

# Chemical stability study of $\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{3-x}$ high-temperature proton-conducting ceramic

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$\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{3-x}$  (BCN) ceramic is known to be an excellent high-temperature proton conductor and is a candidate electrolyte for use in solid oxide fuel cells, hydrogen or steam sensors and steam electrolyzers. In this work, the chemical stability of BCN was investigated systematically by combining XRD and DTA–TG techniques to study its processing compatibility and its feasibility in potential applications. It was found that above 1200 °C, BCN reacted with alumina or zirconia, leading to the loss of barium and an excess of cerium. In cold water, both sintered BCN disks and powder samples had very low solubility and did not hydrolyse, but they were soluble in some mineral acids, especially in HCl with the liberation of  $\text{Cl}_2$ . In boiling water, BCN pellets dissolved readily with decomposition into  $\text{CeO}_2$  and  $\text{Ba}(\text{OH})_2$ . In 1 atm  $\text{CO}_2$ , BCN decomposed to form  $\text{CeO}_2$  and  $\text{BaCO}_3$  below 1200 °C during heating, but during cooling it was stable above 1000 °C, possibly because BCN has different crystal structures at low and high temperatures. At 600–1000 °C, BCN showed a slight mass loss when exposed to a reducing atmosphere, and a slight mass gain in an oxidizing atmosphere. XRD results revealed that BCN demonstrated chemical and structural stability in both reducing and oxidizing atmospheres.

$\text{BaCeO}_3$  doped with rare-earth-metal oxides such as  $\text{Nd}_2\text{O}_3$  is known to exhibit significant protonic conduction in hydrogen or water vapour containing atmospheres at elevated temperatures.<sup>1–6</sup> Their ability to conduct protons makes these systems potential candidates for applications in many novel electrochemical devices such as solid oxide fuel cells, hydrogen or steam sensors, electrolyzers for hydrogen production and high-temperature membrane reactors.

$\text{BaCeO}_3$ -based perovskite oxides are usually formed by a conventional ceramic process involving calcining mixtures of the respective oxides and carbonates at elevated temperatures ( $\geq 1100$  °C) followed by sintering powder compacts at 1400–1600 °C.<sup>1,6</sup> The sample holders used are usually alumina or zirconia. At high temperatures, there is probably reaction between the sample and the sample holder, and this will undoubtedly contaminate the product and affect its electrical properties.

When these materials are used as the electrolytes for solid oxide fuel cells, wet fuels (dilute hydrogen) are supplied. In the cases of steam sensors and electrolyzers, water vapour is present in the working environments. So, the stability of these materials in water vapour containing atmospheres is of particular importance. Tanner and Virkar<sup>8</sup> found that both pure and rare-earth-metal doped  $\text{BaCeO}_3$  were thermodynamically unstable in the temperature range 500–900 °C in an atmosphere of *ca.* 430 Torr  $\text{H}_2\text{O}$  (through a 90 °C water bubbler), and decomposed to form  $\text{CeO}_2$  and  $\text{Ba}(\text{OH})_2$ . However, the water solubility of  $\text{BaCeO}_3$ -based material at lower temperatures is still unreported.

In another promising application of solid oxide fuel cells using readily available city gas as the fuel (of which  $\text{CH}_4$  is the main component), the stability of the electrolyte in  $\text{CO}_2$  containing atmospheres is vital, since by reforming city gas at 800 °C, a quasi-fuel gas atmosphere containing *ca.* 8%  $\text{CO}_2$  is produced. The stability of undoped  $\text{BaCeO}_3$  in a  $\text{CO}_2$  atmosphere has been studied by Scholten *et al.*<sup>9</sup> and Gopalan and Virkar,<sup>10</sup> but there is some discrepancy between their results. Scholten *et al.* found that  $\text{BaCeO}_3$  decomposed below 1185 °C, while Gopalan and Virkar showed that  $\text{BaCeO}_3$  were thermodynamically unstable below 1090 °C. Therefore, the stability of  $\text{BaCeO}_3$  in a  $\text{CO}_2$  atmosphere needs to be reinvestigated.

Following the above observations, the purpose of this work is to systematically examine the chemical stability of Nd-doped  $\text{BaCeO}_3$  in the preparation process and in different environments to investigate the possibility of using this material for practical applications.

