

Synthesis of (Bi, Mn, Fe)-doped ceria electrolytes by low-temperature processes

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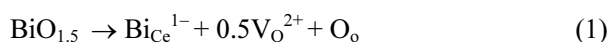
The effects of low temperature processes and the dopants of bismuth, manganese and iron co-doping in $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ materials have been investigated. The CeO_2 -based powders were synthesized by EDTA-citric acid method and their sintering behavior was analyzed by dilatometry (DIL) and density measurement. X-ray diffraction (XRD) and various electron microscopies were used to identify crystalline phases and microstructure. The results show that solubility limit of Mn and Fe in ceria is less than 1 at% while that of Bi is at 8-9 at%. Two electrolytes, $\text{Ce}_{0.9}(\text{Bi}_{0.09}\text{Mn}_{0.005}\text{Fe}_{0.005})\text{O}_2$ and $\text{Ce}_{0.9}(\text{Bi}_{0.1})\text{O}_2$, are selected and sintered to full density at 1050-1100 °C for 1 hr improved by doping trace amount of Mn and Fe. The detail microstructure characterization of the doped samples are discussed.

Key words: Ceria, Sintering, Conductivity, Bismuth, Iron, Manganese.

Introduction

Ceria-based materials are considered as one potential electrolyte to replace zirconia materials for IT-SOFCs since two decades ago [1]. Ceria doped with ions of a lower valence (e.g. Sm^{3+} and Ga^{3+}) usually perform a higher electric conductivity than that of 8YSZ at intermediate temperatures (500 °C-800 °C) [1-4]. The other electrolyte system, $\delta\text{-Bi}_2\text{O}_3$ is also a very high ionic conductivity of $1.0 \text{ S} \times \text{cm}^{-1}$ at 800 °C and known to have same fluorite structure as the doped CeO_2 [5]. However, complex phase transformation, a high coefficient of thermal expansion ($\text{CTE} > 20 \text{ ppmK}^{-1}$ from room to 800 °C), high sublimation and possible reduction problems at high temperature of $\delta\text{-Bi}_2\text{O}_3$ make it cannot be used as a mainstream electrolyte material.

Alternatively, any aliovalent oxides, e.g. Bi_2O_3 , used as a dopant of CeO_2 to promote O^{2-} transportation of ceria by the reaction:



Besides, the sintering temperature of this ceria-based material is also reduced due to a low melting point ($T_m = 825 \text{ °C}$) of Bi_2O_3 [6]. Similar dopants, e.g. rare earth oxides M^{3+} and alkaline earth oxides AE^{2+} , were also used in ceria to achieve the reduction of sintering temperature, possibly due to the formation of low-temperature liquid phase [6-13]. But no solid evidences of glassy boundary are provided to differentiate their statement of fast densification, either by liquid-phase

assistant sintering or solid state sintering by oxygen diffusion enhancement.

In our previous report [13], three (Bi, Mn, Fe) oxides are used as the dopants for ceria and show some solution limitation at the temperatures up to 1400 °C. The objectives of this study are focusing on the sintering behavior at lower sintering temperatures for performing a good electric conductivity. The influences of the dopants on the microstructure are analyzed and discussed.

Experimental

Sample preparation

The chemicals, bismuth (III) oxide (Bi_2O_3 , 99.9% pure, Solar Applied Material Corp., Taiwan), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.5%, Alfa Aesar, USA), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%, Showa, Japan), and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (98%, Alfa Aesar, USA) are adopted to synthesize the powders. The notations of the powders are listed in Table 1. Ethylene diamine tetraacetic acid (EDTA, 99%, Acros, USA) and citric acid (99.5%, Showa, Japan) were used as chelating agents in the EDTA-citric method. The metal oxide and metal nitrate hydrate powders were separately dissolved in HNO_3 ($\geq 65 \text{ wt\%}$, Sigma-Aldrich, USA) and distilled water. Then, each solution was pre-mixed together and stirred for 0.5 hr at room temperature. Next, the mixed metal nitrate solution was drop-by-drop added into the NH_4OH solution (28-30%, J. T. Baker, USA), followed by the addition of citric acid with stirring. The molar ratio of total metal ions to EDTA and citric acid was 1:1:2. The citric acid was often added excessively (more than 1:1:1) in order to stabilize the dissolved metallic ions. After the solution was mixed and stirred, NH_4OH was added to adjust the pH of the solution to 7.0, then stirring for additional

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2.0 hr. The solution was heated on a heat plate with stirring at 85 °C in air for 4 hr to remove the excess water until a viscous gel was formed. The gel was then dried and combusted into fluffy powders at 200 °C, holding for 12 hr in an oven (vacuum oven, SHELAB, USA). At last, the powders were calcined at 800 °C for 1 hr.

