Preparation of doped/ undoped $BaCeO_3$ nano-powders using carbonate co-precipitation

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The aim of this work is to prepare nano-sized powders of $BaCeO_3$, $BaCe_{0.8}Y_{0.2}O_{2.9}$ and $BaCe_{0.8}Sm_{0.2}O_{2.9}$, with round-shaped particles. Synthesis of carbonate precursors is by carbonate co-precipitation with $(NH_4)_2CO_3$ and NH_4HCO_3 as precipitants using concentrations of 0.5-3.0M at temperatures of 30°C, 50°C or 70°C, holding isothermally at the reaction temperature for 1-4 hours. The total cation concentration used was 0.15-0.30M.

TG-DTA and XRD suggest that the precursors are a mix of $BaCeO_3$ and an amorphous phase containing Ce or doped Ce carbonate. Decarbonation is in two stages. The first is Ce/Y/Sm decarbonation at 535-670°C, followed by Ba decarbonation.

After the first stage, the powder is a mix of doped CeO_2 and $BaCO_3$. During or after Ba decarbonation, the Ba and Ce/Y/Sm oxides react at 919-1,100°C to form the mixed oxide, with a very small $BaCO_3$ impurity that will likely disappear upon sintering.

SEM observations suggest that in the precursors, the particles are generally round-shaped and nano-sized (10-40nm), with moderate open agglomeration in clusters of >2μm in size. After high temperature calcination, particles are larger (60-400nm) but aggregated in smaller clusters of up to 2μm or just a few particles linked together or even single particles. The particles are not so rounded after high temperature calcinations, due to either sintering or crystallization of the powder.

Key words: $BaCeO_3$, doped $BaCeO_3$, carbonate co-precipitation, proton conductor

INTRODUCTION

Interest in potential proton-conducting electrolyte materials began in 1981 with the discovery of proton conduction in doped $SrCeO_3$ [1]. Several years later, proton conductivity was discovered in doped $BaCeO_3$ [2, 3], which is supposed to have the best proton conductivity out of the perovskite proton-conductors such as $BaCeO_3$, $BaZrO_3$, $SrCeO_3$ and $SrZrO_3$ [3].

Unfortunately, these materials have drawbacks, as they are unstable in CO_2-containing atmospheres, as they react with CO_2 [4,5], they require high reaction and sintering temperatures and such high temperatures can cause changes in the stoichiometry due to BaO evaporation [6,7]. Thermodynamic studies have shown that when sintering at ~1,600°C, the vapour pressure of Ba can be up to 10^{-5} atm [8].

For example, preparation of single-phase oxides can requires temperatures of 1,250 to 1,500°C, while sintering of pellets of at least 95% density needs temperatures between 1,500 and 1,675°C [3,9]. Attempts have been made using the Pechini process [5,10] and oxalate co-precipitation [11,12] to reduce these temperatures. However, the only success was in reducing the calcination temperatures but pellets still required sintering temperatures of at least 1,450°C.

The best result known so far was for $BaCe_{0.8}Sm_{0.2}O_{2.9}$ powders prepared by an auto-ignition method. These powders could be calcined at ~850°C to be effectively phase pure apart from a small amount of $BaCO_3$ impurity that disappears upon sintering. Pellets prepared from these powders could be sintered to 99% density at 1,300°C [13].

In this work, one of the aims is to determine if doped and undoped $BaCeO_3$ powders can be prepared with nano-sized, rounded particles. Another aim is to see if the resultant powders can be calcined and sintered at lower temperatures. This would be tested by preparing powders using a range of different co-precipitation parameters, such as reaction temperature, duration of isothermal hold, precipitant used, as well as the total cation and precipitant concentrations. This methodology has been used successfully in the preparation of doped CeO_2 compounds that can be sintered at lower temperatures [14-17].