## Experimental

### Sample preparation

$\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{3-x}$  (BCN) was prepared through a conventional ceramic route. The starting materials were  $\text{BaCO}_3$ ,  $\text{CeO}_2$  and  $\text{Nd}_2\text{O}_3$  (all from Alfa). The chemicals, mixed in stoichiometric ratio, were ball-milled in ethanol for 36 h. The resulting slurry was then dried in air and calcined at 1000 °C, which resulted in a single perovskite phase. After calcination, the powder was crushed and ball-milled in ethanol, after which it was pressed into pellets without the addition of binders and sintered in air by two different methods at 1000, 1200 and 1400 °C for 10 h and at 1500 °C for 2 h. In the first method, green pellets were placed on alumina or zirconia plates, while in the second method, pellets were placed on a thick layer of calcined powders of the same composition which was laid between the pellets and the alumina or zirconia plates. The contact surface of the sintered specimens, alumina and zirconia plates was characterized by X-ray diffractometer (Philips PW1078/10).

### Stability in water

Some 1500 °C sintered pellets prepared by the second method ( $>97\%$  theoretical density, no open porosity) were immersed in cold water, while others were immersed in water and heated to boiling point. The pH values in both cases were measured using a pH meter. In cold water, the pellets were intact after one week, while those in boiling water broke into pieces and finally became powders after 6 h. The resulting pellets and powders were dried and examined by XRD.

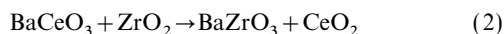
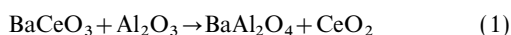
### Exposure to different atmospheres

Some of the 1500 °C sintered pellets from the second method were ground into powders. XRD revealed them to be a single perovskite phase. The powders were examined by differential thermal analysis (DTA) and thermogravimetry (TG), using a Netzsch STA 429 thermal analyser. Samples were heated from 25 to 1400 °C at a heating rate of 2 °C min<sup>-1</sup> and a cooling rate of 5 °C min<sup>-1</sup> in 7% H<sub>2</sub>-93% Ar, air and CO<sub>2</sub>, respectively. After DTA-TG measurements, the powders were characterized by XRD.

## Results and Discussion

### Reaction between BCN and alumina or zirconia

When pellets were sintered in direct contact with alumina, the contact surface of the sintered pellet turned yellow; when laid directly on zirconia, it was grey, while Nd-doped BaCeO<sub>3</sub> was dark brown. With an increase in the sintering temperatures, the change in colour of the contact surface became more obvious. XRD traces of the contact surface of the sintered samples are shown in Fig. 1 and 2. The diffraction peaks belonging to BaCeO<sub>3</sub> were identified easily, but additional peaks due to CeO<sub>2</sub> were also present. Fig. 1 and 2 clearly show that at high sintering temperatures, BCN reacted with the contact substrates and a considerable amount of CeO<sub>2</sub> was formed. XRD patterns of the contact substrates showed that BaAl<sub>2</sub>O<sub>4</sub> was formed on alumina and BaZrO<sub>3</sub> was formed on zirconia. Accordingly, it can be concluded that BCN reacted with Al<sub>2</sub>O<sub>3</sub> or ZrO<sub>2</sub> and decomposed through the following reactions:



The extent of the reaction between the sample and the substrate could be determined by comparison of the relative