After calcining, the powders were ground and sieved by a 200 mesh screen before die-pressing. The powders were die-pressed with a load of 120 MPa lasting for 1.0 min to disc shape of 16.0 mm in diameter and 1.5 mm in thickness. Then sintered the pellets at 1000-1400 °C for subsequent tests.

Characterization

Crystal structure and phase of samples was analyzed using an X-ray diffractometer (XRD, TTRAX 3, Rigaku Ltd., Japan) with Cu K α filtered by Ni. The scanning rate was 4 °min⁻¹ and the scanning range of the 2 θ angle was 20°- 80°. The accelerated voltage was 50 kV at 300 mA.

The die-pressed pellets were sintered in air at a heating rate of 5 °Cmin⁻¹. The apparent density was measured by Archimedes method. The microstructures of the sintered bulk samples were characterized by using a scanning electron microscope (SEM, JSM6510, JEOL, Japan) and two transmission electron microscope (Philips Tecnai F30, the Netherland, and JEOL2010F, Japan). The average grain size is calculated by the following equation.

$$\text{Average Grain Size} = 1.54 \times \frac{L_{\text{eff}}}{MN_{\text{eff}}} \quad (2)$$

where L_{eff} is the summary of each effective length crossed the grains, M is the magnification, N_{eff} is the effective number of the measured grains.

Total electrical conductivity of the sintered sample from 400 °C to 800 °C was measured by a two-probe DC method. Both surfaces of the sinteted samples were coated with a thin Pt layer and then attached an Ag wire by Ag paste. Conductivity of the samples was calculated by Eq. (3):

$$\sigma = \frac{t}{R \times A} \quad (3)$$

where t is the thickness of sample, A is the area of sample and R is the measured resistance of sample.

Dilatometry are used to precisely measure the shrinkage rate of green samples as a function of temperature. Cylindrical samples in a thickness of 1.0 cm were heated at a rate of 5 °C × min⁻¹ in air on the dilatometry instrument (DIL, DIL402C, Netzsch, Germany).

Results and Discussion

Solution limit

Three dopants, Bi, Mn and Fe in CeO₂ were prepared

Table 1. Notations, compositions and impurity phase(s) of synthesized ceria-based powders.

Notation	Ce ⁴⁺	Bi ³⁺	Mn ³⁺	Fe ³⁺	Impure Phase
777	79	7	7	7	BiFeO ₃ (1200-1250 °C) MnFe ₂ O ₄ (1200-1350 °C) Fe ₁₉ Mn (1350-1400 °C)
333	90	3.3	3.3	3.3	BiFeO ₃ (1100 °C) MnFeO ₄ (1100-1300 °C)
811	90	8	1	1	Fe ₂ O ₃ (1350-1400 °C)
E11	80	18	1	1	γ -Bi ₂ O ₃ (800-1200 °C)
F33	80	14	3	3	δ -Bi ₂ O ₃ (800-1200 °C)
T55	80	10	5	5	δ -Bi ₂ O ₃ (800-1200 °C)
9HH	90	9	0.5	0.5	No
T00	90	10	0	0	No

T: Abbreviation of “Ten”; F: Abbreviation of “Fourteen”; E: Abbreviation of “Eighteen”; H: Abbreviation of “Half.”

