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Structural instability of cubic perovskite $Ba_xSr_{1-x}Co_{1-y}Fe_yO_{3-\delta}$

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Abstract

Cubic perovskites $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) are among the most promising oxygen permeable membrane materials and high-performance cathode materials for intermediate temperature solid oxide fuel cells. Here, we show that cubic BSCF becomes unstable in air at intermediate temperatures and gradually transforms to a hexagonal perovskite on cooling. Cubic and hexagonal BSCF polymorphs were observed to coexist below 850–900 °C, and the amount of the hexagonal polymorph was shown to increase at the expense of the cubic polymorph with decreasing temperature. Different chemical composition of the two coexisting phases was inferred, but a complete transformation to the hexagonal polymorph was hindered by slow cation diffusion. Due to the sluggish kinetics, usual cooling rates lead to the meta-stable cubic BSCF, but over time the transition to the stable hexagonal polymorph may be detrimental to applications incorporating BSCF. We show that the transformation of the cubic to hexagonal polymorph of BSCF can be rationalized by the Goldschmidt tolerance factor and accordingly suppressed by appropriate substitutions.

Keywords: Perovskite; Oxygen vacancies; Phase transition; Goldschmidt tolerance factor

1. Introduction

Perovskite oxides of the series $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) are among the most promising oxygen permeable membrane materials [1–5].Very high transport rates have been achieved, which relates to the unusually high concentrations of mobile oxygen vacancies at elevated temperatures. The end member $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) was one of the first materials suggested as an oxygen transport membrane [6–8]. However, undesirable ordering of oxygen vacancies has been reported to occur in SCF at temperatures below 750 °C and pO_2 less than ~0.1 atm, [7–12] yielding an orthorhombic brownmillerite phase, $SrCo_{0.8}Fe_{0.2}O_{2.5}$. The ordered arrangement of oxygen vacancies in the brownmillerite structure, in which one-sixth of the oxygen sites are vacant, reduces the oxygen flux, and the lattice expansion associated with the phase transition results in mechanical instability. Formation of the brownmillerite phase is observed up to a Fe-content $SrCo_{0.1}Fe_{0.9}O_{2.5}$, [13] whilst a minimum substitution level of 20 mol% of Fe is required to prevent formation of the structural analogue of $SrCoO_{3-\delta}$ [14]. Recent reports have, however, demonstrated that the perovskite–brownmillerite phase transition can be suppressed by partial substitution of Ba for Sr. The substitution of considerably larger Ba for Sr also leads to higher levels of oxygen non-stoichiometry, with McIntosh et al. [15] reporting for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ a maximum oxygen content of 2.34 (600 °C, $pO_2 = 1$ atm) and a minimum of 2.19 (900 °C, $pO_2 = 10^{-3}$ atm). Consequently this composition has been proposed as a high-performance cathode material for intermediate temperature solid oxide fuel cells [16,17]. There are, however, questions regarding the long-term stability of such a highly defective material under the operating conditions of an IT-SOFC.

The possibility of stabilization of a hexagonal perovskite polymorph of BSCF at low temperature in air is a particular issue of concern, as hexagonal perovskite polymorphs in the BSCF system are expected based on the crystal structure of the end members. While the crystal structure of $SrFeO_{3-\delta}$ [18] and $SrCoO_{3-\delta}$ [19] (at high temperatures) are based on the cubic packing scheme, $BaFeO_3$ [20] and $BaCoO_3$ [21] are typical

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examples of hexagonal perovskites. Moreover, at low temperature cubic $SrCoO_{3-\delta}$ becomes unstable with respect to Co_3O_4 and $Sr_6Co_5O_{15}$, [22] which is structurally related to the hexagonal perovskites. Both hexagonal and cubic polymorphs have been previously reported for the $Ba_xSr_{1-x}CoO_{3-\delta}$ system [23]. We would therefore expect that part of the cubic perovskite BSCF solid solution may become unstable with respect to a hexagonal polymorph at low temperatures. Of particular interest to us is the nature of the conversion to a hexagonal polymorph since BSCF is a multi-component material according to the Gibbs phase rule.

