JOURNAL OF MATERIALS SCIENCE **37** (2002) 3315–3322

Hydrothermal processing and characterisation of doped lanthanum chromite for use in SOFCs

J. OVENSTONE, K. C. CHAN, C. B. PONTON
School of Metallurgy and Materials Science, Birmingham University,
Birmingham, B15 2TT, UK
E-mail: ovenstone99@yahoo.com

The perovskite powders $Ca_{0.3}La_{0.7}CrO_3$ and $Sr_{0.16}La_{0.84}CrO_3$ have been prepared using hydrothermal processing. The solid solutions were not formed directly in the autoclave, but the hydrothermally produced powders required calcination at a greatly reduced temperature to form the perovskite phase, reducing the tendency to produce hard agglomerates. Pellets with densities in excess of 95% TD were produced.

1. Introduction

The role of fuel cells is becoming ever more important in the future energy strategies of many countries around the world, due to their high energy conversion efficiencies and low environmental pollution attributes. Many major corporations such as Allied Signal and Westinghouse have already developed and tested prototype systems and have even developed vehicles and power generation plants which utilise fuel cell technology.

Solid oxide fuel cells (SOFCs) are of particular interest for fixed site utility, and industrial applications since the high operating temperature (around 1000°C) ensures that all the fuel is used, providing that sufficient oxygen is present. This results in high converion efficiency from the chemical energy stored in the fuel to electrical energy. The high temperatures also improve resistance to poisoning by fuel impurities such as sulphur, which means that they are ideal for use in conjunction with coal gasification plants or hydrocarbon reformers. Furthermore, the high quality by-product heat can also be effectively used in co-generation applications, further increasing the efficiency [1, 2].

SOFCs are constructed from four layered ceramic components, namely, an interconnect, an electrolyte, a cathode, and an anode. The cathode reduces the oxygen gas into O^{2-} ions, which then pass through the thin electrolyte membrane to the anode, where they react with the fuel gas to produce water vapour, and carbon dioxide. The free electrons produced by this reaction travel back to the cathode via an external load circuit, where they can produce more oxygen ions. The interconnect serves as an electrically conductive connector between cells, allowing them to be stacked to produce higher voltages.

The main drawback with SOFCs is the difficulty in the fabrication of some of the components. The choice of materials is limited due to the very demanding conditions, which are encountered during operation. The interconnect, for example, must be resistant to both oxidising conditions (at the oxidant inlet end) and reducing conditions (at the exhaust end), at temperatures in excess of 1000°C. The extent of the difference between the ends depends upon fuel cell and stack design, and upon the operation conditions chosen. It must also be electronically conductive, as well as gas-tight, so as to separate the flows of the oxidant and fuel gases, since contact between them would result in a massive reduction in efficiency. The material must also have a similar thermal expansivity to all the other fuel cell component materials (approximately $12 \times 10^{-6}\ K^{-1}$) [3].

These very stringent conditions for the properties of the interconnect, limit the choice of possible materials to a very narrow group. The material of choice, is usually lanthanum chromite, doped with a group (II) metal such as calcium or strontium to replace the lanthanum on the A sites of the perovskite structure. This doping significantly increases the conductivity of the interconnect material from around $1\ \Omega^{-1}\ cm^{-1}$ to up to $35\ \Omega^{-1}\ cm^{-1}$ when doped with calcium [3, 4].

The main problem with using doped lanthanum chromite, however, is that the material is very difficult to sinter to a high (i.e., gas-tight) density [5]. This is due to the formation of secondary phases such as CrO_3, which are volatile at low temperatures and can then move to the grain surface and deposit as Cr_2O_3, which is impervious to the vapour phase and thus prevents further neck growth. In addition to preventing extensive mass transfer, these phases can also cause local excesses of lanthanum oxide, which forms $La(OH)_3$ causing weakening and hence crumbling of the ceramic due to a large expansion in the lattice parameters [6]. Also, the high mobility of the chromium species can cause problems during the co-sintering of all the fuel cell component materials, as it can migrate from the interconnect into the other components [7]. Therefore a considerable amount of research effort has been applied to the synthesis and improving the sintering properties of doped lanthanum chromite [8–14].

Hydrothermal processing has been shown to have the potential to produce fine, unagglomerated homogeneous powders with enhanced sinteractivity from relatively cheap precursors [15]. Most hydrothermal synthesis processes follow a dissolution/precipitation mechanism, where the driving force for the process is the difference in solubility between the least soluble reactant phase, and the insoluble product. The authors have also demonstrated the usefulness of hydrothermal processing in the production of multi-doped perovskite powders with improved calcination and sintering properties [16, 17]. This paper will describe the synthesis of doped lanthanum chromite and manganite ceramic powders, and the properties of the powders produced.