EXPERIMENTAL

Precursor Preparation

The compositions of interest are $BaCeO_3$, $BaCe_{0.8}Y_{0.2}O_{2.9}$ (BCY20) and $BaCe_{0.8}Sm_{0.2}O_{2.9}$ (BaCeSm20). The reagents used were Ba $(NO_3)_2$ (Aldrich, 99.999%), Ce $(NO_3)_3.6H_2O$ (99.99%, Kanto), Y $(NO_3)_3.6H_2O$ (99.99%, Kanto), Sm $(NO_3)_3.6H_2O$ (99.95%, Kanto), NH_4HCO_3 (min 96%, Kanto) and $(NH_4)_2CO_3$ (min 30% NH_3, Wako Pure Chemicals). These chemicals were used as received. The mixed nitrate solutions were prepared by dissolving appropriate mixtures of the metal nitrates into 300ml of distilled water, with a total cation concentration of 0.15-0.3M. Dissolution was aided by mild stirring at 40°C or room temperature for ~30 minutes. The precipitant $((NH_4)_2CO_3$ or NH_4HCO_3, 0.5-3.0M) was dissolved in 300ml of distilled water at the reaction temperature (room temperature, 50°C or 70°C). In the co-precipitation reaction, the mixed nitrate solution was added dropwise (1-2 drops/ second) to the precipitant

solution that was maintained at the reaction temperature throughout reaction and development time, with gentle stirring. When all of the mixed nitrate solution was added, the reaction mixture was allowed to develop for 1-4 hours at the reaction temperature with gentle stirring. Development times used were 1 hour at 70°C, 2 hours at 50°C or 4 hours at room temperature. In most cases, the reaction mixture was white, although on occasion, the mixture may start out as pale yellow initially.

After the development time, the mixture was filtered by suction filtration and washed three times with water and once with ethanol, with filtration after each washing. After the final filtration, the precipitate was blow-dried with flowing nitrogen for at least 48 hours at room temperature. Finally, the dried solid was crushed in an alumina mortar and pestle, followed by sieving. Powders were calcined in oxygen flowing at 300cm^3 min^{-1} at two temperature ranges to examine the effect of temperature on phase formation. The first stage was for 2 hours at 600-670°C and the second stage was at 919-1,100°C for 4 hours, as suggested by TG-DTA measurements. For lower temperature sintering, some powders were calcined at 850°C for 4 hours.

TG-DTA Measurements

These measurements were carried out on a Seiko EXSTAR 6000 TG/DTA 6200 instrument. Precursor samples of mass 15-35mg were heated in a platinum crucible at 5°C min^{-1} from ambient to 1,100°C in air. This was useful for determination of calcination conditions.

Pellet preparation

Pellets were first pressed uniaxially at <20MPa, followed by isostatic pressing at 200-240 MPa for ~5 minutes. For sintering, pellets were heated at 5°C min^{-1} to temperatures ranging from 1,200 – 1,500°C, holding at these temperatures for 6-12 hours. Pellet densities were determined using the Archimedes method.

SEM Observations

Particle morphologies and extent of agglomeration of calcined and non-calcined powders were observed using a Hitachi S-5000 scanning electron microscope. The calcined powders of interest were those heated to temperatures between 850 – 1,100°C. Powder samples were dispersed into ethanol ultrasonically, with the suspensions spread on to a thin layer of aluminium foil. A small portion of the foil containing the finest particles was cut, fitted onto a copper plate and then coated with tungsten.

X-Ray Diffraction

Phase analysis of non-calcined precursors and those calcined in the temperature regions 530-670°C, 850°C and 919-1,100°C was carried out using a Rigaku RINT2200HF+Ultima+ X-ray diffractometer with a Cu source. Diffraction experiments were carried out over the 2 Theta range 4-85°.
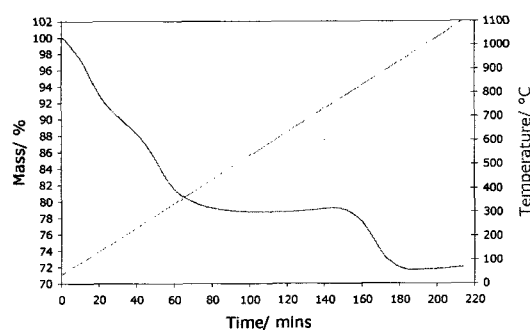
RESULTS/ DISCUSSION
Thermal Decomposition

