Electronic-Ionic Impedance Characteristics of $(Y_{0.08}Sr_{0.92})_{1-x}Ti_{0.6}Fe_{0.4}O_{3-\delta}$ Mixed-Conducting Materials (Postprint)

Authors: single subject, Guo Xingmin

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Abstract

Mixed-conducting materials $(Y_{0.08}Sr_{0.92})_{1-x}Ti_{0.6}Fe_{0.4}O_{3-\delta}$ ($x = 0.05, 0.07, 0.10$) were prepared by the sol-gel method. The phase composition was analyzed by X-ray diffraction (XRD), and the total conductivity and ionic conductivity were measured by AC impedance spectroscopy and electron-blocking electrode method, respectively. The influence of A-site deficiency on the structure, electrical properties, and impedance behavior of $(Y_{0.08}Sr_{0.92})_{1-x}Ti_{0.6}Fe_{0.4}O_{3-\delta}$ mixed-conducting materials was investigated. The results show that all samples possess a single cubic perovskite phase structure. Within the tested temperature range, the total conductivity of $(Y_{0.08}Sr_{0.92})_{1-x}Ti_{0.6}Fe_{0.4}O_{3-\delta}$ ($x = 0.05, 0.07, 0.10$) first increases and then decreases with rising temperature, exhibiting a small polaron conduction mechanism. As the A-site deficiency amount increases, the total conductivity decreases. The total conductivity of $(Y_{0.08}Sr_{0.92})_{1-x}Ti_{0.6}Fe_{0.4}O_{3-\delta}$ ($x = 0.05, 0.07, 0.10$) at 800°C is 0.011-0.26 $S\cdot cm^{-1}$. The total conductivity impedance spectra of $(Y_{0.08}Sr_{0.92})_{1-x}Ti_{0.6}Fe_{0.4}O_{3-\delta}$ only display the high-frequency linear region, indicating that the materials are predominantly electronic conductors. The ionic conduction relaxation time gradually increases with increasing A-site deficiency amount, suggesting that A-site deficiency is detrimental to ionic transport across grain boundaries.

Full Text

Electronic-Ionic Impedance Characteristics of $(Y_{0.08}Sr_{0.92})_{1-x}Ti_{0.6}Fe_{0.4}O_{3-\delta}$ Mixed Conductor Materials

Shan Ke[1], **Guo Xingmin**[2]

[1]Laboratory of New Materials for Power Sources, College of Science, Honghe University, Mengzi 661199, China

[2]State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China

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**Corresponding author: Shan Ke, Tel: 13691055859, E-mail: shankekeshan@163.com*

Abstract

A-site-deficient perovskite (Y0.08Sr0.92)1-xTi0.6Fe0.4O3-δ (x = 0.05, 0.07, 0.10) was synthesized at 1350°C in air by the sol-gel method. The effects of A-site deficiency on the phase structure, electrical and ionic conductivity, and impedance behavior were investigated. All samples exhibited a single cubic perovskite structure without impurity peaks, indicating that co-doping with Y and Fe did not disrupt the SrTiO3 perovskite framework. The tolerance factor for (Y0.08Sr0.92)1-xTi0.6Fe0.4O3-δ (x = 0.05, 0.07, 0.10) was calculated to be 0.9298–0.9544, confirming that the cubic perovskite structure remains stable. As A-site deficiency increased, sample porosity increased and sintered density decreased, suggesting that A-site deficiency hinders densification.

The total electrical conductivity of (Y0.08Sr0.92)1-xTi0.6Fe0.4O3-δ first increased then decreased with rising temperature, exhibiting small polaron conduction mechanism and n-type behavior. Conductivity decreased with increasing A-site deficiency, reaching 0.011–0.26 $\mathrm{S \cdot cm^{-1}}$ at 800°C. The impedance spectra showed only a high-frequency linear region, indicating that electronic conduction dominates. The relaxation time for ionic conduction increased progressively with A-site deficiency, demonstrating that A-site deficiency impedes ionic transport across grain boundaries.