2. Experimental

Metal salts (acetates or nitrates (Aldrich)) were mixed together in aqueous solution in order to give products with the stoichiometry $Ca_{0.3}La_{0.7}CrO_3$ (CLC) and $Sr_{0.16}La_{0.84}CrO_3$ (SLC). The solutions had final concentrations of 0.5 M with respect to the chromium ions. All solids were dried at 70°C for 24 hours in an oven after opening, and stored in a vacuum desiccator prior to use. Solids were weighed to the nearest 0.01 g (0.1% or better). Base was then added, and the mixture thoroughly stirred so that all acid products could be eliminated, assuming full decomposition of the metal salts to their acidic products. The base thus served to drive the reaction to completion by Le Chatelier's Principle, by removing the acidic by-products. The reaction mixture was then hydrothermally processed in an autoclave under autogenous pressure for a period of two hours (discounting heating and cooling times). Syntheses were carried out in one or the other of two autoclaves. The first was a 250 ml, P.T.F.E. lined vessel, equipped with a magnetic stirrer unit, and capable of reaching temperatures of up to 220°C. The second was a 4000 ml, Hastelloy C276 vessel, equipped with a magnetically driven, overhead gas entrainment stirrer, and capable of reaching temperatures of up to 400°C.

Experiments using acid, and using no base were carried out to determine the effect of the base. The effect of the base cation was investigated to see if it played any catalytic role, or whether it is the strength of the base that is important. Therefore a number of different bases, both organic and inorganic, with different cations incorporating sterically hindered and unhindered groups were used. The bases were ammonium hydroxide, tetramethyl ammonium hydroxide (TMAH), tetraethyl ammonium hydroxide (TEAH), sodium hydroxide, calcium hydroxide, and potassium hydroxide (Aldrich). In addition, the base concentration was varied while using ammonia. The reaction temperature was also varied, while using ammonia and KOH as the bases, as was the time of reaction, the reactant concentration, and the solvent.

After hydrothermal treatment, the powders were washed with water and dried by vacuum filtration before further drying in an oven at 130°C for 24 hours. The powders were then characterised by XRD (Philips pw 1050), TG/DTA (Stanton Redcroft STA781), qualitative EDX (Jeol 5410 equipped with a Link 2000 EDX probe), and X-ray sedimentation particle size analysis (Brookhaven XDC). Particle sizes are expressed as mean diameter values based upon their mass. Powder morphology was examined using a Hitachi S4000 FEG SEM. The powders were next calcined at 700°C for two hours to remove the high residual organic content of the powders (up to 50% by mass, measured by TGA), producing the final perovskite solid-solution product. The powders were again characterised by XRD. Finally, the calcined powders were pressed into pellets under a uniaxial pressure of 350 MPa, before being sintered in air at 1600°C for two hours. Densities were measured by Archimedes' method, and are expressed as percentages of the theoretical density (TD) of the product. We define the term yield to refer to the actual mass of product produced, divided by the theoretical mass of product produced assuming 100% conversion of starting materials, multiplied by 100%. All yields are given as a percentage of the theoretical yield.

3. Results and discussion

3.1. Synthesis of the powders

3.1.1. Strontium doped lanthanum chromite

Hydrothermal processing failed to produce the perovskite solid solution directly in the autoclave, however, the calcination temperature and time required to form the perovskite phase were significantly lower than for conventional processing techniques (compare 1000°C for 4 hours for sol gel prepared powder [18] with 625°C for 2 hours for our hydrothermally processed powder. This offers significant advantages in reduction of the formation of hard agglomerates which can seriously hinder sintering. Fig. 1 shows the progressive phase change observed upon calcination of the an as-produced strontium doped lanthanum chromite powder after treatment in an autoclave at 320°C for 2 hours using acetate precursors and ammonia as the base.

3.1.1.1. Effect of base on powder characteristics and reaction yield. All base investigations were carried out at 200°C in water using acetate precursors. Experiments using acid and no base produced zero, and reduced yields, respectively. The use of sodium and calcium hydroxides resulted in the doping of their respective metal ions into the perovskite structure, giving completely different phases from the desired perovskite both before and after calcination (confirmed by XRD). Potassium hydroxide produced a powder, which after calcination, formed the perovskite phase. There was, however, a trace of potassium left in the calcined product (detected by EDX), and a small peak corresponding to KOH in the XRD spectrum. The EDX spectra manifested the same relative intensities for the chromium and lanthanum peaks when compared to the ammonia base reactions, indicating that stoichiometry was maintained. There was, however, no trace of potassium chromate or dichromate in the XRD spectra of either the as-produced or calcined products. The yield was calculated to be 94% after calcination. The doping of the calcium (1.00 Å) and sodium (1.02 Å) ions into the lanthanum chromite can be easily explained after consideration of their ion sizes. The potassium (1.51 Å) ion is far larger and therefore cannot enter the lattice easily.