Figure 1: TGA curve showing typical thermal decomposition behaviour

An example of the thermal decomposition behaviour of the doped/ undoped BaCeO₃ precursors is shown in Figure 1 and is typical of all compositions prepared. There are three decomposition stages. The first stage is the loss of water and other volatiles. The second seems to be decarbonation of Ce, Ce/Y or Ce/Sm mixed carbonate to the oxide, followed by a slight mass gain. The third stage appears to be due to BaCO₃ decomposition. The first stage does not end completely before the second stage ends, as there seems to be an overlap at ~200°C between the end of the first stage and the start of the second stage. The second stage plateaus at 535-670°, depending on sample composition and preparation conditions. For BaCeO₃ precursors, this stage finishes at below 600°C, between 625-655°C for BCY20 precursors and 620-670°C for BaCeSm20 precursors. The third stage plateaus at 919-1,100°C, with no apparent or simple trend between sample parameters and temperatures. As decarbonation is in two stages, this indicates that the precursor is composed of a mix of carbonates.
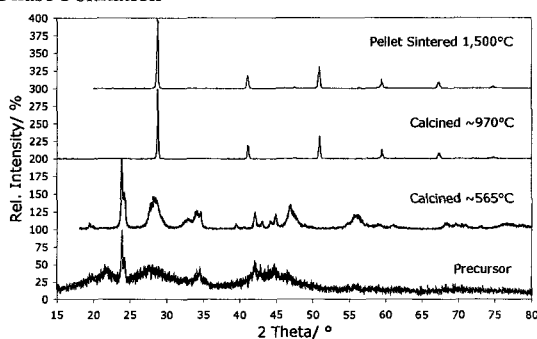
Phase Formation

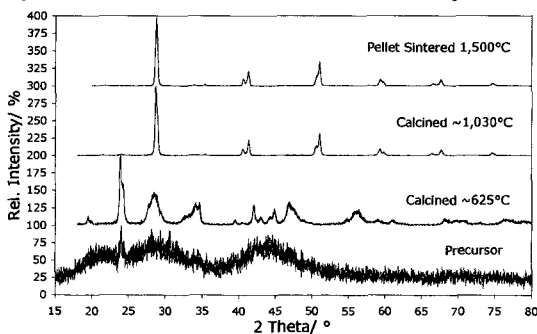Figure 2: Phase formation of BaCeO₃ with temperature

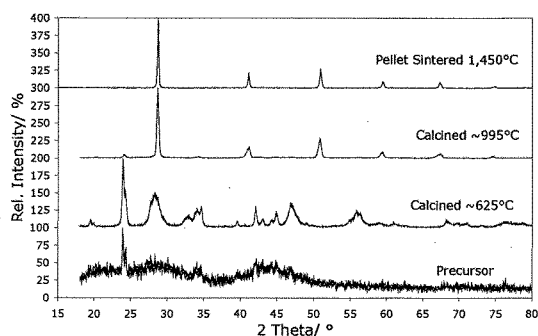Figure 3: Phase formation of BCY20 with temperature

Figure 4: Phase formation of BaCeSm20 with temperature

Figure 2 is a set of X-ray diffraction patterns that show the evolution of crystal phases of a $BaCeO_3$ precursor with temperature. Similar patterns for BCY20 and BaCeSm20 are shown in Figures 3 and 4 respectively. These figures suggest that the precursor is a mixture of crystalline $BaCO_3$ and an amorphous Ce/Y/Sm carbonate, in line with TG-DTA indications that there are two separate compounds in the precursor. The amorphous Ce/Y/Sm carbonate phase decomposes to the oxide, at 535-670°C. In the 919-1,100°C region, the primary phase is of the doped/ undoped $BaCeO_3$, as there is no sign of BaO or doped/ undoped CeO_2 and there may be a slight $BaCO_3$ impurity. This is either from decarbonation being not totally finished or it may be from reaction with CO_2 during measurement. Thus, during this stage, $BaCO_3$ is decomposing to BaO, which is reacting to form the target compound. Upon sintering, the phase is basically the same as for the powder calcined at high temperature, although the $BaCO_3$ impurity disappears during sintering and crystallinity increases.
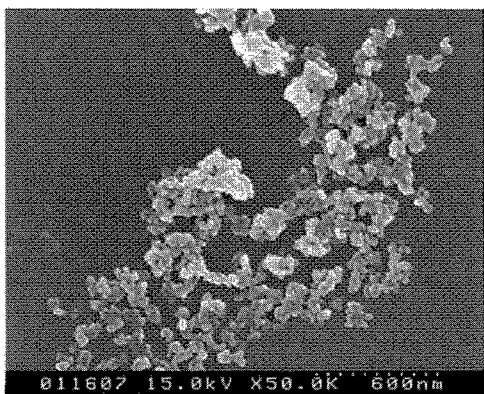
Powder Morphology