Keywords: inorganic non-metallic materials, (Y0.08Sr0.92)1-xTi0.6Fe0.4O3-δ, electrical impedance, ionic impedance, relaxation

Introduction

ABO3 perovskite-structured SrTiO3 maintains structural and performance stability across a wide oxygen partial pressure and temperature range, showing promising applications in fuel cells, oxygen sensors, and oxygen separation membranes. Although stoichiometric SrTiO3 exhibits low electrical conductivity, its A and B sites possess strong doping capabilities that enable modification through substitution. Doped SrTiO3 demonstrates mixed conductor properties with both oxygen ionic conductivity and electronic conductivity, offering catalytic activity and selective oxygen permeability at intermediate to high temperatures. Furthermore, all-ceramic SrTiO3 components exhibit superior structural and chemical stability at elevated temperatures. With high electrical conductivity and compatibility with various electrolyte materials without physical or chemical reactions, co-doping at A and B sites further enables tuning of thermal expansion properties.

In the ideal ABO3 perovskite structure, A and B site elements are present in equal amounts, but non-stoichiometry is practically achievable. Y,Fe-co-doped SrTiO3 (Y0.06Sr0.94Ti0.6Fe0.4O3-δ) exhibits high electronic and ionic conductivity. This study investigates how A-site deficiency affects the crystal structure, densification, electrical properties, and impedance behavior of these materials.

Experimental Methods

1.1 Preparation of (Y0.08Sr0.92)1-xTi0.6Fe0.4O3-δ

Analytical grade strontium acetate (Sr(CH3COO)2·2H2O), tetrabutyl titanate (Ti(CH3CH2CH2CH2O)4), yttrium oxide (Y2O3), and iron(III) oxide (Fe2O3) were used as raw materials to synthesize A-site-deficient (Y0.08Sr0.92)1-xTi0.6Fe0.4O3-δ ($x = 0.05, 0.07, 0.10$) via the sol-gel method. The powders were calcined at 1100°C for 10 h, then uniaxially pressed into pellets at 50 MPa and sintered at 1350°C for 5 h to obtain the final (Y0.08Sr0.92)1-xTi0.6Fe0.4O3-δ samples.

1.2 Material Characterization

Phase analysis was performed using a D/max-A rotating anode X-ray diffractometer operating at 40 kV and 40 mA with Cu-Kα radiation, continuous scanning mode, step size of 0.02°, and scanning range of 10-90°. Sample fracture morphology was examined using a Quanta FEG 650 scanning electron microscope.

Electrical conductivity was measured using a CHI660B electrochemical workstation with impedance spectroscopy in the frequency range of 0.01-10^5 Hz. Platinum paste was applied uniformly to both surfaces of the samples, platinum wires were attached, and the assemblies were fired at 800°C for 30 min to form thin-film electrodes. Ionic conductivity was measured using the electron-blocking electrode method with YSZ (yttria-stabilized zirconia) as the solid electrolyte, since YSZ is a pure oxygen ion conductor. One side of the sintered pellet was coated with platinum paste and attached to a YSZ disc. The composite was fired at 800°C for 30 min, then the edges were sealed with glass to completely isolate the sample periphery from air and close any gaps at the interface. Finally, platinum paste and wires were applied to both sides of the sample/YSZ composite and sintered at 800°C for 30 min to prepare the test specimen.