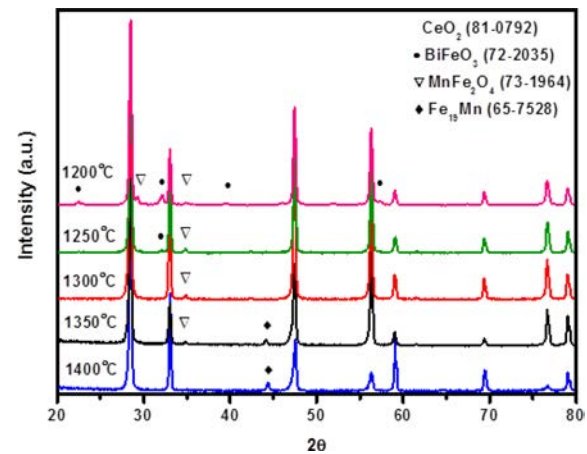


Fig. 1. XRD patterns of 777 sintered at 1200-1400 °C for 5 hr.

by the EDTA-citrate acid method in order to obtain single phasic ceria-based samples. As the doping level is over the solution limit in CeO₂, new phase other than fluorite is possibly formed. Eight Ce_{1-x-y}(Bi_xMn_yFe_y)O₂ powders (Table 1) containing different levels of dopants were synthesized and investigated by XRD. As the pre-heating temperature conducted at >800 °C or higher, impure phases appear. One series of the XRD patterns of 777 sample heat-treated at 1200-1400 °C for 5 hr is shown in Fig. 1. BiFeO₃, MnFe₂O₄ and Fe₁₉Mn are observed from 1200 °C to 1400 °C in sequence. Thus, a sample containing 21 mol% dopant according to the 777 recipe cannot form a fully solid solution in this temperature range.

In order to avoid forming of secondary phase(s), the next approach is to reduce the total doping concentration to 10 at%, as shown in Table 1. The impure phases are classified into two groups: either Fe/Mn-containing phases or Bi-containing phases. The Fe/Mn-phases, including BiFeO₃, MnFe₂O₄ and Fe(Mn)O₃, are observed in 777, 333 and 811 powders after heat-treating at 1100-

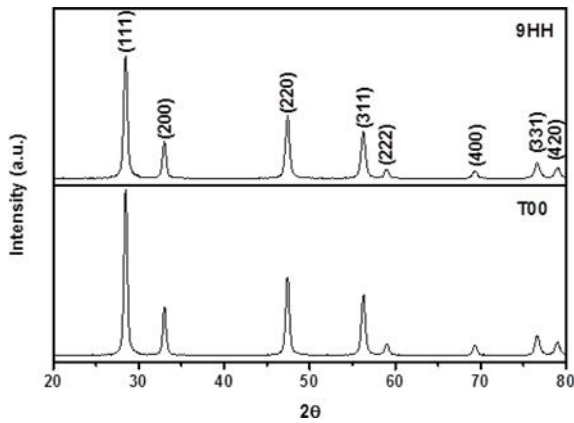


Fig. 2. XRD patterns of 9HH and T00 powders calcined at 800 °C for 1 hr.

1400 °C. That implies that Mn and Fe tend to form new compounds when the doping level is higher than 1 mol%.

On the other hand, only Bi-contained impure phases are identified in E11, F33 and T55 after heat-treating at 800 °C–1200 °C. This implies that the solution limit of Bi^{3+} in CeO_2 at temperatures below 1200 °C may be lower than 10 mol% in the presence of Mn and Fe. The reported solubility limit of Mn and Fe in ceria was 1.0–0.5 mol% [14–16]. While the solubility limit of doped Bi species is around 10.0 at% [6], only 9HH is selected and compared to T00 for the following tests due to the requirements of single-phase (Fig. 2) and favored conductivity.

Sintering behavior

For achieving better electric conductivity, an electrolyte should be sufficiently dense, i.e. $\geq 95\%$ theoretical density (TD). The samples by 800 °C calcined powders were die-pressed into cylindrical-shape for dilatometry analysis. The linear shrinkage rates (R_L) of T00 and 9HH are shown in Fig. 3(a). Both samples start to shrink at around 800 °C and the shrinkage rates reach their maximum at 1009 °C and 1024 °C, respectively, for T00 and 9HH. So the sintering temperature for two samples used is higher than 1025 °C. In addition, the shrinkage rate curve of the 9HH shows that the initial sintering temperature is slightly higher than that of T00 because the melting points of Fe_2O_3 and Mn_2O_3 are both higher than that of Bi_2O_3 . But 9HH shows a higher maximal and narrower