2. Experimental

$Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ ($x=0$, 0.2, 0.5) powders were prepared by spray pyrolysis of nitrate solution containing stoichiometric amounts of the cations. Samples of these were annealed for 10 days in air at 750 °C, and for the same time in flowing oxygen gas at 800 °C, 825 °C and 850 °C. Portions of the raw powders were also calcined at 750 °C for 24 h in air and ball-milled in ethanol. These were used to produce dense ceramics (relative density 98%) via the sintering of compressed powder compacts at 1000 °C in air for 12 h. Thermogravimetric analysis of powders of crushed ceramics was performed using a Netzsch STA 449C TG-DSC. The oxygen stoichiometry of the materials was measured by thermogravimetry in $5\%H_2/N_2$ to form SrO, BaO and metallic Fe and Co. Powder X-ray diffraction measurements were performed using a Bruker D8 ADVANCE diffractometer with a VANTEC position sensitive detector. Scanning electron microscopy was performed using a Hitatchi S-3400N instrument.

3. Results and discussion

The $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ powders were sintered in air at 1000 °C for 12 h and each was confirmed as a single phase cubic perovskite, in line with previous reports [4]. Extended annealing of the sintered powders for 10 days at 750 °C resulted in partial conversion of the cubic parent phase to a lower symmetry polymorph. Indexing of the powder X-ray diffractograms confirmed formation of either a 2H or 4H type hexagonal perovskite structure (Fig. 1) with a considerably smaller unit cell volume than the cubic phase ($\Delta V \sim 7$–9%). We note that fast and moderate cooling rates yielded the meta-stable cubic phase in all cases. Diffractograms taken of the raw powders of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ after extended annealing in air and O_2 (Fig. 2) in the temperature range 800 °C to 850 °C suggest the

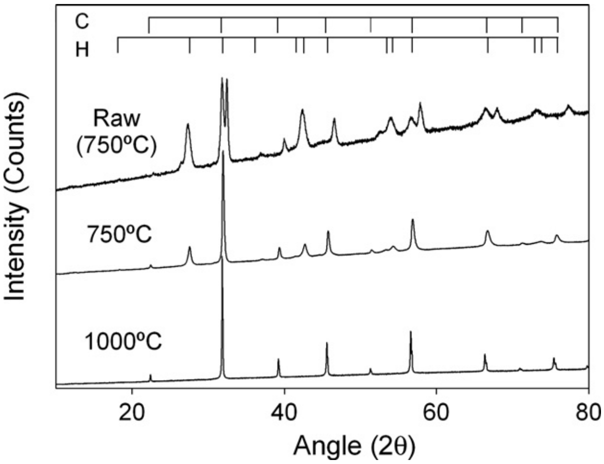

Fig. 1. X-ray powder diffraction data for air-fired samples of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$. Sintered at 1000 °C, sintered powder re-annealed at 750 °C/24 h and raw powder calcined at 750 °C/240 h. Calculated reflections for the cubic ($a=3.99$ Å) and hexagonal 2H ($a=5.60$ Å and $c=4.37$ Å) polymorphs are indicated as “C” and “H” respectively.