Results and Discussion

2.1 Structure and Morphology of (Y0.08Sr0.92)1-xTi0.6Fe0.4O3-δ

[Figure 1: see original paper] shows XRD patterns of (Y0.08Sr0.92)1-xTi0.6Fe0.4O3-δ (x = 0.05, 0.07, 0.10) sintered at 1350°C for 5 h. All samples display a single perovskite structure without impurity peaks, confirming that Y and Fe co-doping does not affect the SrTiO3 perovskite structure type. The perovskite structure type is typically determined by the tolerance factor t, where rA, rB, and rO represent the average ionic radii of A-site, B-site elements, and oxygen ions, respectively. An ideal cubic perovskite structure has t = 1, while materials maintain cubic structure when $0.95 < t < 1.04$. Perovskite structures remain stable for $0.90 < t < 1$, and become orthorhombic when $0.75 < t < 0.9$. Based on ionic radii, the tolerance factor for (Y0.08Sr0.92)1-xTi0.6Fe0.4O3-δ (x = 0.05, 0.07, 0.10) was calculated to be 0.9298–0.9544 using Equation (1), as shown in [Figure 2: see original paper], indicating stable cubic perovskite structures. As A-site deficiency increases, the tolerance factor decreases, suggesting increased lattice distortion.

[Figure 3: see original paper] presents SEM micrographs of (Y0.08Sr0.92)1-xTi0.6Fe0.4O3-δ samples sintered at 1350°C. Porosity increased significantly with A-site deficiency, and sintered density decreased, demonstrating that A-site deficiency is detrimental to the densification of (Y0.08Sr0.92)1-xTi0.6Fe0.4O3-δ.

2.2 Electrical Properties

[Figure 4: see original paper] shows complex impedance plots of (Y0.08Sr0.92)1-xTi0.6Fe0.4O3-δ. Only high-frequency linear regions are observed, indicating that electronic conduction dominates the total conductivity. Material impedance decreased with increasing temperature but increased with A-site deficiency.

[Figure 5: see original paper] illustrates the temperature dependence of total electrical conductivity for (Y0.08Sr0.92)1-xTi0.6Fe0.4O3-δ in air from 400-900°C. Conductivity first increased then decreased with temperature, exhibiting small polaron conduction mechanism and n-type behavior—a trend observed in many mixed conductors. Conductivity decreased with increasing A-site deficiency, possibly due to Fe^{3+} ionization reducing electron hole concentration (Equation (2)). The total conductivity at 800°C ranged from 0.011-0.26 $S \cdot cm^{-1}$, with (Y0.08Sr0.92)0.95Ti0.6Fe0.4O3-δ reaching 0.162 $S \cdot cm^{-1}$.

2.2.2 Ionic Conductivity and Impedance Behavior

[Figure 6: see original paper] shows complex impedance plots for ionic conduction in (Y0.08Sr0.92)0.90Ti0.6Fe0.4O3-δ at different temperatures. At lower temperatures, the spectra display a semicircle that shrinks with increasing temperature. The intercept with the real axis decreases as temperature rises. At higher temperatures, two semicircles appear. As shown in [Figure 6b: see original paper] (with equivalent circuit inset), the intercept represents grain impedance, the mid-frequency arc represents grain boundary impedance, and the low-frequency arc represents sample/electrode interface impedance, indicating that conduction is dominated by oxygen ion relaxation at grain boundaries.

[Figure 7: see original paper] presents the relationship between the imaginary impedance component and frequency for (Y0.08Sr0.92)1-xTi0.6Fe0.4O3-δ during ionic conduction testing. Only single peaks appear, corresponding to grain boundary impedance, indicating one relaxation process. Peak intensity decreases and shifts to higher frequencies with temperature. For (Y0.08Sr0.92)0.95Ti0.6Fe0.4O3-δ, the fmax values at 650, 700, 750, and 800°C are 0.55, 2.55, 5.49, and 21.23 Hz, respectively, corresponding to relaxation times of ~13.4–290 ms. summarizes fmax and τ values, showing that ionic conduction relaxation time increases progressively with A-site deficiency, indicating that A-site deficiency is unfavorable for ionic transport.