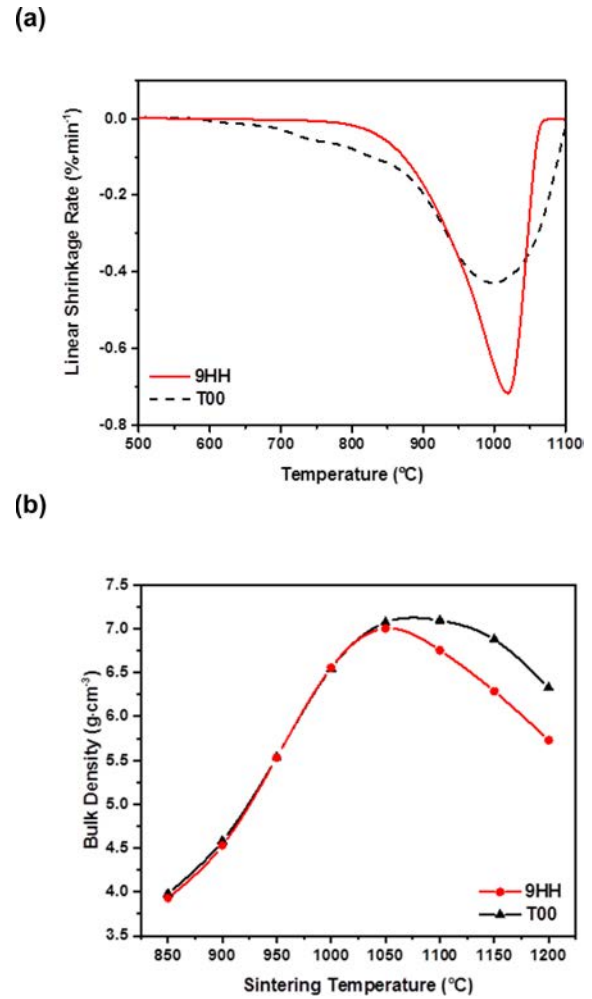


Fig. 3. (a) Linear shrinkage rate and (b) sintering density of 9HH and T00 samples plotted against sintering temperature at a heating rate of 10 °C.min⁻¹.

shrinkage rate than that of T00, possibly due to a higher grain boundary mobility caused by the Mn and Fe dopants [15, 16].

Density results of bulk 9HH sample are shown in Fig. 3(b). The densities of T00 and 9HH samples increase with increasing sintering temperature until 1050 °C, and then decrease above 1050 °C, possibly degrading by Bi sublimation. Our previous work [14] has investigated when Bi_2O_3 containing sample is exposed in oxidation or mild-reducing atmosphere, part of the Bi_2O_3 sublimates at the temperatures ≥ 650 °C, and quickly evaporates while the temperature is greater

Table 2. Pre-annealing and sintering schedules, and sintered densities of 9HH samples.

	Pre-annealing	Sintering	Density
Test A	830 °C for 3 hr @ 10 °C/min	1050 °C for 5 hr @ 10 °C/min	6.875 gcm ⁻³
Test B	830 °C for 3 hr @ 10 °C/min	1050 °C for 1 hr @ 10 °C/min	6.874 gcm ⁻³
Test C	X (no holding)	1050 °C for 1 hr @ 10 °C/min	6.732 gcm ⁻³
Test D	X (no holding)	1050 °C for 1 hr @ 5 °C/min	7.004 gcm ⁻³
Test E	750 °C for 0 hr @ 10 °C/min	1050 °C for 1 hr @ 5 °C/min	7.002 gcm ⁻³

than the melting temperature (825 °C) of Bi_2O_3 -compounds.

Detail tests on the preheating and sintering schedules on the sintering density are tried, and testing conditions are shown in Table 2. The samples could be densified in test A after being pre-sintered at 830 °C for 3 hr and then sintered at 1050 °C for 5 hrs with a heating rate of $10\text{ }^\circ\text{C} \times \text{min}^{-1}$. Since the density is $6.87 \pm 0.005\text{ g} \times \text{cm}^{-3}$, equal to 98.0% TD, other sintering processes (with or without pre-heating) have been also conducted to increase the density. Tests D and E using a heating rate of $5\text{ }^\circ\text{C} \times \text{min}^{-1}$ are effective to improve the final sintered density. As a result, the density of 9HH is successfully improved to $7.00 \pm 0.005\text{ g} \times \text{cm}^{-3}$ after sintering at 1050 °C for only 1 hr at a rate of $5\text{ }^\circ\text{C} \times \text{min}^{-1}$. In summary, the Test D without pre-heating green powders at 830 °C saves ca. 6.25 hr (decreasing from 9.75 to 3.5 hr) over the other tests. Microstructures of 9HH and T00 processed by Test E are shown in Fig. 4, which reveals almost fully dense and no pores. Both samples are densified to >99% TD.

