# CHEMICAL STABILITY OF $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ UNDER DIFFERENT OXYGEN PARTIAL PRESSURE

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$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) is an outstanding material for cathode materials of solid oxide fuel cells (SOFCs). However the chemical stability of BSCF is still not well-understood. In this paper, in situ HT-XRD measurement was performed as a function of temperature and oxygen partial pressure, $p(O_2)$, to evaluate the chemical stability window of BSCF. The results inferred the phase transition of BSCF produced two kinds of impurity phases coexisted with BSCF at 800°C in the relatively higher $p(O_2)$.

## 1. Introduction

A cubic perovskite-type oxide, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) is a promising candidate for a high performance cathode of intermediate temperature solid oxide fuel cells (IT-SOFCs) [1]. Recently, however, there are some reports about the performance degradation of BSCF after long-term measurements [2-4]. This might be caused by a phase transition from cubic to hexagonal at temperatures below 850 ºC. Svarcova *et al.* reported the coexistence of hexagonal and cubic polymorphs after long time annealing at 800°C [5]. More recently, focus has been laid on the annealing time and temperature dependence on the phase transition of BSCF [5-12]. The instability is the obstacles to the future application of BSCF. But chemical stability conditions of BSCF, particularly conditions of oxygen partial pressure, $p(O_2)$, are still insufficiently understood. In this work, we focus on the chemical stability of BSCF under different $p(O_2)$ from intermediate to high temperatures by using HT-XRD. We aim to determine the chemical stability conditions of BSCF in order to ensure the reliability of BSCF.

## 2. Experimental

The powder of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) was synthesized by Pechini method. Firstly, nitrate solutions of $Ba^{2+}$, $Sr^{2+}$, $Co^{2+}$ and $Fe^{3+}$ were prepared. Then the concentration of each solution was determined by a chelate titration for $Ba^{2+}$, $Sr^{2+}$, $Co^{2+}$ and by ICP-AES for $Fe^{3+}$. The nitrate solutions were mixed at a

proper metal ratio. Then ethylene glycol and citric acid were added to the solution and heated up to 473 K to obtain a polymeric precursor. The precursor was firstly calcined at 1073 K, then sintered at 1273 K and 1373 K for 10 h. Conventional powder XRD confirmed that the synthesized powder was a single phase perovskite-type oxide.

X-ray diffractmeter (Bruker D8 Advance: Cu K$\alpha$ radiation) is used for *in situ* high-temperature XRD (HT-XRD) measurement to identify thermodynamically stable phases under a certain condition. HT-XRD measurement was carried out under controlled $p(O_2)$ between room temperature and 1373K. The powder sample was set on a platinum heater in a XRD chamber. $O_2$-$N_2$ gas mixtures were let flow into the chamber to control $p(O_2)$. The oxygen partial pressure was monitored by a zirconia concentration cell placed downstream from the chamber. HT-XRD patterns were measured from 673 K to 1373K after 5- to 20-hour duration at each temperature

**3. Results and discussion**

Figures 1 shows HT-XRD patterns of BSCF at 673 K to 1273 K in 100ppm $O_2$ – $N_2$. No impurity phase was observed below 973 K. At 973 K, however, the peaks assigned to an impurity phase (phase A) appeared. It means that cubic phase of BSCF is not chemically stable under this condition. The intensity of the impurity phase increased up to 1073 K; but that at 1173 K slightly decreased; then, at 1273 K, the peak almost disappeared, indicating that the phase A is not stable at higher temperature than 1273 K.

Figure 2 shows the results of HT-XRD measurement of BSCF in 1%$O_2$-$N_2$ atmosphere. The impurity phase A was observed at 973 K. The intensity of the impurity phase A increased with increase in temperature. At 1173 K, the intensity of the impurity peak is the highest between 973 and 1273 K. The diffraction peak seems to decrease at 1273 K but was still clearly observed This confirms the stable temperature region of the impurity phase A is relatively wider than 100ppm $O_2$-$N_2$.

Fig. 3 shows the HT-XRD results of BSCF in 100%$O_2$ atmosphere. As to the impurity phase A, it is not observed below 973 K, but appeared after a few hour annealing at 973 K. The amount of the phase A increased with increasing temperature to 1273 K. The phase A is stable between 973 and 1273 K in 100%$O_2$. Moreover, the formation of another impurity phase (phase B) was

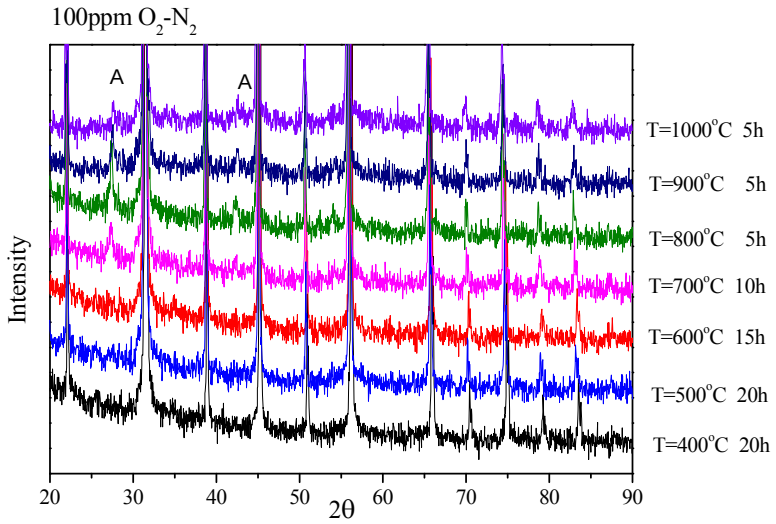



Fig.1. HT-XRD pattern of BSCF from 673 K to 1273 K in 100ppm $O_2$-$N_2$.