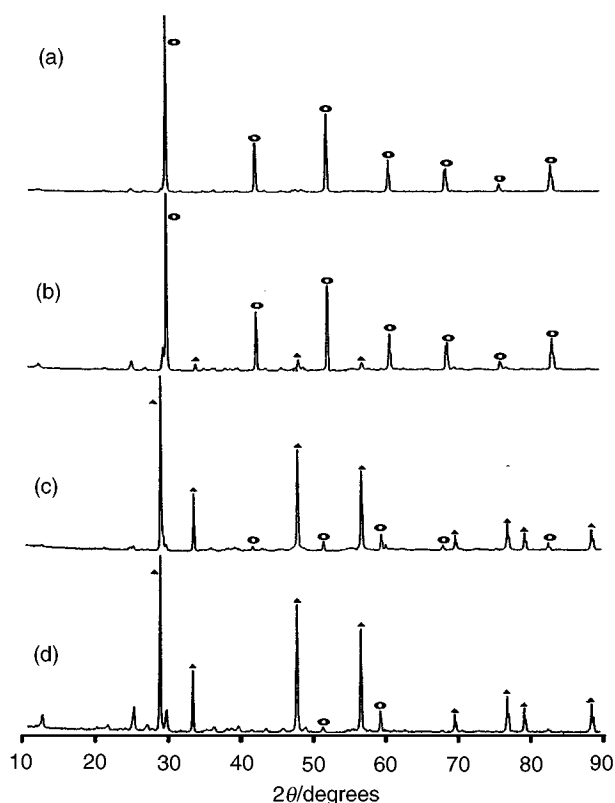


Fig. 1 XRD patterns of the contact surface of the sintered BCN pellet directly on alumina at (a) 1000, (b) 1200, (c) 1400 and (d) 1500 °C. ○, BaCeO<sub>3</sub>; ▲, CeO<sub>2</sub>.

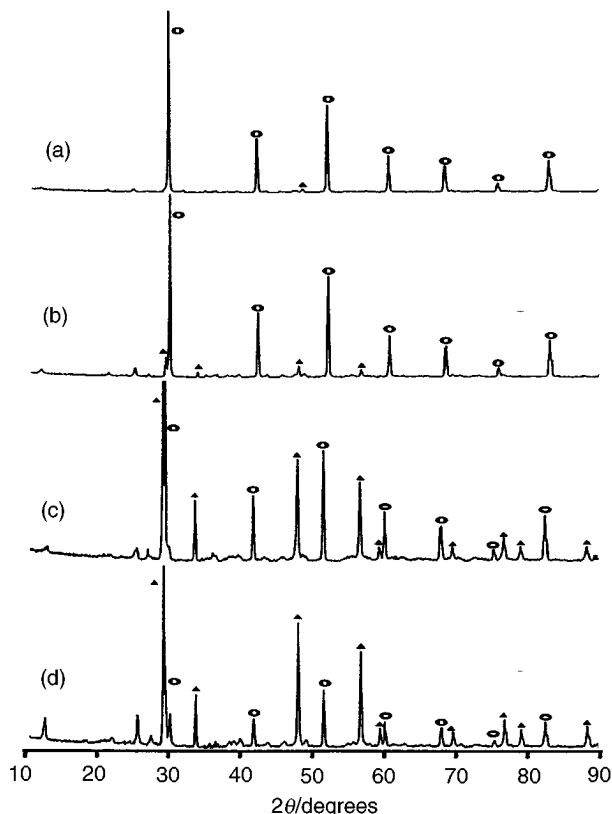


Fig. 2 XRD patterns of the contact surface of the sintered BCN pellet directly on zirconia at (a) 1000, (b) 1200, (c) 1400 and (d) 1500 °C. ○, BaCeO<sub>3</sub>; ▲, CeO<sub>2</sub>.

heights of the CeO<sub>2</sub> and BaCeO<sub>3</sub> peaks. When the specimen was sintered at high temperatures, the reaction between the sample and alumina was greater than that between the sample and zirconia.

The Gibbs energies of the individual compounds and reactions (1) and (2) are listed in Table 1. It can be seen that BaCeO<sub>3</sub> is thermodynamically unstable in contact with alumina or zirconia and the reaction with Al<sub>2</sub>O<sub>3</sub> is more thermodynamically favoured than that with ZrO<sub>2</sub>. When BCN was sintered at high temperature on alumina or zirconia, the contact surface of the sintered specimen showed mainly CeO<sub>2</sub> peaks, and no trace of barium aluminate or barium zirconate was identified. This implies that reactions (1) and (2) took place, and barium reacted with the substrate, leaving CeO<sub>2</sub> on the contact surface of the sintered specimen. This will lead to an excess of CeO<sub>2</sub> in the product. Since the reaction between BCN and Al<sub>2</sub>O<sub>3</sub> proceeded more smoothly than that of BCN and ZrO<sub>2</sub>, the contact surface of the sintered specimen was greyish when sintered on zirconia and yellowish (a typical colour of CeO<sub>2</sub>) on alumina.

