

Short communication

Chemical synthesis of Ca-doped CeO₂—Intermediate temperature oxide ion electrolytes

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Abstract

Nano-crystalline fluorite-like structure CeO₂ and Ca-doped CeO₂ compounds were prepared in the temperature range of 220–400 °C using a precursor method which involves coprecipitation of Ca²⁺ and Ce⁴⁺ ions using oxalic acid from the aqueous calcium chloride and ammonium cerium nitrate solutions. The precipitated products were characterized by employing thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), infrared spectroscopy (IR), laser particle size analysis (LPSA) methods and scanning electron microscopy (SEM). TGA studies show two step weight loss in the temperature range: (i) room temperature to 200 °C and (ii) 200–400 °C for all the investigated precursors. The former loss is attributed to loss of water while the latter is due to decomposition of oxalates. The XRD study reveal a complex pattern for the as-precipitated powders, and surprisingly we see the formation of single-phase fluorite-like structure at about 220 °C for Ce_{1-x}Ca_xO_{2-x} (0 < x < 0.20). However, XRD peaks were found to be very broad that sharpen with increasing temperature. The cubic fluorite-type lattice constant increases with increasing Ca-content, which is consistent with literature, and also follows the expected trend based on the ionic radii consideration. For purpose of comparison, Ce_{1-x}Ca_xO_{2-x} (0 < x < 0.25) samples were also prepared by solid-state reaction using CeO₂ and CaCO₃, and lattice parameter is consistent with precipitation method samples within the experimental error. This result suggesting that doping of Ca is successful by coprecipitation. The particle size of parent and Ca-doped CeO₂ samples prepared by precipitated method was found to be in the range 10–85 nm (from PXRD) in the temperature range 400–1000 °C, while about order of higher size was observed for the ceramic method synthesized samples. The presently employed wet chemical method could be used to prepare ceria and doped materials with nano-sized particles for a large scale production at mild temperature.
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1. Introduction

These days, acceptor doped CeO₂ has been considered as potential oxide ion electrolytes for the development of intermediate temperature solid oxide fuel cells (IT-SOFCs) as well as other applications, including oxygen pumps and sensors for various gases (for, e.g., O₂, H₂, hydrocarbons) due to their high ionic conduction [1]. For example, Gd-doped CeO₂ exhibits oxide ion conductivity of 0.025 S cm⁻¹ [2] at 600 °C which is an order higher than that of conventional Y-doped ZrO₂ (YSZ) (0.003 S cm⁻¹ at 600 °C), and similar to those of La_{0.80}Sr_{0.20}Ga_{0.90}Mg_{0.10}O_{3-δ} perovskite (0.029 S cm⁻¹ at 600 °C) [3]. Such a low-temperature has several advantages over the high temperature electrolyte such as flexibility in the choice

of the electrodes, bi-polar materials, seals, as well as long-term stability and costs [4]. The main concern with the CeO₂ based electrolytes are related to large grain-boundary (especially at low temperatures) impedance which results a huge total resistance of system, and hence shows poor current density [5]. Also, unlike zirconia based electrolytes, CeO₂ based compounds exhibit poor mechanical stability. Accordingly, current research work has been directed to the development of solid electrolytes with optimized microstructure to lower the total resistance by various wet-chemical methods for applications in advanced SOFCs as well as in other solid-state devices.

Conventional solid-state reaction (ceramic) method involves mixing of corresponding metal oxides, nitrates, and carbonates and heat them at elevated temperatures (as high as 2000 °C) for extended duration [6,7]. Numerous solid electrolytes, such as Sr+Mg-doped LaGaO₃, RE-doped CeO₂ (RE=rare earth), Ba₂In₂O₅, Bi₄V₂O₁₁, Ba(Ce,Y)O₃, (Li,La)TiO₃, Li₁₄ZnGe₄O₁₆, Li₄SiO₄, Na_{1+x}Zr₂P_{3-x}Si_xO₁₂