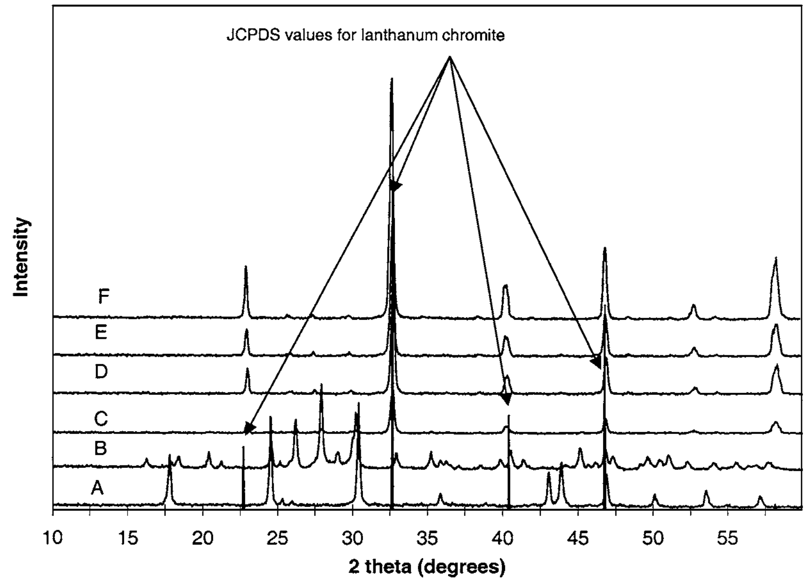


Figure 1 XRD traces showing the progressive phase change of the as-produced powder (A) with calcination at 500°C (B), 675°C (C), 750°C (D), 875°C (E), and 1000°C (F). This powder was produced from acetate precursors in an autoclave at 320°C for two hours using ammonia as the base and water as the solvent.

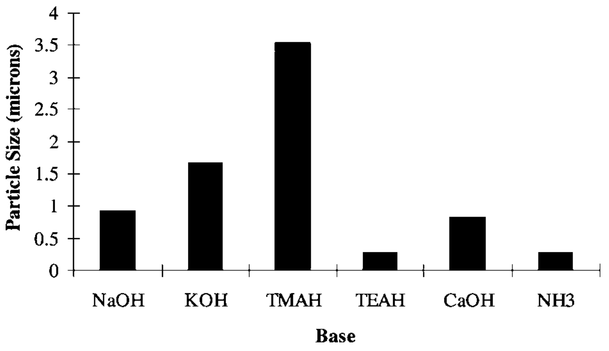


Figure 2 Bar chart showing the changes in particle size of the as-produced powders with changes in the base cation for reactions carried out in water at 200°C for 2 hours.

Ammonia based reactions produced platelet particles of around 0.2 μm in size, but with a yield of just 54% after calcination to the perovskite phase. In contrast, TMAH gave a higher yield of 84% after calcination, but the particle size was larger (3.5 μm), and the powder contained many hard agglomerates. TEAH gave a product yield of only 73% after calcination, but there was a much smaller mean particle size of 0.3 μm. Fig. 2 shows the trend in the particle size with the change in base cation.

Overall, increasing the strength of the base improved the yield, although TEAH, as a base, may also have been sterically hindered by its bulky ethyl groups as a base. Particle growth was also promoted by stronger bases. The influence of the inorganic base cations was also shown, as bases of very similar strength gave very different products and yields.

3.1.1.2. Effect of solvent. Experiments were carried out using acetate precursors and ammonia as the base. The solvent affects both the chemistry and the physical properties of the system. The use of the ethanol or methanol as the solvent instead of water means that the critical temperature of the system will be lower (243°C, 239°C, and 374°C, respectively), altering the fluid's physical properties, such as viscosity and thermal conductivity. The pressure within the reactor vessel is also very much increased by the use of organic solvents. A number of side reactions took place involving the production of an unsaturated organic molecule from the solvent molecules as they decomposed. This was demonstrated by the decolouration of potassium permanganate solution as the product gases were bubbled through. In addition to the unsaturated compound, an ester (identified by its characteristic smell) was also produced together with a water molecule. Since three molecules were produce from a single molecule, this reaction was particularly significant at the higher reaction temperatures, as it could accelerate suddenly, without warning, causing large increases in pressure.

$$3C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + C_2H_4 + 2H_2O$$

The use of organic solvents resulted in a large increase in yield at a reaction temperature of 200°C (54% for water, 78% for methanol, and 87% for ethanol) when using precursor acetates. The particle size was between 0.15 μm, and 0.3 μm, in the order water > ethanol > methanol. With precursor nitrates, there was also a large increase in yield when organic solvents were used (68% for water, 73% for ethanol, and 85% for methanol). This time, however, the water and methanol produced different crystalline phases after hydrothermal processing, whereas the ethanol again produced an amorphous phase. Using a 50 : 50 mixture of water/methanol with precursor nitrates produced an 86% powder yield after calcination, with a mean particle size of 0.1 μm. Fig. 3 shows the effect of changing the solvent on the yield of the product. The reversal of yields between the ethanol and methanol reactions using acetates and nitrates may be explained by the improved solubility of acetates in ethanol as opposed to methanol. For nitrates this would be reversed due to the higher polarity of the methanol. The improved yields obtained when using the organic solvents over water may be due to the increased pressure present in

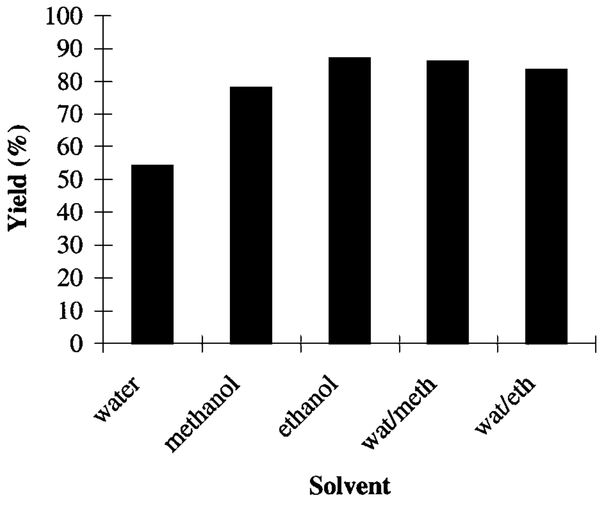


Figure 3 Bar chart showing the effect of changing the solvent on the yield of the powder after calcination at 700°C. These reactions were carried out at 200°C using ammonia as the base.

the vessel due to their lower boiling points. In addition, as more of the solvent is in the gas phase at this temperature, the effective concentration of the reactants in the remaining fluid is higher.