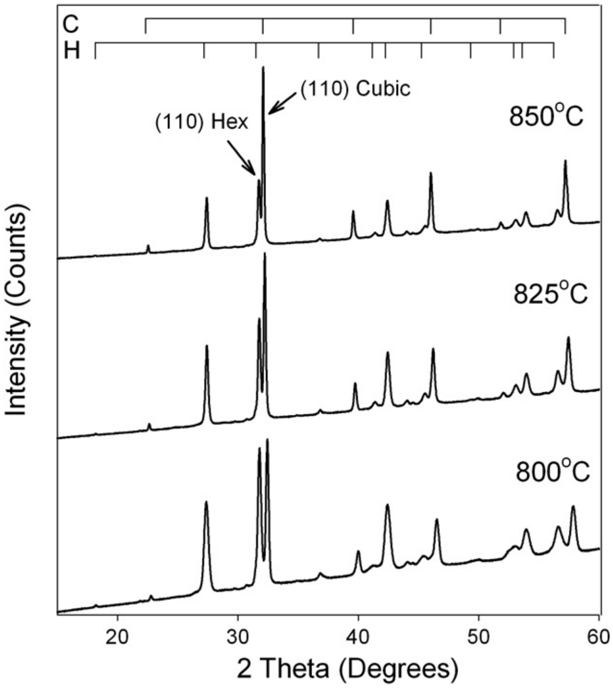

Fig. 2. Diffraction patterns for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ annealed in O_2 at 800 °C, 825 °C, and 850 °C for 240 h. Calculated reflections for the cubic and hexagonal 2H polymorphs (labelled “C” and “H” respectively) are indicated.

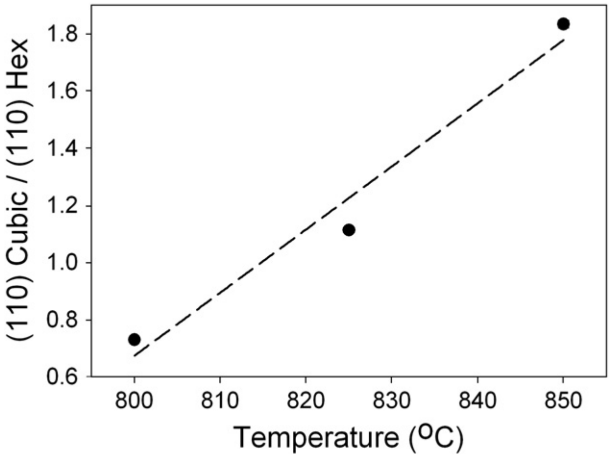

Fig. 3. The ratio of the integrated intensities of the cubic (110) peak to the hexagonal 2H (110) peak, as a function of annealing temperature.

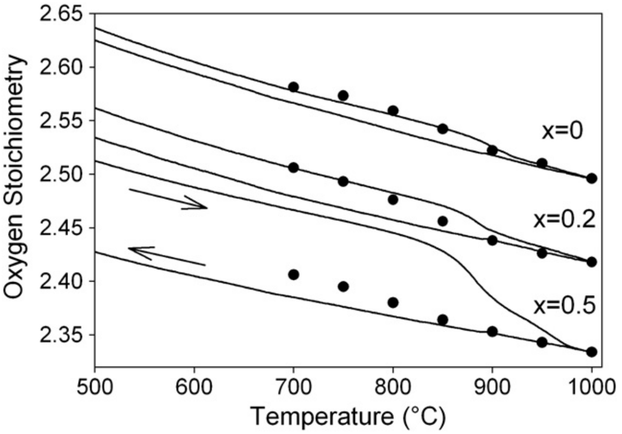

Fig. 4. Oxygen stoichiometry of two-phase mixtures of $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ ($x=0$, 0.2, 0.5) upon heating and subsequent cooling at 5 K/min, showing the cubic to hexagonal phase transition during heating only. Data of oxygen stoichiometry of the cubic polymorph measured at isothermal conditions (~200 min) is shown for comparison (solid points).

existence of a two-phase region separating the cubic and hexagonal forms: the cubic:hexagonal phase ratio is clearly temperature dependent (Fig. 3). Over the same region the unit cell edge of the cubic phase increases sharply from 3.90 Å (800 °C) to 3.94Å (850 °C), suggesting some compositional variation, probably in Ba/Sr stoichiometry as the change in oxygen content is expected to be relatively small over this temperature range. An increase in the hexagonal *a*-axis and shortening of the *c*-axis is also seen, though the effect is smaller. Similar observations were also observed for $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ ($x=0$, 0.2).