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($0 < x < 3$), and Na- β -alumina, as well as electrodes (mixed ionic and electronic conductors), including Sr-doped LaMnO_3 , LiCoO_2 , LiFePO_4 were prepared regularly by solid-state reactions. Because of very low diffusion of coefficients of ions in solids, solid-state reaction requires intermittent grinding, and repeated heating and grinding, for extended period of time to form the desired single-phase compound. For example, Ca-doped CeO_2 was typically synthesized by mixing CeO_2 and CaCO_3 , and heating the mixed powder first at 1100°C for 5 h, and resulting powder was ground and calcined at 1300°C for 10 h, and then heated at 1450°C for 15 h in air [8a]. Such high temperature treatment usually results in large particle sizes, (large crystallites) and hence, low surface area. A high surface (which depends on the size of the particles) is the key requirement of electrodes for their best performance in SOFCs, proton exchange membrane fuel cells (PEMFCs), gas sensors and catalysis. Therefore, the current research is directed on the development of electrode materials with nano-sized particles with large surface area for application to advanced ionic devices. Another major drawback of solid-state reaction method is the contamination during the repeated mixing with milling balls and reacting vessels and during the sintering.

Several soft-chemical methods, including hydrothermal, sol-gel, precipitation, and Pechini polymerization techniques have been employed to prepare novel solid electrolyte and electrode materials. The resulting powders generally show finer crystallite/particle sizes and exhibit better physical properties compared to those of solid-state reaction. Chemical methods generally involve first the preparation of the appropriate precursors in which the constituents are mixed in an atomic scale and decomposed at a relatively lower temperature to form single-phase compounds compared to solid-state reaction [6,7]. For example, nano-crystalline powders of rare earth doped CeO_2 was prepared (at 700°C) from nitrate solutions by a sol-gel process [7b,d], hydrothermal [9a], and coprecipitation reaction using ammonia carbonate [9b] and oxalic acid [7c] as the precipitating agents while the solid-state reaction require about 1650 – 1800°C to prepare the same materials [8,9].

In the present study, we report a new precursor method for preparation of nano-crystalline powders of CeO_2 and Ca-doped CeO_2 at low temperatures ($\leq 400^\circ\text{C}$). This method involves coprecipitation of Ca^{2+} and Ce^{4+} ions from the corresponding aqueous halides and nitrate solutions, respectively at room temperature. Various solid-state techniques that include powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), infrared spectroscopy (IR), laser particle size analyzer, scanning electron microscopy (SEM) methods were employed for characterization of precursor and products evolved during the decomposition.

2. Experimental

2.1. Synthesis

The $x \approx 0.1$ member of $\text{Ce}_{1-x}\text{Ca}_x\text{O}_{2-\delta}$ series shows the highest oxide ion conductivity for the ceramic method [8]. Therefore, we have selected three compositions with $x = 0, 0.10$ and 0.20

to demonstrate a new coprecipitation method for preparation. A typical reaction involves the following steps; the required amounts of CaCl_2 and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ were dissolved in de-ionized water at room temperature in separate beakers and mixed together. To this mixed solution, the solution of appropriate amounts of oxalic acid (1 mole for divalent and 2 moles for tetravalent cations) was added under constant stirring at room temperature (RT). Light brown/yellow coloured precipitate was formed spontaneously that changes to white after a few hours. The completion of precipitation reaction was tested by adding additional oxalic acid after holding solution overnight, and found that no additional precipitate was formed, suggesting that all ions (Ca^{2+} and Ce^{4+}) were precipitated. The precipitation was filtered, washed with a large amount of de-ionized water for several times, and dried at RT in ambient atmosphere.

For purpose of comparison, we have prepared Ca-doped CeO_2 by solid-state reaction using appropriate amounts of high purity ($>99.5\%$) CeO_2 and CaCO_3 . Before the final sintering in the shape of cylinders at 1500°C for 24 h, the powder reactant mixtures were annealed at 1000 – 1350°C for 24 h twice with intermediate grinding using mortar and pestle.