3.1.1.3. Effect of changing the precursors. At low temperatures (200°C), when water or methanol was used as the solvent, the use of nitrates as the precursors resulted in a 14% increase in the yield, but at higher temperatures, the yield fell to below that for acetates. Particle size was unaffected by the change in precursors, but the nitrates did tend to produce less agglomerated powder.

When ethanol was used, however, the yield using nitrates was 14% less than with acetates at 200°C, and the particle size increased from 0.2 μm to 1.1 μm. Again, the nitrate-derived powder, was amorphous. The changes in yield and crystallinity maybe explained by the difference in solubility of the metal salts under hydrothermal conditions, since the increase in yield with increasing temperature using acetates may be due to their expected greater solubility at higher temperatures. This would not be true for the nitrates, since they are highly soluble throughout the temperature range in water and methanol.

The use of precursor nitrates also produced large rod-like clusters of particles after calcination, regardless of solvent or temperature, although the particles themselves appeared similar to those derived from acetates (see Fig. 4). The reason for the formation of the macrostructures has yet to be explained.

3.1.1.4. Effect of synthesis temperature. There was an increase in the yield with reaction temperature over a reaction time of two hours, as shown in Fig. 5. XRD showed that the crystal phase of the as-produced powder also changed as the synthesis temperature was increased (see Fig. 6). The change in the asproduced phases may explain the increasing yields, as the activation energy towards a second more stable intermediate is overcome at the higher temperature. Particle size is unaffected by the synthesis temperature. This suggests that the product at the higher temperature either nucleates all at once, or is so insoluble as to be incapable of undergoing further dissolution and precipitation. When nitrates are used instead of acetates, however, the trend in yield is reversed; as the temperature increases, the yield falls. Again there is a change in the crystalline phase of the as-produced powder as the synthesis temperature is increased. In this case, the particle size increased with synthesis temperature. This would suggest that the nitrate ions can increase the solubility of the high temperature product, causing it to undergo more dissolution precipitation, increasing the particle size, but lowering the yield at higher temperatures due to the formation of highly soluble species which would not precipitate.

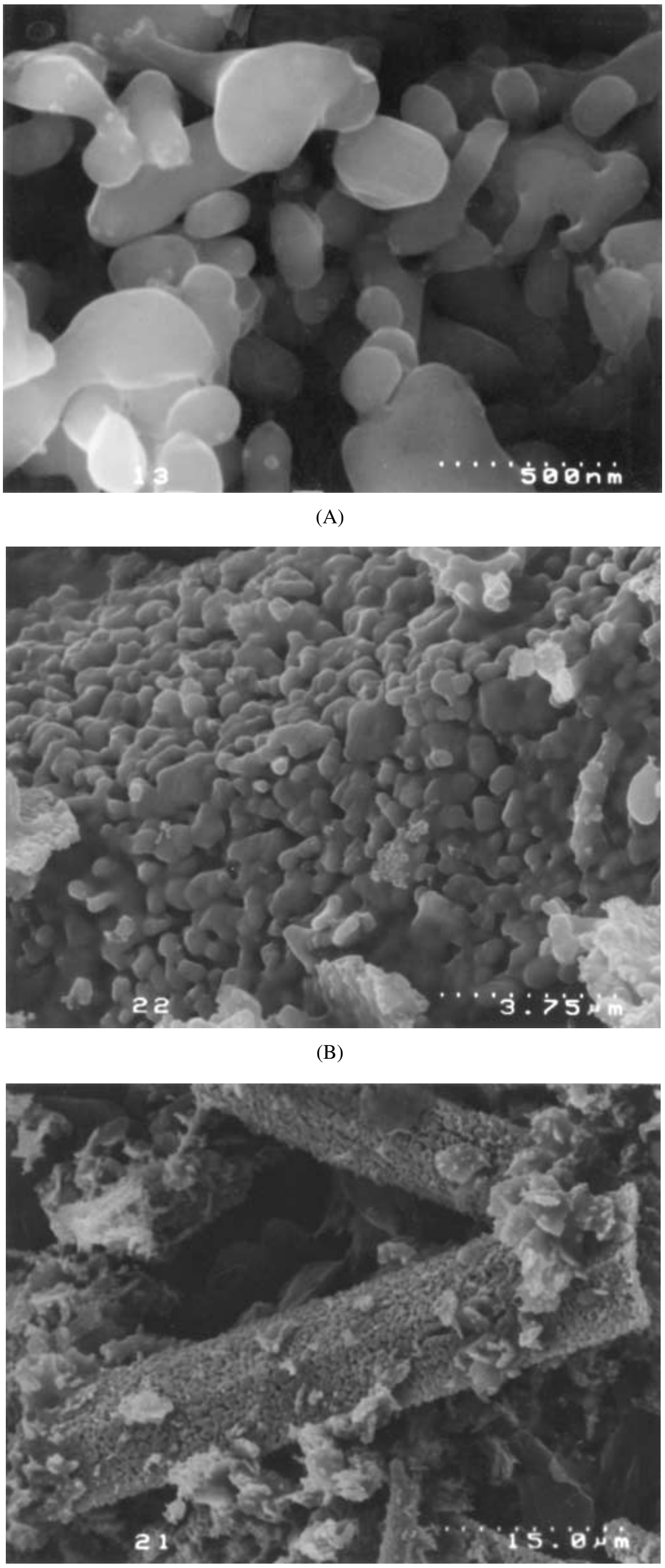
3.1.1.5. Effect of reaction time. The time of synthesis had little effect on yield, or on the phase formed in the autoclave. Therefore the reaction has reached completion after the first two hours. At 200°C, however, there was some particle growth from 0.3 μm to 1.5 μm with an increase in reaction time from two hours to twenty four hours. This is due to the dissolution/precipitation mechanism, which results in the loss of the material smallest particles back into solution, and then its reprecipitation onto the larger particles in the dispersion.