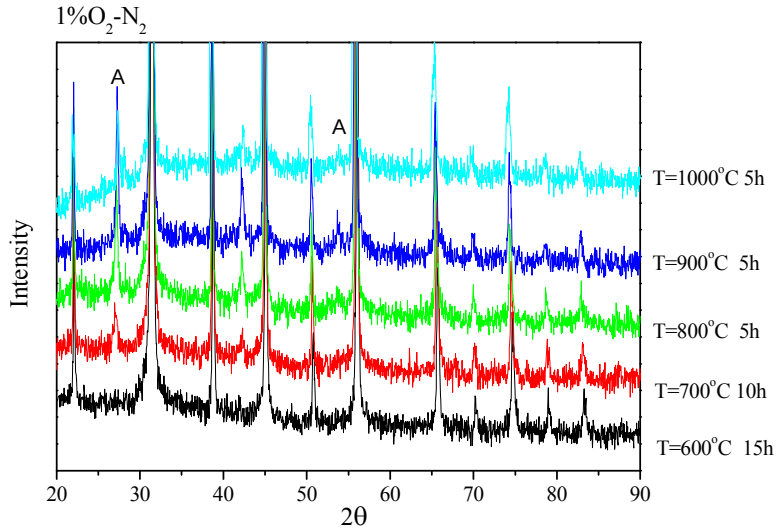



Fig.2. HT-XRD pattern of BSCF from 873 K to 1273 K in 1% $O_2$-$N_2$.

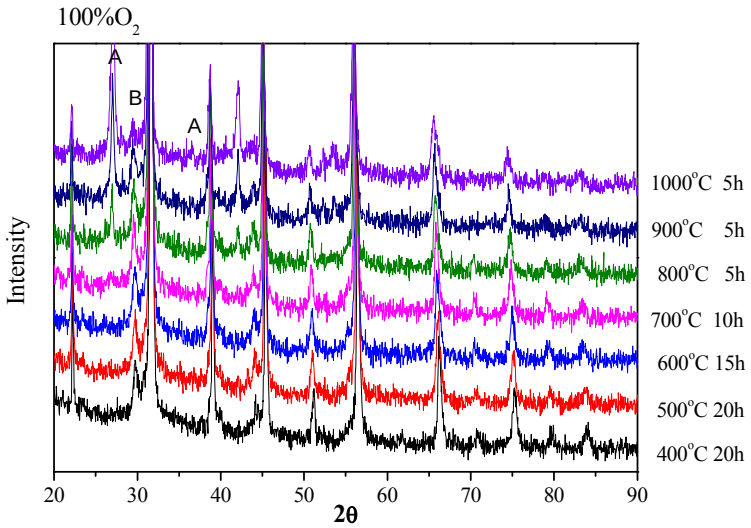
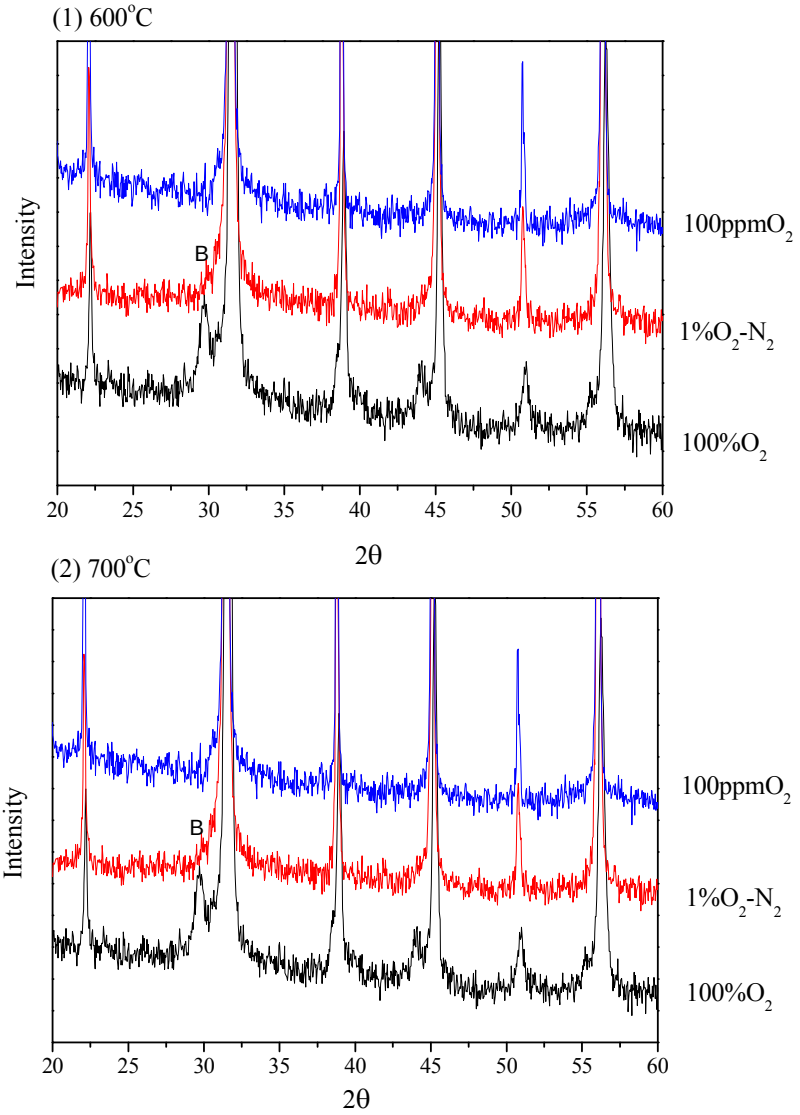