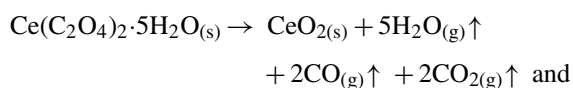
2.2. Thermal and structural characterizations of precursors and its decomposition products

The precursor powder was subjected to thermogravimetric analysis (TGA) in ambient atmosphere at heating and cooling rate of 5°C min^{-1} using Setaram TAG 16/18 DSC/TGA dual chamber balance. Powder X-ray diffraction (PXRD) (Rigaku powder X-ray diffractometer ($\text{Cu K}\alpha$)), FTIR (Nicolet FTIR spectrometer (Nexus 470) using KBr), and a scanning electron microscope (SEM) (JEOL JXA-8200 electron probe microanalyzer) were employed for the materials characterization. The particle size distribution of powder was measured using a laser particle size analyzer (NanoTec Analysette 22, Fritsch). The powder was dispersed homogeneously in water using ultrasound for determination of particle sizes.

3. Results and discussion

3.1. TGA, XRD and IR investigations

The TGA curves of the as precipitated powder precursors of $x = 0$ and 0.10 members of $\text{Ce}_{1-x}\text{Ca}_x\text{O}_{2-\delta}$ are shown in Fig. 1. We see clearly two weight losses in the range of temperature (i) room temperature to 200°C and (ii) 200 – 400°C . No further weight loss or gain was found in the temperature range of 400 – 900°C , suggesting that the single-phase materials may be formed at about 400°C which has been confirmed later by PXRD results. The mass remaining after the decomposition decreases with increasing Ca content. For example, the mass remaining for $x = 0$ and $x = 0.10$ members are $\sim 47.5\%$ and $\sim 40\%$, respectively. The TGA result of $x = 0$ and 0.10 members could be explained using following proposed decomposition reactions:



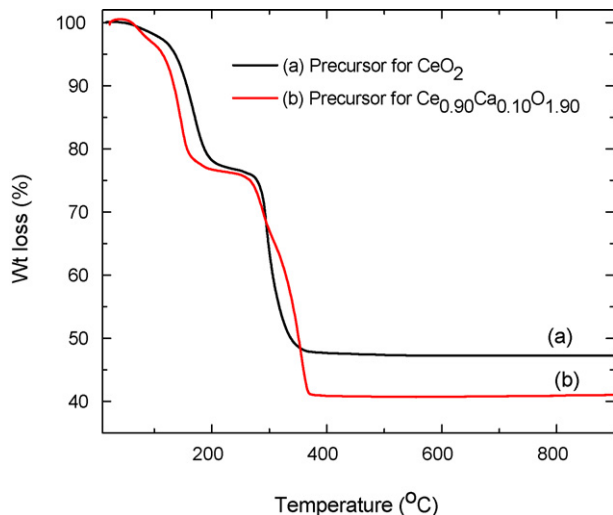
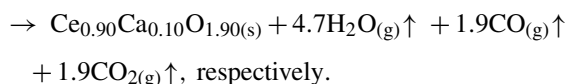
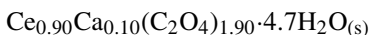


Fig. 1. TGA curves show the decomposition of precursor for the preparation of (a) CeO_2 and (b) $\text{Ce}_{0.90}\text{Ca}_{0.10}\text{O}_{1.90}$ in air.



The first loss observed in the TGA curves is due to water degradation and the second step is due to the decomposition of oxalate and formation of the fluorite-type structure CeO_2 . In order to confirm presence of Ce^{4+} ions in the precursors, we have decomposed the precursor $\text{Ce}(\text{C}_2\text{O}_4)_2 \cdot 5\text{H}_2\text{O}$ in Ar at 800°C overnight. The PXRD study of the resultant product shows the formation of a single-phase fluorite-like structure CeO_2 (Fig. 2) [10], suggesting that Ce ions in the +4 state in the as precipitated precursors. If the Ce ions are present in the +3 state in the precursor, one may expect the formation of Ce_2O_3 instead of CeO_2 . Further investigations are required, however, to confirm the proposed decomposition reactions.