3.1.1.6. Effect of reactant concentration. Increasing the reactant concentration from 0.125 M to 1 M, with respect to the metal ions, resulted in a decrease in particle size from around 2 μm to 0.2 μm. There is also a trend towards increasing yield from 68% to 78% as the concentration was increased. This could be explained in terms of the reaction undergoing a single rapid nucleation due to the greatly increased number of ion interactions in the solution at higher concentration. As the base concentration was increased from 0.5 M to 5 M, the yield also increased from 54% to 82%. The degree of crystallinity also increased, as did the mean particle size, from 0.3 μm to 1.5 μm. The higher base concentration therefore resulted in a stronger driving force to completion of the reaction, but also provided a medium in which the product was more soluble, resulting in more growth by dissolution/precipitation.

3.1.2. Calcium doped lanthanum chromite

As with SLC, the CLC solid solution did not form directly in the autoclave, but formed an intermediate phase, which transformed into the solid solution upon calcination. The calcination temperature required to form the solid solution was again significantly lower than for powders produced using conventional techniques (compare 1000°C for 4 hours using sol gel techniques [18] to 700°C for 2 hours for the hydrothermally produced powder). The asproduced powders typically consisted of hexagonal platelet particles (Fig. 7A), which shrunk, and sintered together upon calcination (Fig. 7B).

3.1.2.1. Effect of base on the product powder. The reaction conditions used were the same as those for strontium doped lanthanum chromite. Also, as with SLC, the use of sodium or potassium hydroxide as



(A)

(B)

(C)

Figure 4 SEM micrograph of SLC powders after calcination at 875°C. (A) shows an acetate derived powder, while (B) and (C) show a nitrate derived powder. Ammonia was used as the base.

a mineraliser had to be rejected due to doping into the perovskite structure by the respective metal ions. Using TMAH resulted in a very low yield, while TEAH did not produce the desired phase, or even an appropriate intermediate. Ammonium and potassium hydroxide both produced higher yields of the correct perovskite phase after calcination (75% and 83%, respectively). Considerable washing of the KOH product was, however, required, to remove the excess base, which rather than doping into the perovskite structure, adhered to the powder surface. Fig. 8 shows the XRD traces of the as-produced powders prepared from acetate precursors in water using different bases.

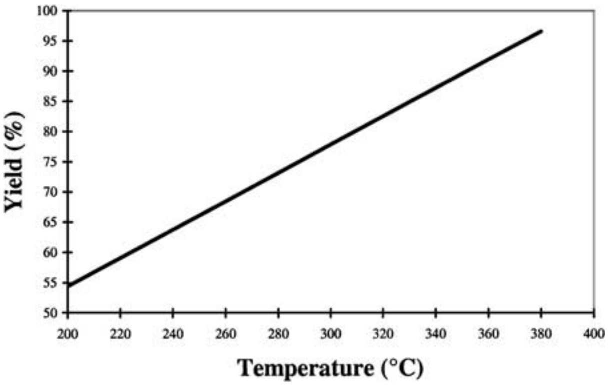


Figure 5 Graph of yield against synthesis temperature for powders prepared from acetate precursors in water using ammonia as the base.