When a pellet of BCN was placed on a thick layer of calcined powders of the same composition and sintered, both the surface and the inner part of the sintered pellet had the same dark brown colour. XRD showed that the pellet had a single perovskite phase, indicating that no reaction had taken place between the sample and the substrate. XRD patterns revealed that the calcined powder layer was a mixture of CeO<sub>2</sub> and perovskite phase, indicating its reaction with the substrate. So the thick layer of calcined powders acted as a buffer and prevented the reaction between the pellet and the substrate. Therefore, using a thick layer of calcined powders in the sintering process seems to be an effective way to obtain sintered samples with desired BCN compositions.

At low sintering temperatures (< 1000 °C), BaCeO<sub>3</sub> exhibited kinetic stability over alumina or zirconia, and BaCeO<sub>3</sub>-based thin films have been successfully fabricated on alumina

**Table 1** Gibbs energy values (in kJ mol<sup>-1</sup>) of some compounds and reactions (1) and (2)

T/K	BaCeO <sub>3</sub> <sup>a</sup>	BaZrO <sub>3</sub> <sup>a</sup>	BaAl <sub>2</sub> O <sub>4</sub> <sup>b</sup>	CeO <sub>2</sub> <sup>b</sup>	Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	ZrO <sub>2</sub> <sup>b</sup>	ΔG <sub>f</sub> (1)	ΔG <sub>f</sub> (2)
298	-1623.86	-1664.43	-2368.84	-1105.95	-1687.20	-1111.42	-163.73	-35.10
1000	-1411.77	-1465.58	-2550.17	-1183.52	-1774.62	-1180.04	-547.30	-57.29
1300	-1317.35	-1379.47	-2659.12	-1229.97	-1834.42	-1222.96	-737.32	-69.13
1500	-1254.32	-1322.07	-2739.12	-1263.94	-1882.51	-1254.76	-866.23	-76.93
1700	-1191.46	-1264.92	-2824.22	-1300.06	-1934.11	-1289.32	-998.71	-84.20
1800	-1160.09	-1236.44	-2868.53	-1318.77	-1961.14	-1307.27	-1066.07	-87.85

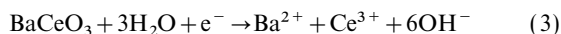
<sup>a</sup>Ref. 11. <sup>b</sup>Ref. 12.

substrates by Kelder *et al.*<sup>13</sup> and Jiang *et al.*<sup>14</sup> using low-temperature synthesis techniques.

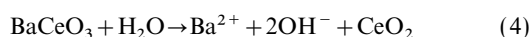
### Stability in water

When the sintered pellet from the second method was immersed in cold water (298 K), the pH value was unchanged after one week. The pellet was intact, had good mechanical strength and exhibited no mass change. XRD revealed that the pellet remained a single perovskite phase. When HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub> was added dropwise to the cold water, the pellet dissolved gradually and a yellowish powder was finally obtained, which was identified as CeO<sub>2</sub> by XRD. When HCl was added to the cold water, many bubbles appeared on the surface of the pellet, the pellet dissolved readily and a small amount of light blue powder was obtained, which was identified as Nd<sub>2</sub>O<sub>3</sub> by XRD. When BCN sintered specimens were ground into powders and then placed in cold water, no apparent dissolution was observed, and the pH value was only slightly increased after one week.

Yokokawa *et al.*<sup>15</sup> constructed an electrochemical potential diagram to analyse the solid-liquid equilibria between SrCeO<sub>3</sub> and the aqueous species. They found that SrCeO<sub>3</sub> was in equilibrium with Sr<sup>2+</sup> and Ce<sup>3+</sup> at P(O<sub>2</sub>) = 1 bar. Analogously, it can be assumed that BaCeO<sub>3</sub> has the following dissolution reaction:

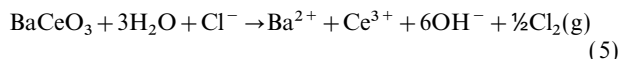


and the standard Gibbs energy for this reaction is 142.2 kJ mol<sup>-1</sup>, indicating that BaCeO<sub>3</sub> cannot dissolve in cold water according to this reaction. In the presence of HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>, BaCeO<sub>3</sub> dissolved in cold water and CeO<sub>2</sub> was formed, so the following reaction took place:



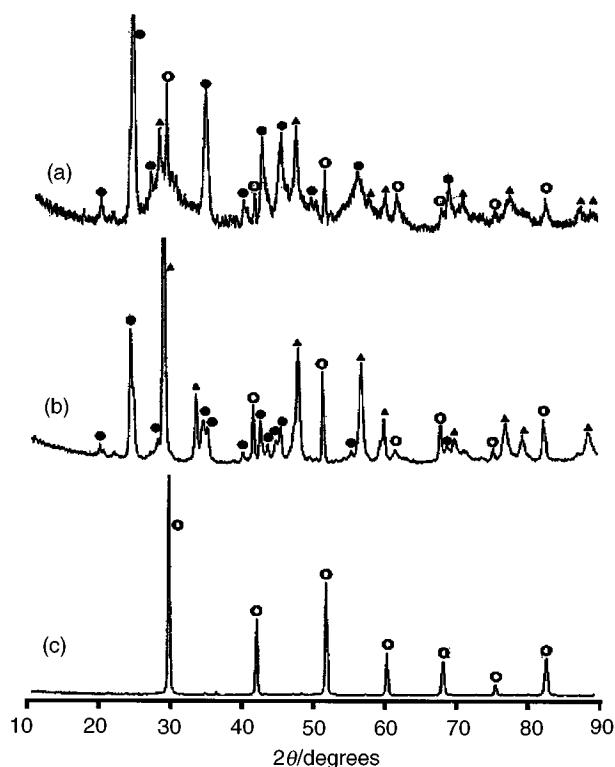
The standard Gibbs energy for this reaction can be calculated to be -242.9 kJ mol<sup>-1</sup>, indicating that BaCeO<sub>3</sub> is thermodynamically unstable in the presence of water. This reaction may be kinetically inert in cold water, since hydrolysis of BaCeO<sub>3</sub> leads to an increase of the pH value, while no apparent increase of the pH value was detected in our work. But in the presence of acid, reaction (4) can proceed much more readily and this is consistent with our experimental observations.

In hydrochloric acid, the bubbles on the surface of the pellet are due to the evolution of Cl<sub>2</sub> through the following redox reaction:



Consequently, the perovskite structure was destroyed and Nd<sub>2</sub>O<sub>3</sub> precipitated from the solution. Uchida *et al.*<sup>18</sup> also found that SrCeO<sub>3</sub> dissolved in hydrochloric acid to evolve Cl<sub>2</sub>.

In boiling water, the pellet began to chip and finally broke into small pieces. The pH increased gradually up to 14, indicating that the hydrolysis reaction according to eqn. (4) took place. After the pellet was boiled in water for 6 h, it disintegrated completely into a powder. XRD patterns of the resulting powder, as shown in Fig. 3(a), revealed a mixture of CeO<sub>2</sub>, BaCO<sub>3</sub> and a small amount of BaCeO<sub>3</sub>. The presence



**Fig. 3** XRD patterns of the sintered BCN sample after exposure to different environments. (a) BCN pellet after 6 h in boiling water, (b) BCN powders after DTA-TG measurement in CO<sub>2</sub> atmosphere and (c) BCN powders after DTA-TG measurement in H<sub>2</sub> atmosphere. ●, BaCO<sub>3</sub>; ▲, CeO<sub>2</sub>; ○, BaCeO<sub>3</sub>.

of BaCO<sub>3</sub> arises from the following reaction with the existence of CO<sub>2</sub> in ambient atmosphere:



Tanner and Virkar<sup>8</sup> found that both pure and rare-earth-metal doped BaCeO<sub>3</sub> were thermodynamically unstable in the temperature range 500–900 °C in an atmosphere of ca. 430 Torr H<sub>2</sub>O and decomposed to form CeO<sub>2</sub> and Ba(OH)<sub>2</sub>. They concluded that the perovskite decomposed through a bulk-decomposition mechanism which involved dissolved H<sub>2</sub>O within the BaCeO<sub>3</sub> lattice. As shown in this work, in cold water, BaCeO<sub>3</sub> had a very low solubility and consequently negligible hydrolysis. But in boiling water, it showed significant hydrolysis, and this fast hydrolysis may be accelerated by high solubility. Therefore, our work confirms the bulk-decomposition mechanism. The instability of doped BaCeO<sub>3</sub> in H<sub>2</sub>O-containing environments may restrict its use as an electrolyte material, especially as electrolytes for electrolyzers.