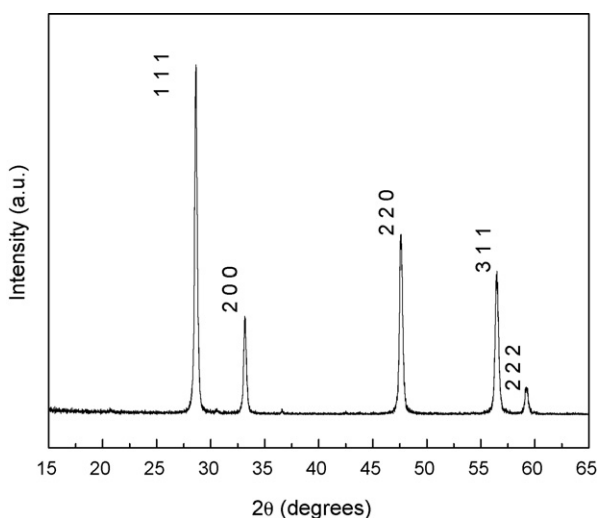


Fig. 2. Powder XRD ($\text{Cu K}\alpha$) patterns for as precipitated precursor of CeO_2 heated at 800°C in Ar atmosphere overnight. We see the indication of formation of fluorite-type structure with a lattice constant of $5.399(2) \text{ \AA}$.

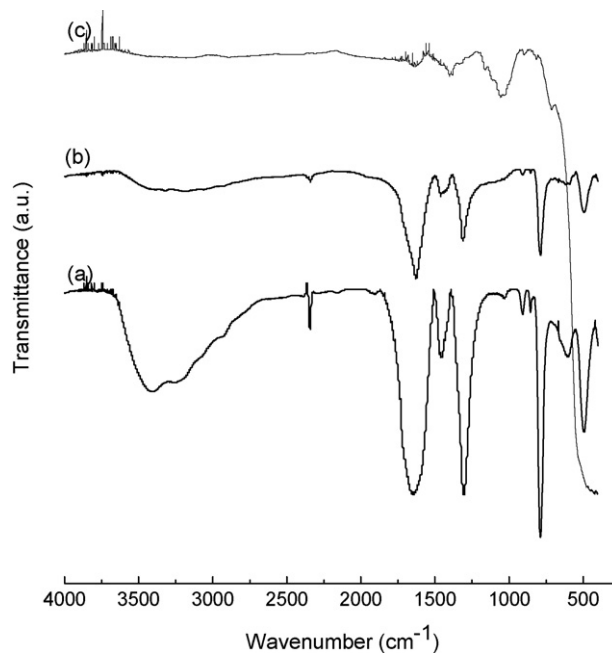


Fig. 3. IR spectra of (a) as precipitated precursor for the preparation of CeO_2 , (b) sample “a” heated at 220°C , and (c) sample “a” heated at 1000°C .

Fig. 3 shows the IR spectra of the as precipitated precursor of $x=0$ member and its decomposition products obtained at 400 and 1000°C . The IR spectra shows presence of OH (3500 cm^{-1}) and CO (1720 cm^{-1}) groups in the precursor and are absent in the samples obtained in the temperature range 400 – 1000°C [11]. IR spectrum of sample prepared in the temperature range of 400 – 1000°C is similar to that of the commercially available CeO_2 .

Fig. 4 shows the PXRD patterns of the as precipitated precursors and its decomposition products obtained at 220 , 400 , 800 and 1000°C for 6 – 12 h. We see clearly that as precipitated precursors are crystalline compounds, they show several peaks, indicating complex structure that becomes cubic fluorite-type structure at relatively low-temperature in the range 220 – 400°C (Fig. 4A). Very interestingly, we see clearly characteristic diffraction peaks related to fluorite-like structure at around 220°C . The peaks are broad, suggesting presence of small particle sizes. These peaks gradually sharpen with increasing heat treatment temperature, indicating an increase of particle sizes. Using coprecipitation method, we could readily prepare CeO_2 and $10 \text{ mol}\%$ Ca-doped CeO_2 at below 400°C . Fig. 4B shows the powder diffraction patterns for the precursor and its decomposition products of $10 \text{ mol}\%$ Ca doped CeO_2 .