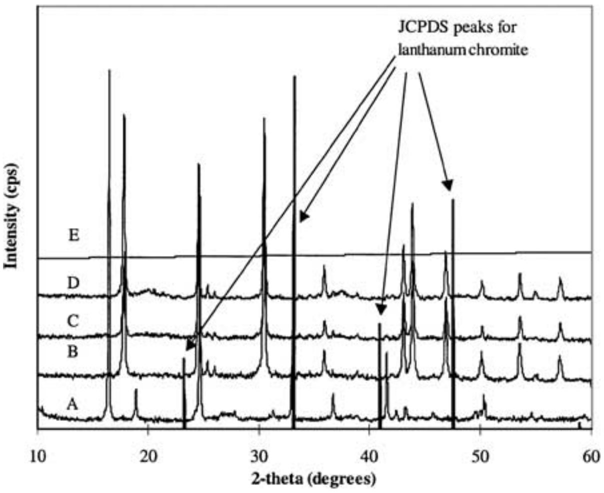
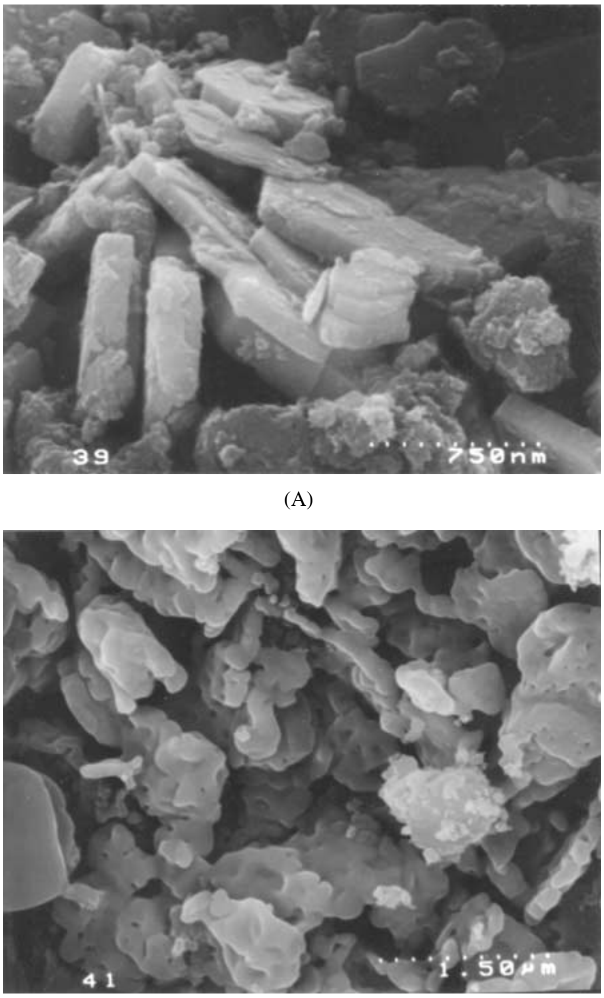


Figure 6 XRD traces showing the phases produced by hydrothermal treatment at (A) 150°C, (B) 200°C, (C) 320°C, (D) 350°C, and (E) 380°C. Experiments were carried out in water using acetate precursors and ammonia as the base.

Overall, increasing the strength of the base did not result in improved yield, but the strong influence of the base cation was again shown, as bases of very similar strength gave very different products and product yields. The stronger organic bases showed poor yields, probably due to the formation of stable co-ordination complexes with the calcium ions (1.00 Å) which are considerably smaller than the strontium ions (1.26 Å). These bases may have been too sterically hindered to co-ordinate with the larger strontium ions.

3.1.2.2. Effect of solvent on product powder. The use of ethanol or methanol reduced the tendency for the as-synthesised powders to agglomerate. Fig. 9 shows the changes in particle size with solvent. It is clear that the use of organic solvents or even mixtures of water and organic solvent has a strong effect on the particle size and reduces particle agglomeration. The use of methanol also resulted in a 6% increase in yield to 81% at 200°C. This can again be explained in terms of increased pressure using organic solvents and an increase in effective concentration in the remaining fluid.

The intermediate phase produced in both solvents was microcrystalline in nature with smaller XRD peaks. The methanol reaction, however, produced a slightly different intermediate phase, which again formed the perovskite structure after calcination.



(A)

(B)

Figure 7 (A) SEM micrographs of the CLC powder prepared at 320°C for 2 hours from acetate precursors and ammonia in water. (B) The same powder after calcination at 675°C for 2 hours.

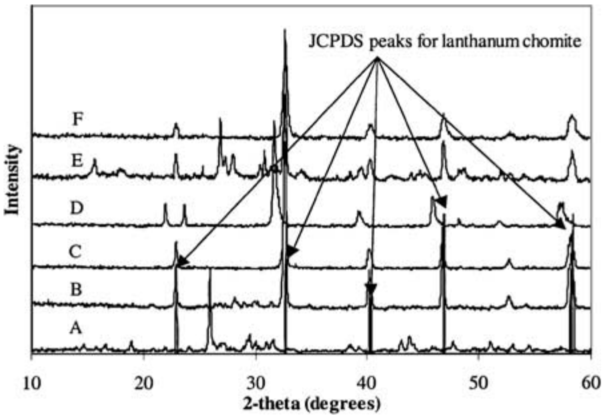


Figure 8 XRD traces showing the different products from reactions using different base cations. (A) A = NaOH, (B) KOH, (C) TMAH, (D) TEAH, (E) CaOH, and (F) NH_3.

