

Synthesis and Characterization of $\text{BaZr}_x\text{Ce}_{0.8-x}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$

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Introduction

Proton Conductive Ceramics has become known for allowing the reduction of operating temperature of Intermediate Temperature Solid Oxide Fuel Cell, known as IT-SOFC [1]. The most studied materials are the perovskite type oxides as $\text{BaCeM}^{\text{III}}\text{O}_{3-\delta}$ (BCM^{III}) (M^{III} = metals with valence 3+), that exhibit good proton conductivity. However, it has low chemical stability in the presence of acidic gases such as CO_2 and SO_2 [1]. Compounds with adequate chemical stability under CO_2 atmospheres can be provided by doping the cerates with zirconium. In particular, $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ showed an outstanding mixed ion conduction (by proton and oxide ion), in IT-SOFC operating conditions [1,2]. Thus, the aim of this study was to obtain the $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb) and $\text{BaCe}_{0.8}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BCYYb) and evaluate the effect of zirconium on chemical stability under CO_2 containing atmospheres of this oxide system.

Experiments

The compounds were synthesized by EDTA-Citrate gel Method [1,2]. After gelling, it was dried at $150^\circ\text{C}/2\text{h}$ and $250^\circ\text{C}/2\text{h}$ and pyrolysed at $400^\circ\text{C}/4\text{h}$, in air. Finally, it was heat treated at $1100^\circ\text{C}/10\text{h}$, also in air. These compounds were characterized by X-Ray Diffraction (XRD). The compounds were submitted to a 5mol% CO_2 (N_2 balance) atmosphere at different temperatures: 400°C , 500°C , 600°C and 700°C , for 4 hours, and they were also characterized by X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR).

Results and Discussion

The XRD patterns (Fig. 1) showed that EDTA-Citrate gel Method can provide materials under perovskite crystal structure, for both samples, however, the inclusion of Zr leads to a more symmetrical crystalline structure.

In the Fig. 2, it can be seen that there is no formation of BaCO_3 when the samples are submitted to an heat treatment at 400°C and 500°C in CO_2 atmosphere. At 600°C , the BZCYYb sample was relatively stable with small formation of BaCO_3 , while BCYYb sample revealed to be quite unstable at 600°C , demonstrating the key role of zirconium for chemical stability. At 700°C , both samples proved unstable. The chemical stability results were confirmed by FTIR.

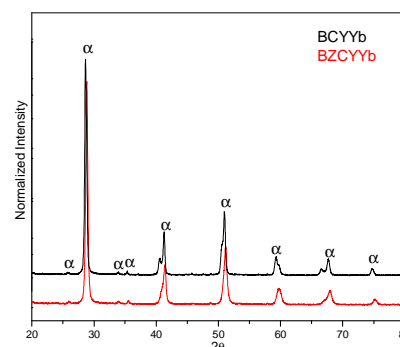


Fig. 1. XRD patterns of BZCYYb and BCYYb after heat treated at $1100^\circ\text{C}/10\text{h}$ in air. α - perovskite.

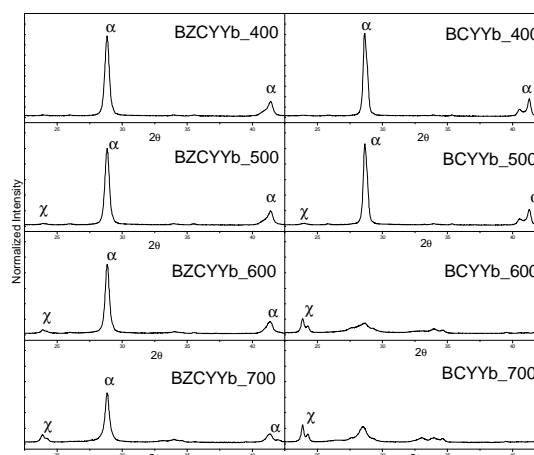


Fig. 2. XRD patterns of BZCYYb and BCYYb after submitted to heat treatment in 5mol% CO_2 . α - BZCYYb perovskite and χ - barium carbonate.

Conclusions

The BZCYYb compound presented perovskite crystalline structure with higher symmetry. The BZCYYb and BCYYb compounds were stable under CO_2 atmosphere at 400°C and 500°C , whereas just BZCYYb was stable at 600°C .

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References

- [1] S. Wang; F. Zhao, L. Zhang, F. Chen. Solid State Ionics, v.213, p.29–35, 2012.
- [2] F. Zhao; C. Jin; C. Yang; S. Wang; F. Chen. Journal of Power Sources, v.196, p.688–691, 2011.