The lattice constant was obtained by least-squares refinement of PXRD data and is shown in Fig. 5. For comparison, we give the lattice parameters of $\text{Ce}_{1-x}\text{Ca}_x\text{O}_{2-x}$ ($0 < x < 0.25$) prepared by solid-state reactions. We see that lattice parameter obtained from both precipitation and solid-state methods are comparable for the $x=0$ and 0.10 members, and is also similar to the literature data. The lattice parameter obtained for $x=0$ in the Ar ($a \approx 5.4 \text{ \AA}$) (Fig. 2) is slightly lower than that of the air decomposed product ($a \approx 5.409 \text{ \AA}$) (Fig. 4A). The slight difference in the lattice parameter may be attributed to small variation in the

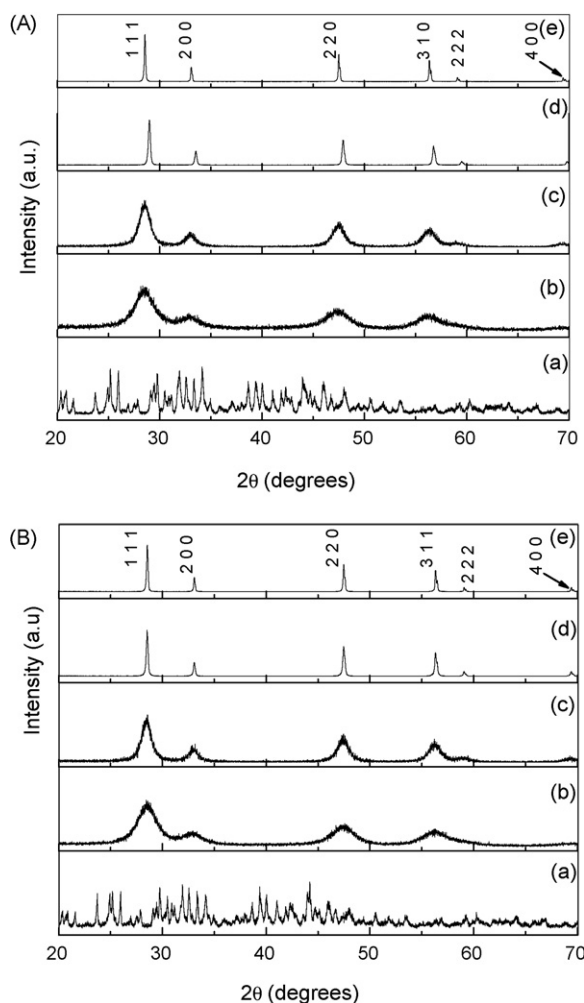


Fig. 4. (A) Powder XRD (Cu K α) patterns showing the formation of CeO₂ (a) as precipitated precursor, (b) sample “a” heated at 220 °C in air, (c) sample “b” heated at 400 °C in air, (d) sample c heated at 800 °C in air and (e) sample “d” heated at 1000 °C in air. We see the indication of formation of fluorite-type structure at 220 °C. The corresponding diffraction patterns for formation of Ce_{0.90}Ca_{0.10}O_{1.90} are shown in (B).

oxygen content. Also, it must be mentioned that the CeO₂ sample prepared in Ar looks dark black in colour (believed due to carbon deposition from oxalate), while it looks dirty white in air. The variation of lattice parameter of the parent CeO₂ and Ca-doped CeO₂ suggests that the present coprecipitation method is successful in the preparation of Ca-doped CeO₂. The lattice constant increases with increasing the Ca content up to $x=0.1$ in Ce_{1-x}Ca_xO_{2-x} suggesting that solid solution is limited up to 10 mol% under the investigated temperature. The increase in the lattice constant is in good agreement with effective ionic radii considerations ($r_{\text{Ca}^{2+}_{\text{CN}=8}} = 1.12 \text{ \AA}$ and $r_{\text{Ce}^{4+}_{\text{CN}=8}} = 0.97 \text{ \AA}$) [12]. The lattice parameter reported in the present study for $x=0$ and $x=0.10$ is consistent with Joint Committee for Powder Diffraction Studies (JCPDS) card numbers 34:10,062 and 51:0231, respectively, and also with that reported in the literature [8]. The lattice constant for $x=0.20$ is found to be slightly lower than $x=0.10$ and also with the literature. A similar behaviour is observed for the solid-state reaction method. For solid-state reac-