### Reaction in CO<sub>2</sub> atmosphere

Fig. 4 shows the DTA-TG diagrams of the solid-state reaction of the mixture BaCO<sub>3</sub>-CeO<sub>2</sub>-Nd<sub>2</sub>O<sub>3</sub> in a CO<sub>2</sub> atmosphere. At 1200 °C, there is a large mass loss accompanied by an apparent endothermic peak, which corresponds to the decomposition of

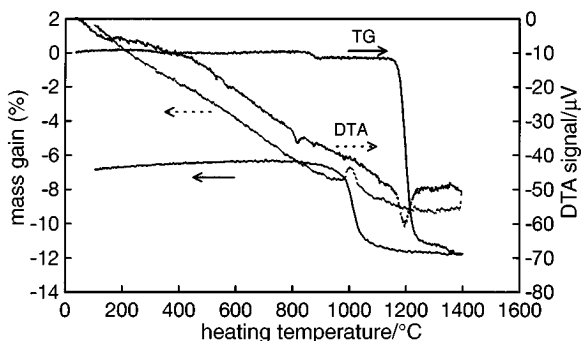


Fig. 4 DTA-TG results of 50% BaCO<sub>3</sub>-45% CeO<sub>2</sub>-5% Nd<sub>2</sub>O<sub>3</sub> in CO<sub>2</sub> atmosphere

BaCO<sub>3</sub>. The subsequent slow mass loss is due to the decomposition of BaCO<sub>3</sub> and the formation of BaCeO<sub>3</sub>. During cooling, at 1000°C, BaCeO<sub>3</sub> began to decompose. Surprisingly, the decomposition of BaCeO<sub>3</sub> did not go to completion and no mass loss occurred below 900°C. The powders obtained after DTA-TG measurements were examined by XRD, which, as shown in Fig. 3(b), showed a mixture of BaCO<sub>3</sub>, CeO<sub>2</sub> and perovskite phase. This means that there is only partial decomposition of BCN. The DTA-TG trace of air-sintered BCN powder in a CO<sub>2</sub> atmosphere is shown in Fig. 5. With increasing temperature there is a gradual mass gain, indicating that BCN reacts with CO<sub>2</sub> through the following reaction:

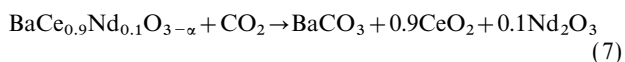


Fig. 5 also shows that when the temperature increased up to 1000°C, BCN decomposed almost completely. Above 1100°C, BaCO<sub>3</sub> began to decompose and the formation of BaCeO<sub>3</sub> initiated. At 1400°C, a single perovskite phase was obtained. During the subsequent cooling process, at 1000°C, BaCeO<sub>3</sub> started to react with CO<sub>2</sub>, and there was no mass change below 800°C. The XRD pattern of the powder after DTA-TG measurement was the same as that shown in Fig. 3(b).

Taniguchi and Gamo<sup>16</sup> studied Gd-doped BaCeO<sub>3</sub> in air and CO<sub>2</sub> atmospheres and found that this material reacted with CO<sub>2</sub> when the CO<sub>2</sub> partial pressure was more than 0.17 atm (1.8 × 10<sup>4</sup> Pa) and decomposed to form BaCO<sub>3</sub> and a fluorite-type oxide based on ceria. They found that the crystal structure changed gradually from orthorhombic to tetragonal above 550°C and finally to cubic at 800°C as the temperature increased in air. They claimed that the cubic phase was very stable physically and chemically and was hardly affected by CO<sub>2</sub>. Our result is in partial agreement with theirs. As the temperature was increased, BCN probably started from an orthorhombic structure, which was readily attacked by CO<sub>2</sub> and was unstable below 1200°C. During subsequent cooling, BCN may start from a cubic structure and was