3.1.2.3. Effect of synthesis temperature. As can be seen from Fig. 10, increasing the synthesis temperature of the reaction resulted in a significant increase in the yield for reactions using ethanol or water. This increase was not observed when methanol was used as the solvent. The yields shown are after calcination at 1000°C for two hours. Particle size was largely unaffected by the synthesis temperature, although the tendency for

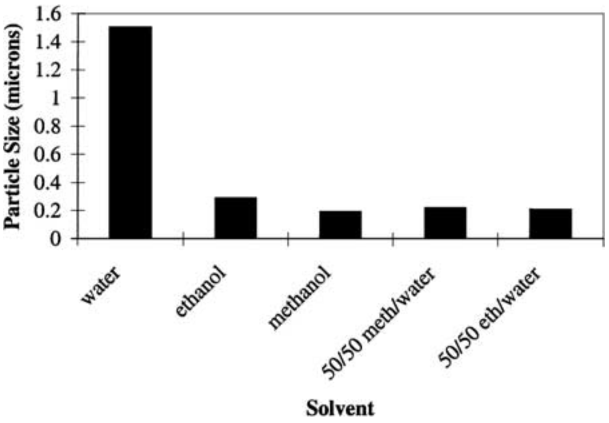


Figure 9 Changes in as-produced particle size with solvent for reactions at 200°C using acetate precursors and ammonia as the base.

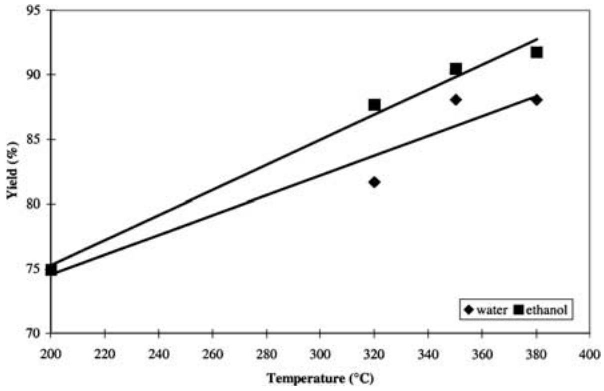


Figure 10 Yield vs hydrothermal processing temperature for CLC using acetate precursors and ammonia as the base.

powders to form agglomerates was reduced at higher synthesis temperatures. The crystallinity of the as-synthesised powders also increased with temperature. The temperature behaviour then is rather similar to that for the strontium doped material.

3.1.2.4. Effect of changing the precursors. There was a marked effect on the powder yields and particle morphology when using nitrates as precursors instead of acetates. At 200°C, the nitrates gave a 15% increase in yield (90%) over the acetates, but there was no further increase in yield as the temperature was increased. As the synthesis temperature increased, the nitrate-derived particles decreased in size, from being larger than the acetate-derived particle size to being smaller. The as-synthesised phase was also different to that produced from the acetates, suggesting a different chemical reaction mechanism.

3.1.2.5. Effect of reactant concentration. Above a concentration of 0.3 moles per litre of metal ions, there is no increase in yield. Particle size is unaffected by concentration, as is the morphology. This is in sharp contrast to the strontium doped material. This may be due to the calcium salts having lower solubility than their strontium counterparts, so that dissolution/precipitation is limited. Increasing the base concentration, from 0.6 M to 4.8 M, resulted in a tenfold reduction in particle size from 1.3 μm to 0.13 μm, but with no change in yield. Again, these results contrast significantly with the strontium doped material. The reduction in size may be explained by a single homogeneous nucleation step occurring due to the increased solubility of the precursors in the highly basic solution. The precipitate may then be insoluble under these conditions, preventing further dissolution/precipitation.

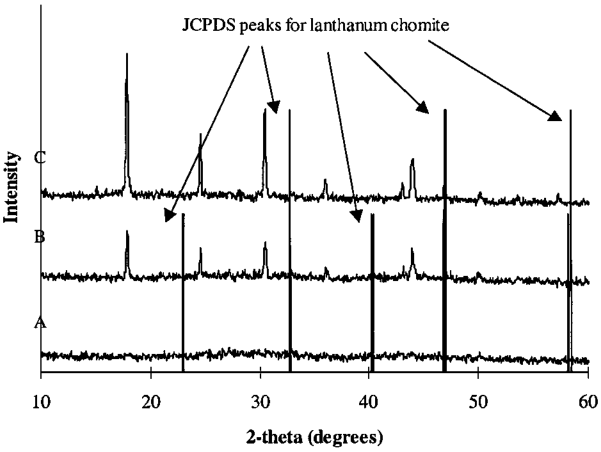


Figure 11 XRD traces showing the change in crystallinity with increasing hydrothermal processing time for CLC. (A) 2 hours, (B) 4 hours, and (C) 12 hours.

3.1.2.6. Effect of synthesis reaction time. As the reaction time for the experiment was increased, there was a marked increase in the crystallinity of the as-synthesised powder, formed in ethanol at 300°C (Fig. 11). This was also observed to a lesser extent with the other solvents (water or methanol). The temperature of formation of the perovskite phase during calcination, however, was unaffected, as confirmed by XRD analysis of powders calcined over a range of temperatures. As this occurs, there is also a small decrease (10%) in the particle size, and an increase in the tendency of the powder to agglomerate. Again these results can be explained interms of the elimination of the smallest particles and growth of the remaining particles by dissolution/precipitation. The yield was unaffected by increasing the reaction time from 2 to 12 hours.