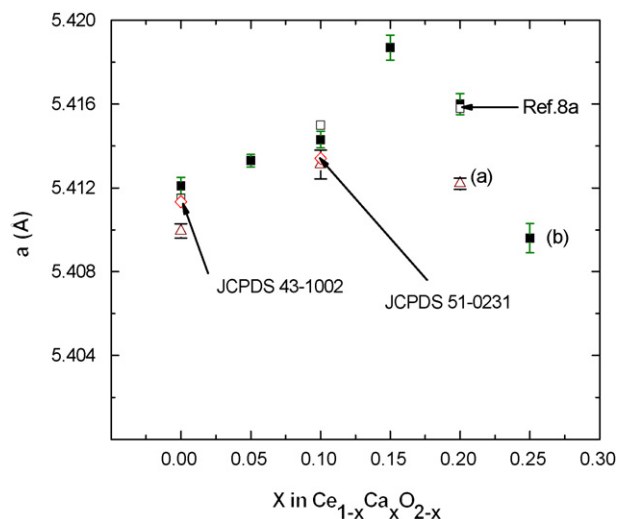


Fig. 5. Comparison of variation of cubic lattice parameters as a function of Ca content in Ce_{1-x}Ca_xO_{2-x} between coprecipitation and solid-state reaction. The lattice parameter increases with increasing in Ca content suggesting that doping has been successful. Also, the lattice parameter reported in the present work is very similar to the literature data [8].

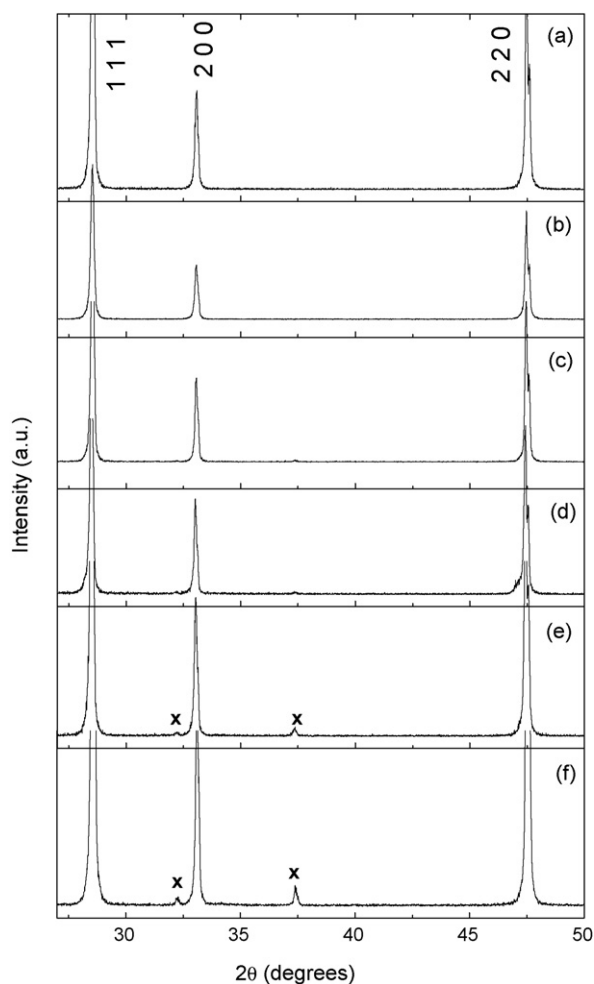


Fig. 6. Powder XRD (Cu K α) patterns for Ce_{1-x}Ca_xO_{2-x} prepared by solid-state reaction at 1500 °C for 24 h. (a) $x=0$; (b) $x=0.05$; (c) $x=0.10$; (d) $x=0.15$; (e) $x=0.20$ and (f) $x=0.25$. x denotes un-reacted CaO.

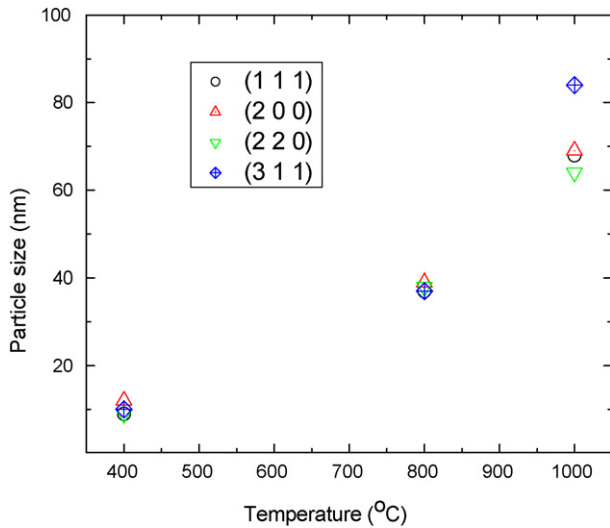


Fig. 7. Variation of particle size as a function of sintering temperature for $\text{Ce}_{0.90}\text{Ca}_{0.10}\text{O}_{1.90}$ prepared by precipitation method.