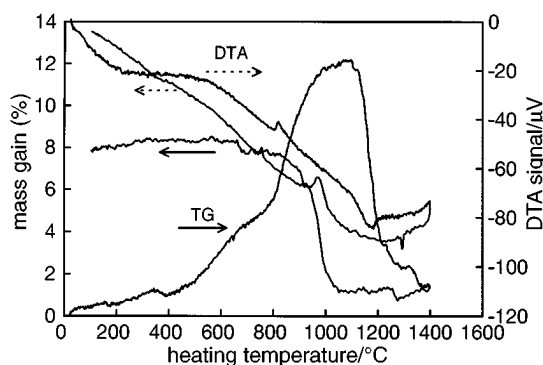


Fig. 5 DTA-TG diagrams of BCN in CO<sub>2</sub> atmosphere

chemically stable at 1000°C in 1 atm CO<sub>2</sub>. Below 1000°C, BCN may transform from cubic to orthorhombic and hence lose its stability. From the above observations, it seems that BCN reacts with CO<sub>2</sub> through an equilibrium reaction as expressed in eqn. (7), which depends on the temperature, CO<sub>2</sub> partial pressure and structure of the perovskite phase. Despite the fact that BaCeO<sub>3</sub>-based materials decompose to form BaCO<sub>3</sub> and CeO<sub>2</sub> in CO<sub>2</sub>-containing atmospheres, it is expected that sintered BaCeO<sub>3</sub>-based ceramics may be kinetically stable due to the interfacial nature of the decomposition reaction with CO<sub>2</sub>. This is because CO<sub>2</sub> cannot dissolve in BaCeO<sub>3</sub> and the reaction must occur at the solid/gas interface. Taniguchi *et al.*<sup>17</sup> studied the operating properties of solid oxide fuel cells using BaCe<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>3-x</sub> electrolytes with 80% H<sub>2</sub>-20% CO<sub>2</sub> as fuel gas and found that BaCe<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>3-x</sub> could still be applied very well as a practical electrolyte for low-temperature fuel cells, although there was a larger cell voltage degradation rate (due to the reaction of the electrolyte with CO<sub>2</sub>) compared with that for pure H<sub>2</sub> as fuel gas.

#### Stability in reducing and oxidizing atmospheres

Fig. 6 shows the DTA-TG results for BCN powders in H<sub>2</sub>. It can be seen that, below 400°C, there is some mass gain, which may be caused by the adsorption of gas on the surface of the sample. With an increase in temperature, there is a gradual, small mass loss. Before the DTA-TG measurements, the powder was dark brown, but it became grey afterwards. When the grey powder was subsequently heated in air, it changed back to dark brown. When a sintered dark brown BCN pellet was fired at 900°C in an H<sub>2</sub>-containing atmosphere, it showed a green colour, but it maintained integrity and good mechanical strength. When it was refired at 900°C in air, it became dark brown and still demonstrated integrity and good mechanical strength. The colour change from dark brown to grey may be caused by the partial reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup>, and when subsequently fired in air, Ce<sup>3+</sup> was oxidized to Ce<sup>4+</sup>, and it changed back to dark brown. Uchida *et al.*<sup>18</sup> also found that in SrCeO<sub>3</sub>-based materials, when heat-treated in H<sub>2</sub>, some of the Ce<sup>4+</sup> was reduced to Ce<sup>3+</sup>.

Fig. 7 shows the DTA-TG results of BCN powders in air. It can be seen that with increasing temperature, there is a slight mass gain. There is no colour change before and after DTA-TG measurements. XRD patterns of the powders from the DTA-TG measurements in both H<sub>2</sub> and air revealed a single perovskite phase, as shown in Fig. 3(c), indicating that BCN was chemically and structurally stable in both idealised reducing and oxidizing atmospheres.