Microstructure containing glassy boundaries

Detailed microstructures of sintered 9HH and T00 were observed by TEM. Fig. 5(a) shows the grains in 9HH with narrow size distribution. An average grain size of 95 nm and no abnormal grain growth after the sintering process are noted for both samples. In addition, amorphous phase is found at the grain boundary of 9HH with a thickness of about 1.1 nm, as shown in Fig. 5(b). The amorphous phase is continuous at the binary boundary, implying the densification of the 9HH relying on the glass phase.

Fig. 6(a) shows the EDS spectra of the selected area shown in Fig. 5(b). Positions of “a” and “b” are at the center of the grains, while “c” and “d” are at the triple-grain boundary. The spectra were obtained by semi-quantitative analysis. Detailed comparison of the EDS intensity for each element is shown in Figs. 6(b) and 6(c). The strongest X-ray dispersive peak of Mn overlaps with that of Ce at 6.0 keV, and Fe overlaps with that of Ce and Cu at 0.7 keV. This overlapping certainly influences the semi-quantitative analysis of Mn and Fe, makes the interpretation of Mn and Fe contents doubtful. Below we only report the Bi-results.

Table 3 shows that Bi contents in the grain are $\leq 5\text{ mol}\%$, while Bi contents at the triple-grain boundaries are greater than 5 mol%, and possibly up to 10.6 mol%. This implies that Bi is repelled from the grains and may diffuse to the grain boundary or surface if forming a liquid phase at sintering temperature. As a result, the liquid phase at the grain boundary can dramatically improve the densification. That is why T00 and 9HH achieve a full density at temperatures as low as 1050–1100 °C.

The microstructure of T00 is shown in Fig. 5(c), fine grains and narrow grain size distribution are noted.

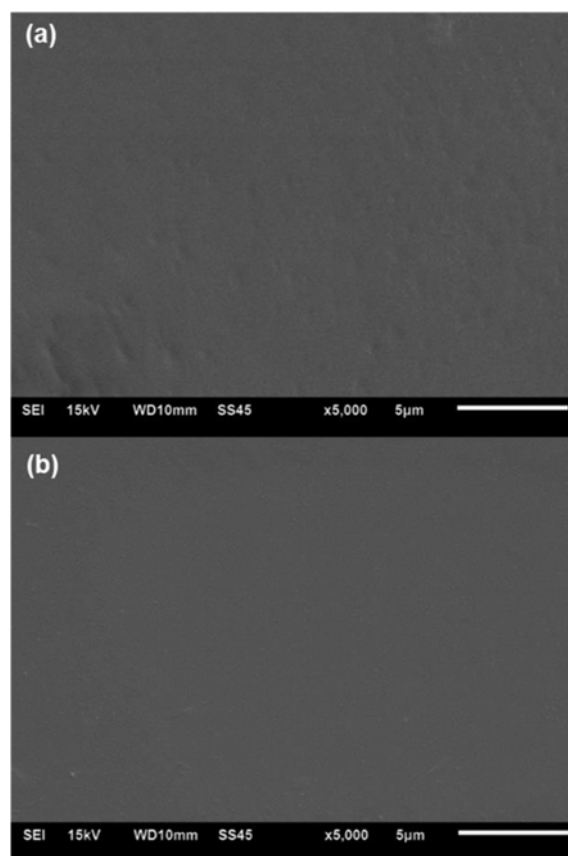


Fig. 4. SEM images of the polished surface of (a) 9HH sintered at 1050 °C for 1 hr and (b) T00 sintered at 1100 °C for 1 hr.

Table 3. Bismuth content of the selected area shown in Fig. 5(b) by EDS analysis.