Figure 5: Example SEM image of carbonate precursor

Figure 5 shows an example of a SEM image of precursor powders. In most cases, the particles are rounded, with sizes usually in the 15-40nm range, with varying degrees of agglomeration. In most cases, the particle aggregation is moderate and open, with particle clusters that are more than 2μm in size. There have been a few cases of powders with hard agglomeration or particles grouped in rods or fibres.
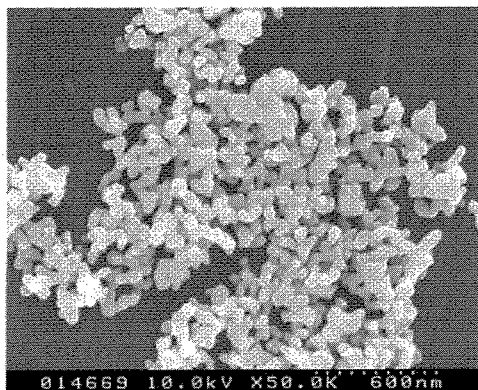

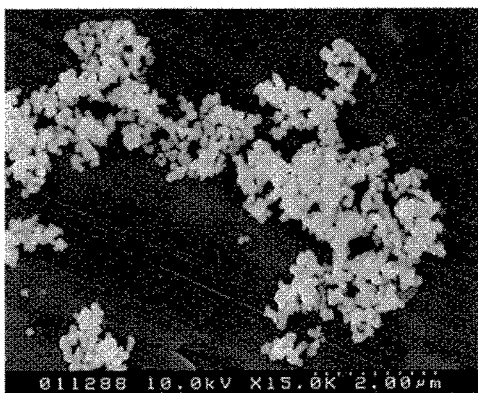Figure 6: SEM image of powder calcined at ~850°C

Figure 7: SEM image of powder calcined at high temperature

Figure 6 shows a SEM image from a powder calcined at 850°C and Figure 7 shows a SEM image from a powder calcined at between 919 and 1,100°C. In the calcined oxides, there are differences in particle size, morphology and agglomeration. Particle size increases with calcination temperature to a range of 40-120nm at ~850° or 60-400nm at 919-1,100°C. Agglomeration can loosen or breaks down considerably, with particle clusters being less than 2μm in size. Clusters can also be comprised of just a few particles and one can also observe instances of single particles. Particles show some changes in shape, as they can become slightly less rounded at ~850°C. After calcination at 919-1,100°C, the particles become much less rounded and appear to show some signs of sintering. The change in particle shape is due to crystallinity increasing with temperature.
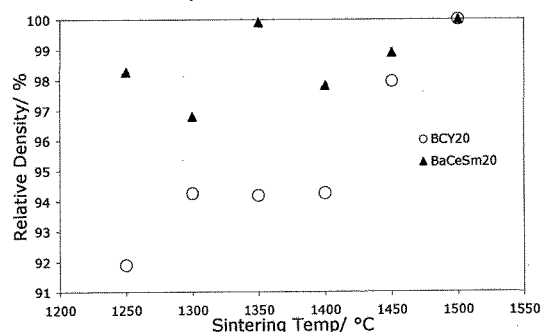
Powder Sinterability

Figure 8: Sintering progress for BaCeSm20 and BCY20

Examinations of powder sinterability have been focused on BCY20 and BaCeSm20, while $BaCeO_3$ will be looked at later. For sintering at 1,350-1,500°C, pellets were made from powders calcined at 900-1,050°C. For lower temperature sintering, powders were calcined at 850°C, as the smaller particle size should make it easier for sintering.

For BaCeSm20, the best result has been the sintering of pellets at 1,250°C that were 97-98% dense, which is at least as good as previously reported attempts at low temperature sintering [13]. This is the limit of sintering BaCeSm20 so far, as a pellet sintered at 1,200°C had a density of only 86.1%.