In Nd-doped BaCeO<sub>3</sub> material, the following defect reactions (Kröger-Vink notation) exist.

defect caused by doping:

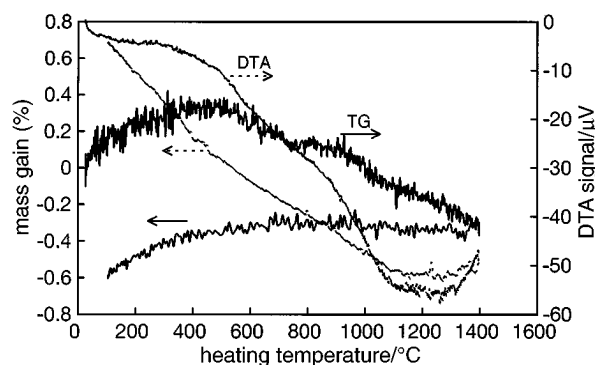
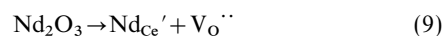


Fig. 6 DTA-TG diagrams of BCN in H<sub>2</sub> atmosphere

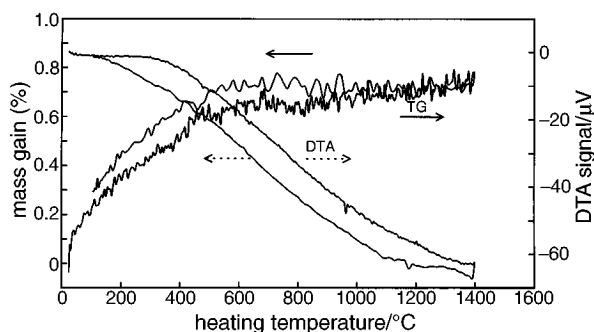
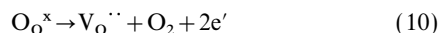
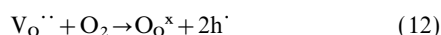


Fig. 7 DTA-TG diagrams of BCN in air

in a reducing atmosphere:



in an oxidizing atmosphere:



In  $\text{H}_2$  atmosphere, the slight mass loss was caused by the formation of the oxide vacancies. When BCN was heated in air, the slight mass gain was the result of the annihilation of the oxide vacancies and formation of the oxide lattice ions. The slight mass change does not affect the integrity and mechanical strength of the electrolyte ceramic, which satisfies the requirements of practical fuel cell applications, in which the anode is the reducing atmosphere and the cathode is the oxidizing atmosphere. Moreover, Iwahara *et al.*<sup>19</sup> found that combustion products such as CO and  $\text{C}_2\text{H}_4$  produced by reforming city gas in the anode compartment did not affect the performance of the solid oxide fuel cell using  $\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{3-\alpha}$  as the electrolyte.

## Conclusions

At temperatures  $\geq 1200^\circ\text{C}$ , BCN reacted with alumina or zirconia to form  $\text{BaAl}_2\text{O}_4$  or  $\text{BaZrO}_3$ , leading to a loss of barium and an excess of cerium in the product. At temperatures below  $1200^\circ\text{C}$ , the reaction between  $\text{BaCeO}_3$  and alumina or zirconia was kinetically unfavourable.

In cold water, BCN had a very low solubility, but it dissolved readily in some mineral acids. In boiling water, BCN had a high solubility and a strong hydrolysis reaction which led to the decomposition of the ceramic into  $\text{CeO}_2$  and  $\text{Ba}(\text{OH})_2$ . The instability of doped  $\text{BaCeO}_3$  in  $\text{H}_2\text{O}$ -containing environments at elevated temperatures may restrict its use as an electrolyte material, especially in electrolyser applications.

In 1 atm  $\text{CO}_2$ , BCN decomposed to form  $\text{CeO}_2$  and  $\text{BaCO}_3$  below  $1200^\circ\text{C}$  with an increase in temperature, but during cooling it was stable above  $1000^\circ\text{C}$ , possibly because BCN

has a different crystal structure at low and high temperatures. Despite the decomposition reaction of  $\text{BaCeO}_3$  with  $\text{CO}_2$ ,  $\text{BaCeO}_3$ -based materials could still be applied very well as practical electrolytes for low-temperature fuel cells. At  $600\text{--}1000^\circ\text{C}$ , although BCN exhibited a slight mass loss when exposed to a reducing atmosphere, and a slight mass gain in an oxidizing atmosphere, it demonstrated chemical and structural stability, integrity and good mechanical strength which fulfil the requirements of materials as electrolytes for solid oxide fuel cells.

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