tion, the lattice constant increases with increase in Ca content up to 15 mol% and it decreases with further increase in Ca content ($x = 0.20, 0.25$). In this region, we found diffraction peaks due to un-reacted CaO (Fig. 6), suggesting the solid solution may be limited to $x \approx 0.15$ under the investigated condition.

3.2. Particle size and microstructure of CeO_2 and Ca-doped CeO_2

Fig. 7 shows the variation of average particle sizes determined using 111, 200, 220 and 311 diffraction peaks using the Scherrer method as a function of heat treatment for 10 mol% Ca-doped CeO_2 prepared by the precursor method. The particle size was found to be in the range 20–80 nm at 400–1000 °C. The results clearly show that particle size increases with increasing temperature, which is expected based on the shape of diffraction peaks. Very interestingly, the particle size distribution determined using

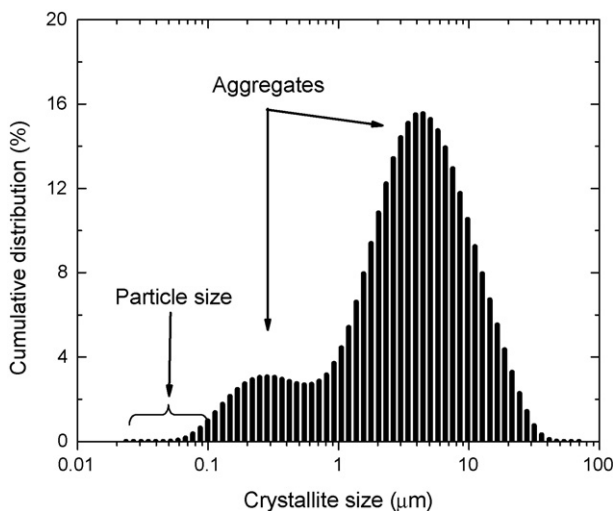


Fig. 8. Histogram of the size of particles and aggregates of $\text{Ce}_{0.90}\text{Ca}_{0.10}\text{O}_{1.90}$ prepared by coprecipitation at 800 °C.

laser particle size analyzer also show a similar range, but, aggregates of particles with a maximum size of 10 μm were also observed (Fig. 8). Fig. 9 shows the SEM images for chemical method synthesized CeO_2 and $\text{Ce}_{0.9}\text{Ca}_{0.1}\text{O}_{1.9}$. We clearly see the smaller particle sizes and large aggregates for the samples