Results of sintering BCY20 in the 1,250-1,500°C range were not quite as good, with pellet densities of around 94% obtained at 1,300-1,400°C. At 1,250°C, however, pellet densities were slightly below 92%, less than the 'target' density of 94-95%. This shows improvement in sinterability, relative to powders prepared by conventional solid-state methods.

It may be possible to improve the sintering results by further changes like sintering for longer times such as 10 or more hours or by calcination at 800-825°C. Alternatively, trying some other sets of BCY20 or BaCeSm20 powders prepared under different conditions may yield a powder that could have better sinterability at lower temperatures but it is likely that one may not be able to sinter at temperatures much below 1,200°C.

CONCLUSIONS

Carbonate co-precipitation is capable of producing powders of $BaCeO_3$, BCY20 and BaCeSm20 that have rounded, nano-sized particles that may be used for attempts at lower temperature synthesis and sintering of these materials.

The resultant precursors are mixtures of $BaCO_3$ and amorphous Ce, Ce/Y or Ce/Sm carbonates. Thermal decomposition is in three stages. The first stage is loss of water and volatiles, which is almost finished when the second stage begins. In the second stage (535-670°C), the amorphous Ce/Y/Sm carbonate decomposes to the relevant oxide. In the final stage (919-1,100°C), $BaCO_3$ decomposes to BaO. During this stage, BaO appears to be reacting with the Ce/Y/Sm oxide to form the doped/ undoped $BaCeO_3$. On occasion, there can be a very small amount of $BaCO_3$ impurity, which disappears on sintering.

In terms of sinterability, BaCeSm20 is able to be sintered to at least 97% density down to 1,250°C and BCY20 could only be sintered to ~94% density at 1,300-1,400°C. Currently, BaCeSm20 appears to have better sinterability than BCY20. Further thought on processing, calcination and sintering conditions may yield improvements, although it is predicted that the lowest temperature limit for sintering may be in the 1,100-1,200°C region.

REFERENCES

[1] H. Iwahara, T. Esaka, H. Uchida, N. Maeda, Solid State Ionics, **3/4**, 359-363 (1981)

[2] A. Mitsui, M. Miyayama, H. Yanagida, Proceedings of the 3rd Meeting on Chemical Sensors, pgs 43-, Tokyo, Japan (1984)

[3] H. Iwahara, H. Uchida, K. Ono, K. Ogaki, Journal of the Electrochemical Society, **135** [2], 529-532 (1988)

[4] H. Uchida, A. Yasuda, H. Iwahara, Denki Kagaku, **57**, 153- (1989)

[5] M. J. Scholten, J. Schoonman, J. C. van Miltenburg, H. A. J. Oonk, Solid State Ionics, **61**, 83-91 (1993)

[6] D. Shima, S. M. Haile, Solid State Ionics, **97**, 443-455 (1997)

[7] S. M. Haile, G. Staneff, K.H. Ryu, Journal of Materials Science, **36**, 1149-1160 (2001)

[8] R. Saha, R. Babu, K. Nagarajan, C. K. Matthews, Thermochimica Acta, **120**, 29- (1987)

[9] A. Tomita, T. Hibino, M. Suzuki, M. Sano, Journal of Materials Science, **39**, 2493-2497 (2004)

[10] V. Agarwal, M. Liu, Journal of the Electrochemical Society, **143** [10], 3239- (1996)

[11] S. D. Flint, R. C. T. Slate, Solid State Ionics, **77**, 15- (1995)

[12] F. Chen, O. T. Sorensen, G. Meng, D. Peng, Solid State Ionics, **100**, 63- (1997)

[13] A. Chakroborty, A. Das Sharma, B. Maiti, H. S. Maiti, Materials Letters, 57, 862-867 (2002)

[14] T. Mori, T. Kobayashi, Y. Wang, J. Drennan, T. Nishimura, J. G. Li, H. Kobayashi, Journal of the American Ceramic Society, **88** [7], 1981-1984 (2005)

[15] J. G. Li, T. Ikegami, T. Mori, Acta Materialia, **52** [8], 2221-2228 (2004)

[16] Y. R. Wang, T. Mori, J. G. Li, T. Ikegami, Journal of the American Ceramic Society, **85** [12], 3105-3107 (2002)

[17] J. G. Li, T. Ikegami, Y. R. Wang, T. Mori, Journal of Solid State Chemistry, **168** [1], 52-59 (2002)