	$\text{BiO}_{1.5}$ (mol%)
a	3.7 mol%
b	4.5 mol%
c	6.7 mol%
d	10.6 mol%

Amorphous boundaries of T00 are not as obvious as that in 9HH after examining more than 50 grains. Thus, the evaporation of Bi_2O_3 -rich glass in T00 during sintering at 1100 °C for 1 hr might be apparent, and eliminate most of Bi-containing glass phase.

Electric conductivity

The conductivity and degradation behavior of the ceria materials are shown in Fig. 7. The comparable cases of 811 and 777 by Chiu [13] and T00 by Dikmen [6] are also plotted in Fig. 7. The conductivity of T00 testing in air is the highest in the range of 450–800 °C, e.g. $1.34 \times 10^{-2}\text{ S} \times \text{cm}^{-1}$ at 800 °C. The reason is due to a clean grain boundary of T00, as shown in the TEM microstructure in Fig. 5(c).

9HH performs the next highest conductivity, e.g.

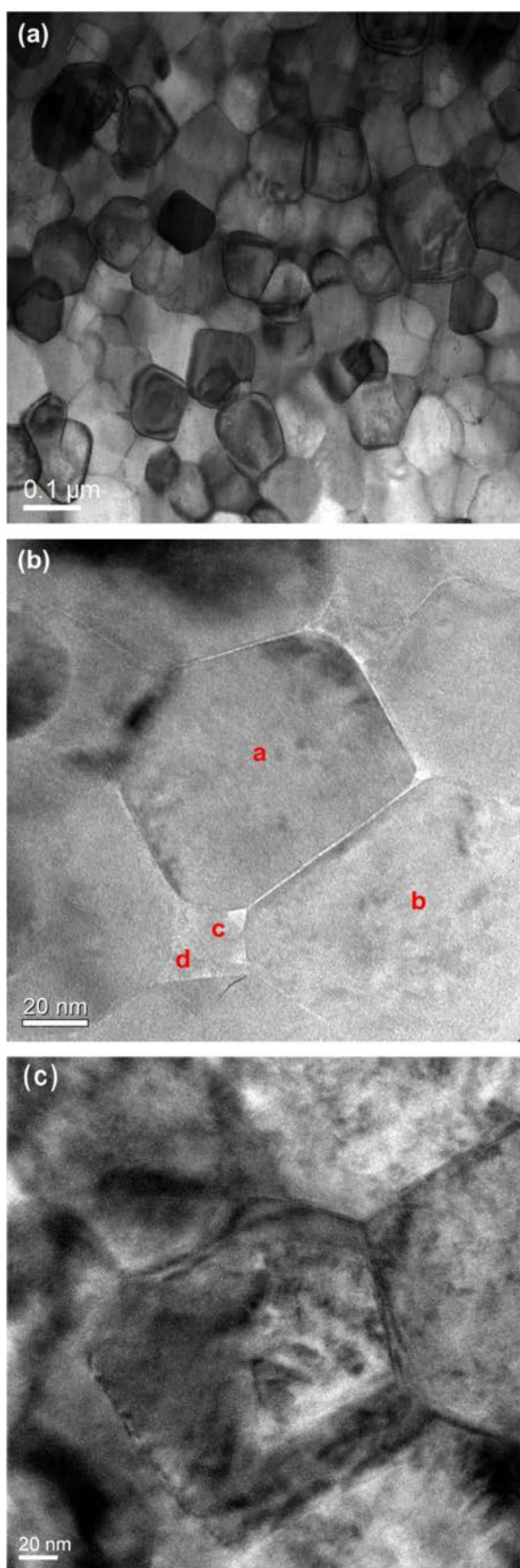


Fig. 5. TEM BF images of (a) sintered 9HH, and (b) grain boundaries of the 9HH sample, (c) TEM BF micrograph of 1100 °C/1 hr sintered T00 sample.