3.2. Sintering properties

All attempts to sinter the as-synthesised powders failed due to the high organic content of the powders (up to 50%), the volatilisation of which, caused extensive cracking in the discs. With some of the discs, cracking due to the formation of volatile chromium compounds such as CrO_3 occurred, but in most, the calcination stage removed these phases. No further volatiles formed during sintering at 1600°C for 2 hours in air.

For strontium doped lanthanum chromite, the best densities achieved were in excess of 95% theoretical density (TD), and were obtained from acetate precursors and ammonia base in ethanol at 350°C for 12 hours, giving a yield of 90%. Densities in excess of 90% TD were achieved by a number of reactions: (1) nitrate precursors, 380°C, water, ammonia base, 2 hours, 88% yield; (2) acetate precursors, 350°C, ethanol, KOH base, 2 hours, 93% yield; (3) acetate precursors, 200°C, methanol, ammonia base, 2 hours, 87% yield.

For calcium doped lanthanum chromite, the best sintered densities achieved after sintering at 1600°C for 2 hours in air were, 1.96% theoretical (TD) (acetate precursors, 200°C, water, ammonium hydroxide base, 2 hours, 65% yield); 2.96% TD (acetate precursors, 200°C, water, TEAH base, 2 hours, 73% yield); and 3.93% TD (acetate precursors, 320°C, water, ammonia base, 2 hours, 84% yield).

4. Conclusions

It has been shown that inorganic bases are unsuitable for use as mineralisers for lanthanum chromite due to the tendency to dope metal ions into the lattice. The size and shape of the powder particles can be controlled by varying the synthesis conditions. Fine, unagglomerated powder has been formed after calcination at a temperature of only 700°C for two hours calcium doped lanthanum chromite and 625°C for two hours for strontium doped lanthanum chromite after hydrothermal processing. These values represent significant reductions in the temperatures of formation of the perovskite phases from conventional synthetic routes (1000°C, 4 hours for CLC and SLC) (Sakai, 1990). The reduction is due to the formation of a high energy intermediate phase in each case. Yields of calcined powder have exceeded 90% for SLC and 95% for CLC. Sintered densities of 96% TD (SLC), and 90% TD (CLC) have been achieved for dry pressed pellets of the calcined powder, pressed uniaxially at 350 MPa and then sintered at 1600°C for 2 hours. The current work holds potential for producing powders with morphologies that are suitable for co-sintering techniques, which are used in SOFC fabrication.

Acknowledgements

The authors would like to thank the School of Metallurgy for providing the funding for this project. Special thanks also go to Dr. I. MacLaren for his help during the course of this work.

References

1. K. KORDESCH and S. GNTUR, in "Fuel Cells and Their Applications" (Weinheim, 1996).
2. K. KENDALL, *Am. Ceram. Soc. Bull.* **70**(7) (1991) 1159.
3. N. Q. MINH, *J. Amer. Ceram. Soc.* **76**(3) (1993) 583.
4. D. B. MEADOWCROFT, *Brit. J. Appl. Phys.* **2**(2) (1969) 1225.
5. G. H. JONKER, *Physica* **20** (1954) 1118.
6. D. B. MEADOWCROFT and J. M. WIMMER, *Am. Ceram. Soc. Bull.* **58** (1979) 610.
7. N. SAKAI, T. KAWADA, H. YOKOKAWA and M. J. DOKIYA, *J. Jap. Ceram. Soc.* **101**(11) (1993) 1195.
8. G. M. CHRISTIE, P. H. MIDDLETON and B. C. H. STEELE, *J. Europ. Ceram. Soc.* **14** (1994) 163.
9. M. R. DeGUIRE, S. E. DORRIS, R. B. POEPPEL, S. MORISETTE and U. BALACHANDRAN, *J. Mater. Res.* **8**(9) (1993) 2327.
10. P. H. DUVIGNEAUD, P. PICATE and F. CAMBIER, *J. Europ. Ceram. Soc.* **14** (1994) 359.
11. K. FUKAYA, S. HAYASHI and H. SAITO, *J. Mater. Sci. Lett.* **7** (1988) 457.
12. R. KOC and H. U. ANDERSON, *J. Mater. Sci.* **27** (1992) 5837.
13. N. SAKAI, T. KAWADA, H. YOKOKAWA, M. DOKIYA and I. KOJIMA, *J. Amer. Ceram. Soc.* **76**(3) (1993) 609.
14. N. M. SAMMES and R. RATHARAJ, *J. Mater. Sci.* **29** (1994) 4319.
15. W. J. DAWSON, *Am. Ceram. Soc. Bull.* **67**(10) (1988) 1673.
16. J. OVENSTONE and C. B. PONTON, in Proceedings of The Second International Conference on Solvothermal Reactions (1996) p. 114.
17. *Idem.*, in Proceedings of The Second International Conference on Solvothermal Reactions (1996) p. 239.
18. N. SAKAI, T. KAWADA, H. YOKOKAWA, M. DOKIYA and T. IWATA, *J. Mater. Sci.* **25** (1990) 4531.

Received 19 October 2000
and accepted 29 March 2002