It is evident that the long-term annealing of the raw powders (with considerably higher surface area) yields a considerably higher fraction of the hexagonal polymorph than for the sintered and re-annealed samples. Also, the measured unit cells for both the hexagonal and cubic forms in the sintered and annealed samples do not approach the values expected from the annealed raw powders. A larger cubic and smaller hexagonal cell is seen, along with peak broadening of the hexagonal phase. It is therefore proposed that formation of the hexagonal polymorph goes via a nucleation and growth mechanism and is inhibited by slow diffusion, probably of Ba/Sr. Thermogravimetric analysis confirm these slow kinetics: Fig. 4 compares the oxygen contents of mixed phase powders of cubic and hexagonal $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ ($x=0$, 0.2 and 0.5) obtained after long-term annealing in air at 750 °C for 10 days with those obtained by annealing the pure cubic form under isothermal conditions (~200 min) in the range 700–900 °C. For each of the compositions the hexagonal–cubic phase transition occurs in the region 850–900 °C. The phase fraction of the hexagonal polymorph obtained after the long-term annealing increases with increasing Ba-content as expected, and no reversibility is seen for the transition in any of the faster cooled data. The deviation of the isothermal and fast-cooled data below ~900 °C indicates the formation of minor amounts of the hexagonal polymorph, but it can be seen that only the $x=0$ and $x=0.2$ compositions attain similar phase fractions (related to the sample oxygen content) as obtained after 10 days annealing at 750 °C.

The coexistence of the hexagonal and cubic polymorphs in $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ can be rationalized by analysis of the reduced Gibbs phase rule at constant absolute pressure, $Ph+F=C+1$, where Ph, F and C reflects the number of phases,

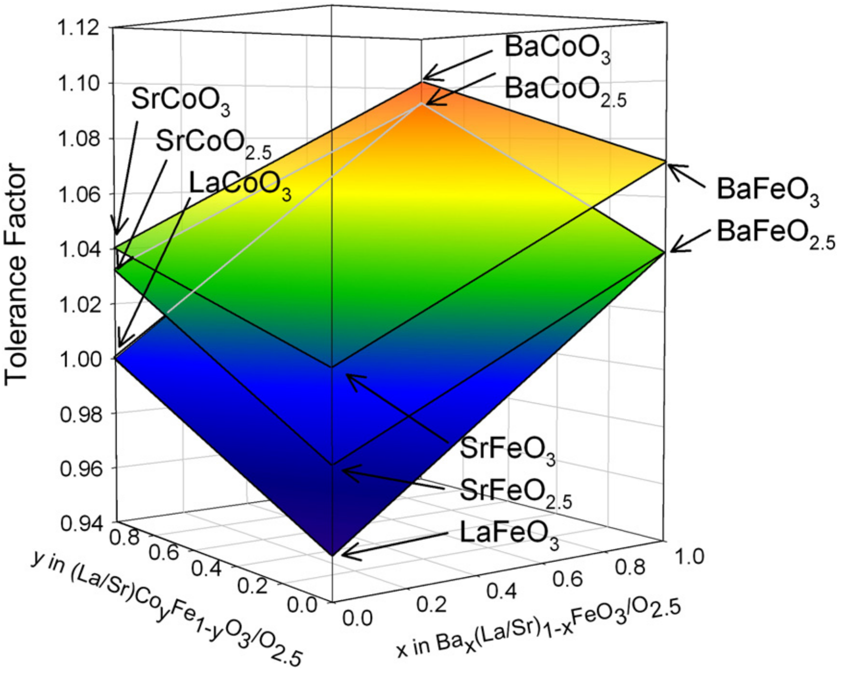

Fig. 5. Calculated Goldschmidt tolerance factors *t* of $Ba_xSr_{1-x}Co_yFe_{1-y}O_3$, $Ba_xSr_{1-x}Co_yFe_{1-y}O_{2.5}$ and $Ba_{1-x}La_xCo_yFe_{1-y}O_{2.5+y/2}$ materials versus composition. *t* has been calculated using ionic radii from Shannon [27].

