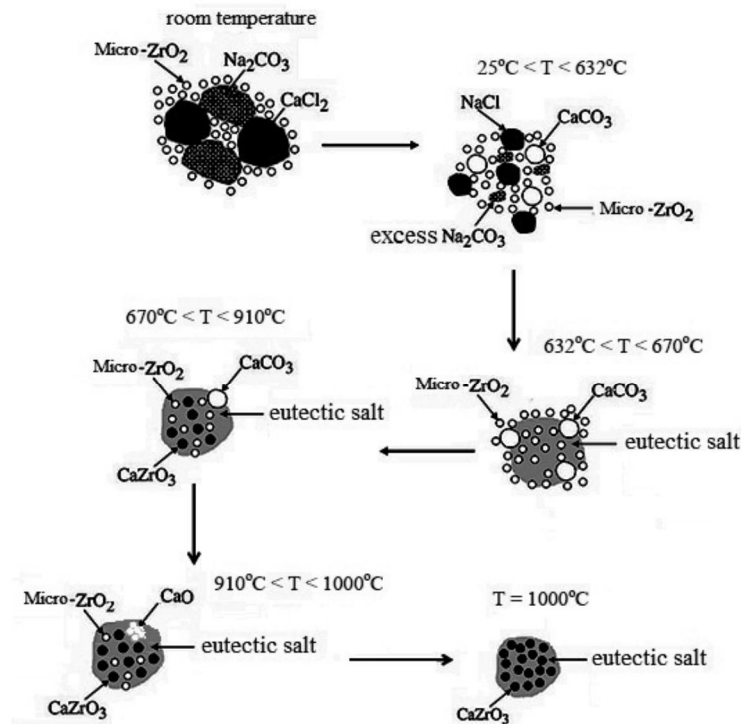


Fig. 7. Schematic diagram illustrating the synthesis of CaZrO_3 powder by heating micro-ZrO_2 , CaCl_2 and Na_2CO_3 .

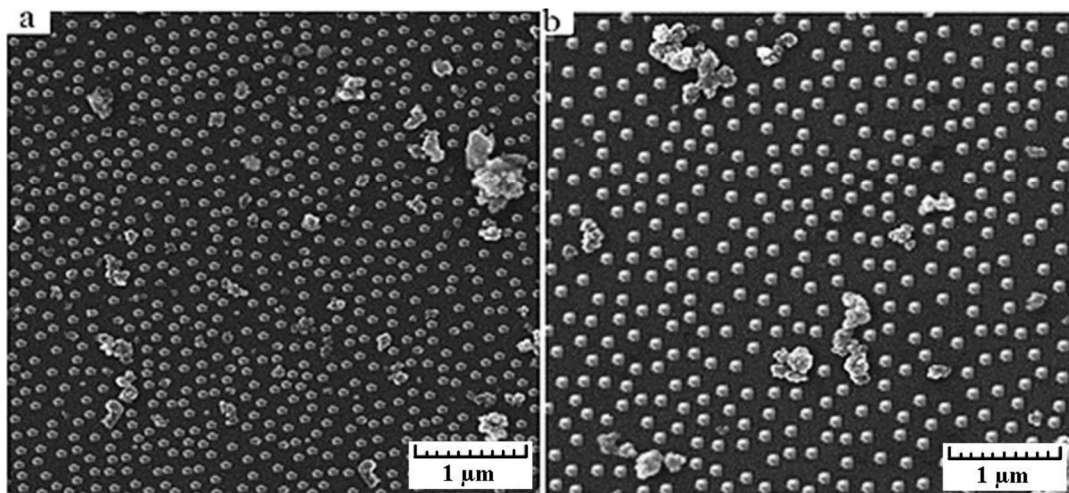


Fig. 8. SEM micrographs of (a) nano- ZrO_2 (b) synthesized CaZrO_3 .

of the synthesized CaZrO_3 and those of the as-received ZrO_2 . The morphology and particle size of the synthesized CaZrO_3 grains is similar to ZrO_2 grains, therefore, “template-Growth” mechanism play a dominant role in the low temperature molten salt synthesis of CaZrO_3 particles. (Figure 8 and Figure 9).

4. CONCLUSIONS

1. Calcium zirconate were synthesized via molten salt method, using nano and micro- ZrO_2 and $\text{CaCl}_2 - \text{Na}_2\text{CO}_3$ salt mixtures.
2. The synthesis temperature for n- ZrO_2 and

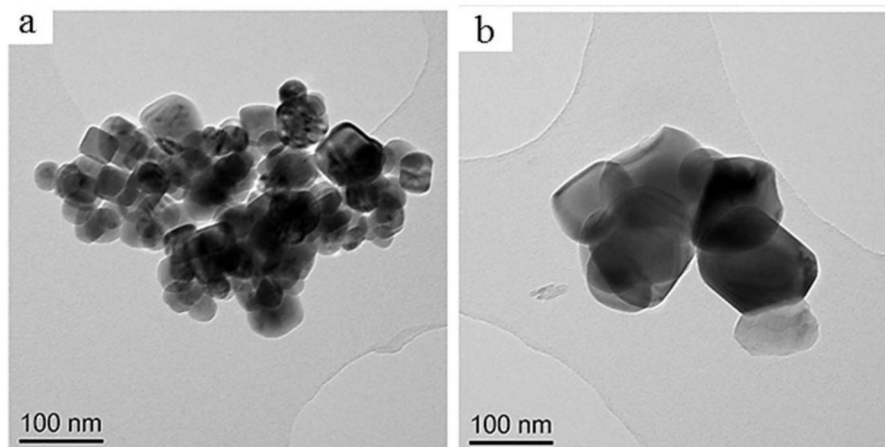


Fig. 9. TEM micrographs of (a) nano-ZrO₂ (b) synthesized CaZrO₃.

m-ZrO₂ samples are lowered to 800°C and 1000°C respectively and soaking time of the optimal synthesis condition for both of them was reduced to 3h.

3. Particle size of synthesized CaZrO₃ from the n-ZrO₂ and m-ZrO₂ samples are 70-80 nm and 250-400 nm, respectively.
4. Similarity of morphology and particle size of the synthesized CaZrO₃ to ZrO₂ grains showed that "template growth" is dominant mechanism in synthesis process.

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