Conclusions

A-site-deficient (Y0.08Sr0.92)1-xTi0.6Fe0.4O3-δ exhibits n-type electronic conduction with total conductivity first increasing then decreasing with temperature. Conductivity decreases as A-site deficiency increases, ranging from 0.011–0.26 $\mathrm{S \cdot cm^{-1}}$ at 800°C, with (Y0.08Sr0.92)0.95Ti0.6Fe0.4O3-δ reaching 0.162 $\mathrm{S \cdot cm^{-1}}$. The total conductivity impedance spectra show only high-frequency linear regions, confirming electronic conduction dominance. The ionic conduction relaxation time increases with A-site deficiency, demonstrating that A-site deficiency impedes ionic transport across grain boundaries.

References

1. Boukamp B. A., The amazing perovskite anode, *Nature Materials*, 2(5), 294(2003)
2. Li X., Zhao H., Gao F., La and Sc co-doped SrTiO3 as novel anode materials for solid oxide fuel cells, *Electrochemistry Communication*, 10(10), 1567(2008)
3. Litzelman S. J., Rothschild A., Tuller H. L., The electrical properties and stability of SrTi0.65Fe0.35O3-δ thin films for automotive oxygen sensor applications, *Sensors and Actuators B*, 108(1/2), 231(2005)
4. Kharton V. V., Kovalevsky A. V., Viskup A. P., Transport properties and thermal expansion of Sr0.97Ti1-xFexO3-δ (x=0.2-0.8), *Journal of Solid State Chemistry*, 156(2), 437(2001)
5. Hui S. Q., Petric A., Electrical conductivity of yttrium-doped SrTiO3: influence of transition metal additives, *Materials Research Bulletin*, 37(7), 1215(2002)
6. Yoon J. S., Yoon M. Y., Kwak C., Y0.08Sr0.92FexTi1-xO3-δ perovskite for solid oxide fuel cell anodes, *Materials Science and Engineering B*, 177(2), 151(2011)

7. Fagg D. P., Kharton V. V., Frade J. R., Stability and mixed ionic-electronic conductivity of (Sr, La)(Ti, Fe)O3-δ perovskites, *Solid State Ionics*, 156(1/2), 45(2003)
8. Hui S., Petric A., Evaluation of yttrium-doped SrTiO3 as an anode for solid oxide fuel cells, *Journal of European Ceramic Society*, 22(9/10), 1673(2002)
9. Fu Q. X., Mi S. B., Wessel E., Influence of sintering conditions on microstructure and electrical conductivity of yttrium-substituted SrTiO3, *Journal of European Ceramic Society*, 28(4), 811(2008)
10. Kurokawa H., Yang L., Jacobson C. P., Y-doped SrTiO3 based sulfur tolerant anode for solid oxide fuel cells, *Journal of Power Sources*, 164(2), 510(2007)
11. Li X., Zhao H., Gao F., Synthesis and properties of Y-doped SrTiO3 as anode material for SOFC, *Journal of Power Sources*, 166(1), 47(2007)
12. Zhao H. L., Cheng Y. F., Xu N. S., Oxygen permeability of A-site nonstoichiometric BaxCo0.7Fe0.2Nb0.1O3-δ perovskite oxides, *Solid State Ionics*, 181(5-7), 354(2010)
13. Liu M. F., Zhao L., Dong D. H., High sintering ability and electrical conductivity of Zn doped La(Ca)CrO3 based interconnect ceramics for SOFCs, *Journal of Power Sources*, 177(2), 451(2008)
14. Shan K., Guo X. M., Synthesis and electrical properties of mixed-conducting YxSr1-xTi0.7Fe0.3O3-δ, *Materials Letters*, 121, 251(2014)
15. Shan K., Guo X. M., Synthesis and electrical conductivity of Y0.06Sr0.94Ti1-xFexO3-δ as a mixed conductor, *Materials Science and Engineering of Powder Metallurgy*, 18(6), 857(2013)

Note: Figure translations are in progress. See original paper for figures.