degrees of freedom and the number of components respectively and 1 represents temperature. Consider the well known phase transition between hexagonal and cubic $SrMnO_{3-\delta}$ [24]. The phase transition temperature between the two perovskite polymorphs in this material has been shown to decrease with decreasing partial pressure of oxygen, proving that the phase transition corresponds to an invariant phase equilibrium ($F=0$, $C=3$, Ph$=3$, at fixed pO_2 or fixed T). The interesting question is how this situation is changed upon chemical substitution of the material. In BSCF, the two additional components (C=5) implicitly generate two additional degrees of freedom, and the coexistence of the two polymorphs thus does not necessarily correspond to an invariant phase equilibrium. Consequently the separation of cubic and hexagonal polymorphs by a two-phase region in T-pO_2 space is in good accord with thermodynamic principles. The composition of the two coexisting phases within this two-phase region will naturally respond to a change in the state parameters: A change in temperature or partial pressure of oxygen will imply that the composition of the two condensed phases will change, as indicated by our diffraction data. Based on the crystal structure of the end members, we expect that the Ba-content is higher in the hexagonal polymorph than in the cubic. We therefore propose that the main compositional variation in between the two polymorphs is on the Ba/Sr-site.

The perovskite structure is predicted for ABO_3 compounds when the ionic ratio of A is considerably larger than the ratio of the B cation [25]. Cubic perovskites are based on a cubic close packing of AO_3 with B cations in octahedral positions. Deviations from cubic symmetry, leading to orthorhombic or rhombohedral polymorphs, can be rationalized using the Goldschmidt tolerance factor, $t=(r_A+r_O)/\sqrt{2}(r_B+r_O)$, where r_A, r_B and r_O are the respective radii of A cation, B cation and O anion in the appropriate coordination. The ideal cubic structure is formed for $t=1$, when the A cation matches in size with the O^{2-} ions to form cubic close-packed layers, and the B cation matches the size of the interstitial sites formed by the oxygens to give an array of corner-shared BO_6 octahedra. For $t<1$, lower symmetry arrangements with tilted BO_6 octahedra are commonly seen whilst for $t>1$ hexagonal structures with near hexagonal close-packed layers of the A cations and O^{2-} anions are formed. The hexagonal structure is a variant of the oxygen packing in perovskite oxides, leading to a structure with chains of face-sharing BO_6 octahedra. Theoretical consideration of the stability of hexagonal and cubic polymorphs of $AeMnO_3$ (Ae=Ca, Sr, Ba) has shown that increasing the size of the Ae cation favours edge sharing octahedral and the hexagonal perovskite structure [26].

Fig. 5 displays calculated Goldschmidt tolerance factors, using the ionic radii taken from Shannon [27], for phases $A_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$ (A=Ba, La), with fixed oxidation state of Fe/Co. The high tolerance factor of the $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ series points to the meta-stability of the cubic polymorph at low temperature. Increasing temperature leads to an increase of the oxygen non-stoichiometry, and concomitant reduction of the transition metal cations on the Co/Fe-sites as required by charge compensation. Since the reduced cations tend to be larger in size than the oxidized ones, their presence will favour formation of the cubic perovskite structure at high temperature. An obvious remedy to avoid formation of the hexagonal phase at low temperature is to lower the tolerance factor by substitution, for example, of La for Ba or Sr as illustrated in Fig. 5.

4. Conclusions

We have demonstrated that the cubic perovskite phase of BSCF transforms gradually to a hexagonal polymorph at lower temperatures. A two-phase region consisting of both polymorphs is proposed. This sluggish but reversible transition is accompanied by a significant increase in the oxygen non-stoichiometry. It is anticipated that the structural instability will adversely affect the performance of devices incorporating BSCF as membrane or electrode where long-term stability of operation is required. Previous observations of declining oxygen fluxes at moderate temperatures using $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ as oxygen permeable membrane may be attributable to this effect [2,28].

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