Fig.3. HT-XRD pattern of BSCF from 673 K to 1273 K in 100% $O_2$..

observed from 673 to 1273 K. Its characteristic peaks increased with the annealing time from 673 to 973 K, while the peak intensity of the phase B seems to decrease at higher temperature than 973 K. At temperature above 700°C, the impurity phase A appeared in addition to the impurity phase B even under 100%$O_2$ atmosphere. Such complicated phase relation infers that there exist at least two decomposition processes for BSCF.

Fig.4 shows the HT-XRD results of BSCF at 600°C, 700°C and 800°C in 100ppm $O_2$, 1% $O_2$ and 100% $O_2$ atmosphere. The impurity phases were not observed at temperatures below 873 K in 1%$O_2$-$N_2$ and 100ppm$O_2$-$N_2$. This shows BSCF is, at least kinetically, stable under these conditions.

The formation of impurity phases greatly depends on $p(O_2)$ and temperature. Considering the fact that single phase BSCF can be obtained by sintering at 1373 K in air, and that only the diffraction peaks of BSCF were observed at 1273 K in 100ppm $O_2$-$N_2$ in Fig. 3, we can speculate that BSCF should be stable under relatively reducing condition. In addition, compared to BSCF, the chemically stable condition of the phase A should be more oxidizing condition, while that of the phase B should be much more oxidizing.


(1) 600°C
Intensity
B
100ppmO2
1%O2-N2
100%O2
20
25
30
35
40
45
50
55
60
2θ
(2) 700°C
Intensity
B
100ppmO2
1%O2-N2
100%O2
20
25
30
35
40
45
50
55
60
2θ

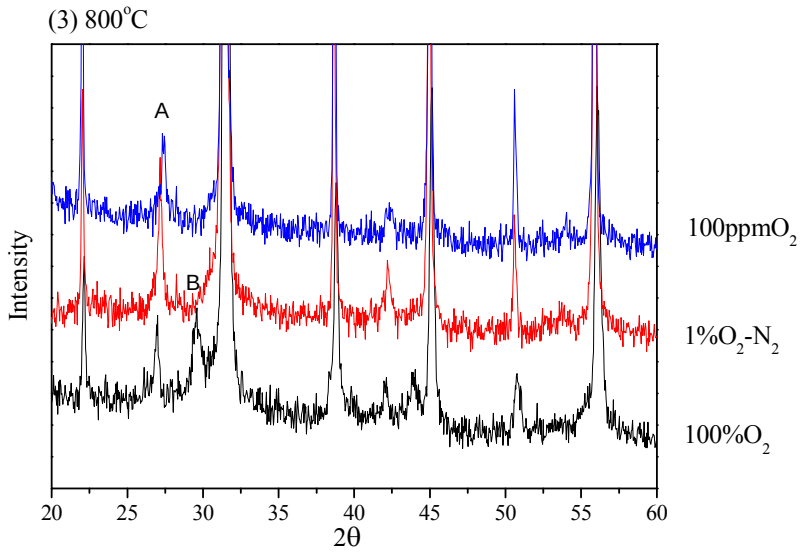



Fig.4. Dependence of HT-XRD results on oxygen partial pressure at (1) 600°C, (2) 700°C, and (3)800°C respectively.

## 4. Conclusions

The HT-XRD measurement of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) were employed with $p(O_2)$ from 1 to $10^{-5}$ bar in $O_2$-$N_2$ gas system. The results confirmed the instability of BSCF at intermediate temperature. It was inferred that the decomposition reactions of BSCF should have $p(O_2)$ dependence. The further investigation of BSCF based on this chemical stability analysis is extremely essential and will provide us a reliable evaluation of the reported electrochemical properties of BSCF.

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