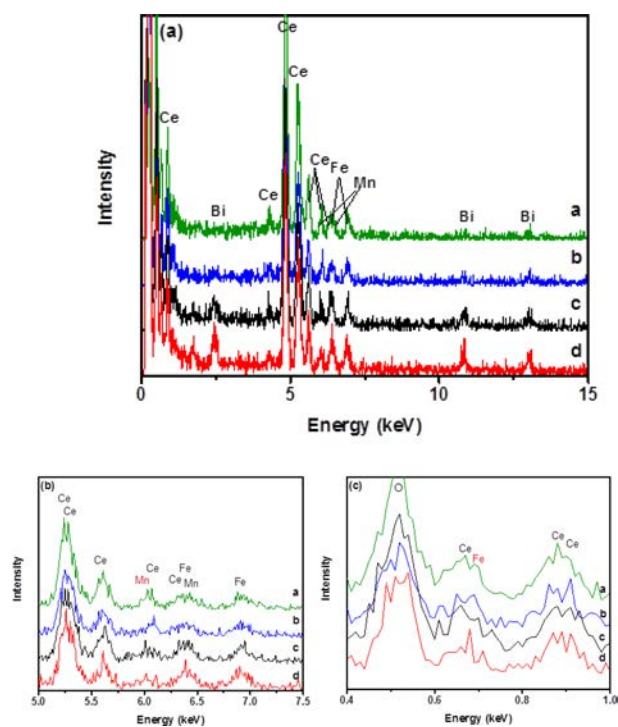


Fig. 6. EDS spectra of selected area shown in Fig. 5(b). The energy of the plot is in the range of (a) 0-15, (b) 5.0-7.5 keV, and (c) 0.4-1.0 keV

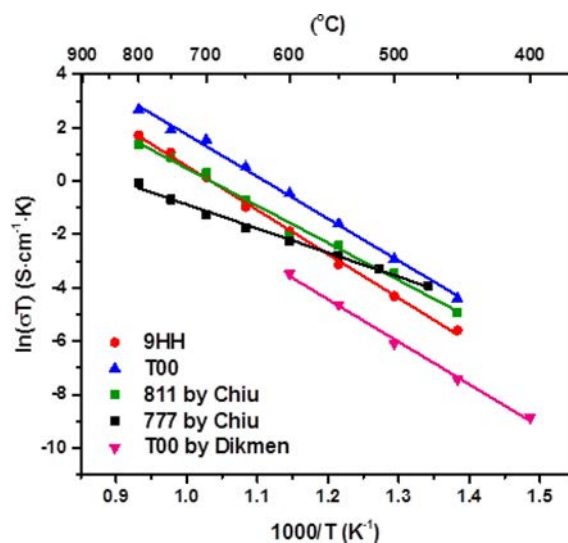


Fig. 7. Arrhenius plot of conductivity of 9HH and T00 in the temperature range of 450 °C-800 °C. The reference data of Ce_{0.9}Bi_{0.1}O₂ reported by Dikmen is also plotted for comparison.

$5.15 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at 800 °C, which may be due to two reasons: One is favored for improving the conductivity, more oxygen vacancies is resulted from the solid solution of Bi, Mn and Fe in CeO₂. The other, glassy boundary, is degrading the conductivity performance.

Activation energies of the ceria materials are measured from the slopes of the conductivity lines in Fig. 7 and summarized in Table 4. The activation

Table 4. Conductivity at 800 °C and activation energy of (Bi, Mn, Fe)-doped ceria materials and data reported by others.

Sample (Sintering Temp.)	Impure Phase	$\sigma_{800^\circ\text{C}}$ (S·cm ⁻¹)	E _a (eV)	Note
T00 (1100 °C)	No	--	*1.37 ± 0.04	Dikmen [6]
T00 (1100 °C)	No	1.34 × 10 ⁻²	1.36 ± 0.03	--
9HH (1050 °C)	No	5.15 × 10 ⁻³	1.42 ± 0.03	--
811 (1050 °C)	No	3.59 × 10 ⁻³	1.20 ± 0.05	Chiu [13]
777 (1250 °C)	BiFeO ₃ and MnFe ₂ O ₄	8.83 × 10 ⁻⁴	0.78 ± 0.02	Chiu [13]

*The activation energy of T00 reported by Dikmen is 1.02 ± 0.04 eV, which is not corresponded to the value calculated from the linear fitting line in his report. The activation energy in this table, 1.37 ± 0.04, was recalculated from the linear fitting line.

energies of all materials except 777 are similar, in the range of 1.31 ± 0.12 eV implying that T00, 9HH and 811 contain similar conductive species at 450-800 °C. The conductivity mechanism in 777 might be strongly influenced by the metallic phase at grain boundary caused by sublimation of Bi species, or by the formation of secondary phases (i.e. BiFeO₃ and MnFe₂O₄) after sintering.