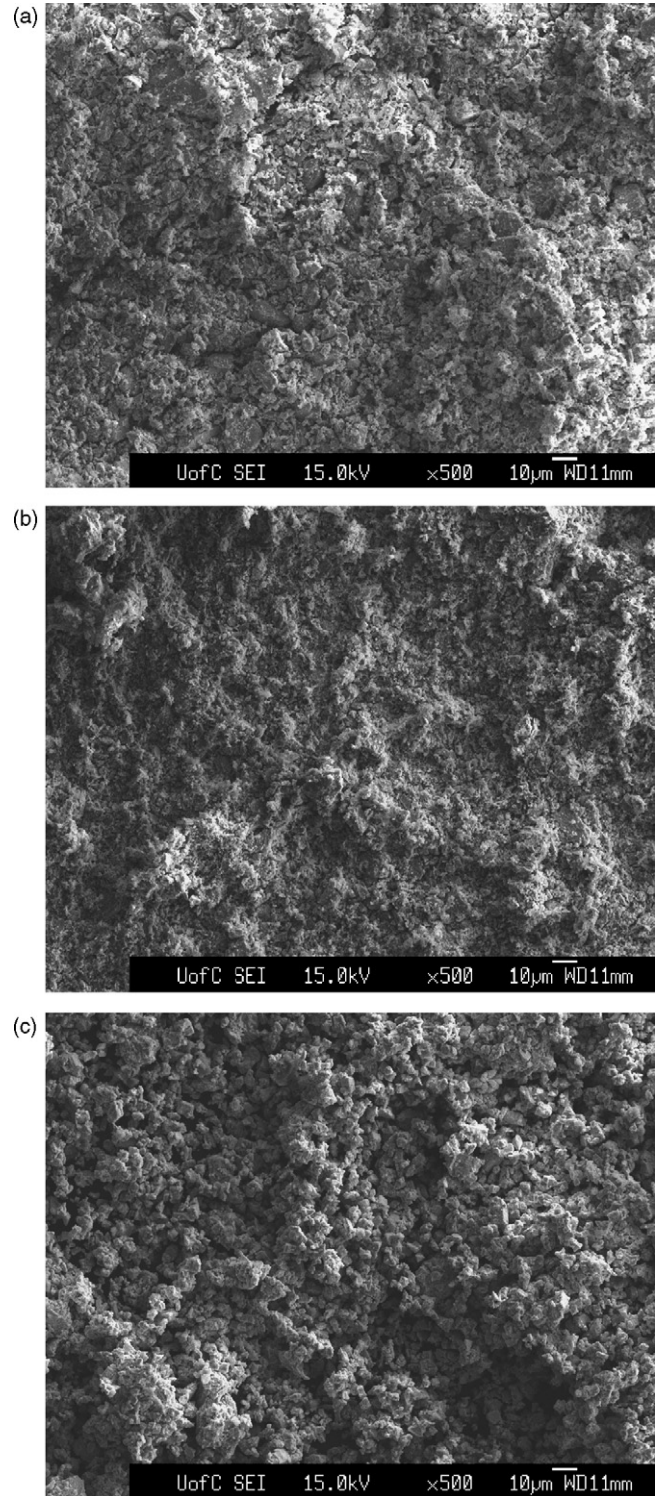


Fig. 9. Scanning electron microscopy images of powders for (a) CeO_2 prepared from the precursor at 800 °C, (b) $\text{Ce}_{0.90}\text{Ca}_{0.10}\text{O}_{1.90}$ prepared from the precursor at 800 °C, and (c) $\text{Ce}_{0.90}\text{Ca}_{0.10}\text{O}_{1.90}$ prepared by solid-state reaction at 1500 °C.

prepared by the coprecipitation method. For purpose of comparison, we have also shown the SEM images of $\text{Ce}_{0.9}\text{Ca}_{0.1}\text{O}_{1.9}$ prepared by the solid-state method. As expected, the solid-state reaction method yields higher particle size due to high temperature preparation. It is obvious that wet-chemical method gives much smaller particles/aggregates compared to conventional high temperature solid-state reactions. However, a further experimental study using transmission electron microscopy (TEM) is required to confirm these results. The present method can be used to prepare large quantities of nano-sized CeO_2 and Ca doped CeO_2 for practical applications that require large surface area materials. Our recent work is directed to prepare other ceria based fast oxide ion conductors, e.g., rare earth doped CeO_2 , using a similar coprecipitation method, to understand the role of synthesis method on the electrical conductivity.

4. Conclusions

Fast oxide ion conducting Ca-doped CeO_2 was prepared by coprecipitation method at relatively low temperature. This method involves coprecipitation of Ce and Ca ions from the aqueous solutions using oxalic acid as a precipitating agent. TGA studies show two abrupt weight losses in the temperature range from RT to 200 and 220–400 °C that are due to water degradation, and decomposition of oxalates and formation of CeO_2 , respectively. Powder XRD and LPSA studies confirm the formation of nano-size materials. XRD and SEM studies show that the particle size increases with increasing heat treatment temperature. The lattice parameter increases with increase in Ca content up to $x=0.10$ in $\text{Ce}_{1-x}\text{Ca}_x\text{O}_{2-x}$ and is consistent with solid-state preparation methods. The increase in lattice parameter is due to replacement of smaller Ce^{4+} ions by larger Ca^{2+} ions. The described method is very simple and inexpensive, and can be employed for the production of large scale of CeO_2 and Ca-doped (up to 10 mol%) CeO_2 based materials with uniform particle size distributions for fuel cells as well as catalysis applications.

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