Conclusions

Triple-doped (Bi, Mn and Fe) CeO₂-based materials are successfully synthesized by an EDTA-citrate method. Several second phases appear with the dopant concentrations higher than the solution limit in CeO₂. Based on the XRD analysis results, the solubility limits of Mn and Fe co-existing with Bi dopant are ≤1.0 at%, and the solubility limit of Bi co-existing with Mn and Fe is 9.0 at%. The maximal total doping concentration of Bi, Mn and Fe in ceria is 10 at%. The conditions to obtain a single phase of fluorite structure are calcining at 800-1100 °C for 1 hr.

Dense T00 (only 10 mol% Bi-doped CeO₂) and 9HH (9 mol% Bi-0.5 mol% Mn-0.5 mol% Fe doped CeO₂) samples are successfully obtained by sintering to 1050 °C at a rate of 5 °Cmin⁻¹ and holding for 1 hr without holding at 800 °C. Glassy phase is noted staying at triple and binary grain boundaries of 9HH. But glass phase is hardly detected in T00 possibly due to an extensive evaporation of Bi species at the sintering/annealing stages. But the glass boundary is retained by the Mn and Fe dopants in 9HH, and makes the electric conductivity of 9HH initially worse than that of T00 in short annealing time (≤20 hr).

The activation energy of the conductivity of these CeO₂-based electrolytes is in the range of 1.32 ± 0.12 eV. Those pure fluorite materials show same electric conductive mechanism at the temperatures ≤800 °C.

Acknowledgements

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References

1. H. Inaba, H. Tagawa, Solid State Ionic 83 (1996) 1-16.
2. L. Minervini, M.O. Zacate, R.W. Grimes, Solid State Ionic 116 (1999) 339-349.
3. K. Eguchi, J. Alloys Compd. 250 (1997) 486-491.
4. V.V. Kharton, F.M. Figueiredo, L. Navarro, E.N. Naumovich, A.V. Kovalevsky, A.A. Yaremchenko, A.P. Viskup, A. Carneiro, F.M.B. Marques, J.R. Frade, J. Mater. Sci. 36 (2001) 1105-1117.
5. W.S. Jang, S.H. Hyun, S.G. Kim, J. Mater. Sci. 37 (2002) 2535-2541.
6. S. Dikmen, P. Shuk, M. Greenblatt, Solid State Ionic 112 (1998) 299-307.
7. W. Zajac, J. Molenda, Solid State Ionics 179 (2008) 154-158.
8. S.A. Muhammed Ali, M. Anwar, A.M. Abdalla, M.R. Somalu, A. Muchtar, Ceram. Int. 43 (2017) 1265-1271.
9. H. Bi, X. Liu, L. Zhu, J. Sun, S. Yu, H. Yu, L. Pei, J. Hydrog. Energy 42 (2017) 11735-11744.
10. K. Venkataramana, C. Madhuri, Y. Suresh Reddy, G. Bhikshamaiah, C.V. Reddy, J. Alloys and Compd. 719 (2017) 97-107.
11. I.V. Zagaynov, S.V. Fedorov, A.A. Kononov, O.S. Antonova, Mat. Let. 203 (2017) 9-12.
12. A. Arabaci, Metal. Mat. Trans. A 48 (2017) 2282-2288.
13. C. Chiu, in "doped ceria-based fluorite type electrolyte materials for IT-SOFC", (National Taiwan University, 2017) p.50-65.
14. Y.H. Cheng, Y.Y. Chen, W.C. Wei, J. Ceram. Processing Research 19[5] (2018) 388-393.
15. S. Boyapati, E.D. Wachsman, N. Jiang, Solid State Ionics 140 (2001) 149-160.
16. N. Jiang, R.M. Buchanan, F.E.G. Henn, A.F. Marshall, D.A. Stevenson, E.D. Wachsman, Mater. Res. Bull. 29 (1994) 247-254.