Structural Analysis of Multiphase La₁₋ₓSrₓCo₁₋ₓFeₓO₃₋δ

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Abstract. Multiphase $La_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ has been synthesized by sol-gel method and characterized by powder X-diffraction. Structure refinements of multiphase were undertaken to analyze compositions of compounds, and structure parameters were determined by Rietveld method, respectively. It was found that products were easier to be prepared in the condition of a precursor dealed with by high-speed disintegrator, and products synthesized at 1173K were composed of two phases of which $La_{0.75}Sr_{0.25}Co_{0.2}Fe_{0.8}O_{3-\delta}$ is an orthorhombic structure with space group Pbnm and $La_{0.46}Sr_{0.54}Co_{0.2}Fe_{0.8}O_{3-\delta}$ trigonal structure with space group R-3c. Structure geometry becomes more regular with increasing Sr content.

Introduction

The traditional $La_{1-x}Sr_xMnO_3$(LSM) cathode performs adequately at 1273K, however, its poor oxygen ionic conductivity results in high electrode resistance at lower temperatures. The mixed conductivity in the cathode can be improved by two approaches: mixing an ionically conducting material with an electrically conducting material to create a two-phase cathode [1, 2], or replacing the present materials with perovskites displaying high mixed conductivity on B-site of Co, Fe, and Ni, etc. [1, 3]. Further reduction of the SOFC operation temperature to 773K calls for better cathode materials than LSM. Studies of the $(La,Sr)(Co,Fe)O_3$ have been one of the most popular topics in the cathode research toward to intermediate temperature operation [4-6]. $LaCoO_3$ substituted with Sr and Fe on the A and B sites, a perovskite-type complex oxide with a very high electronic conductivity and high oxide ion conductivity over a wide temperature range [7-9], has been shown to possess the superior surface oxygen exchange/bulk diffusion characteristics at intermediate temperatures. It is therefore interesting and important whether we can prepare multiphase $La_{1-x}Sr_xCo_{1-x}Fe_xO_{3-\delta}$ materials as composite cathodes of IT-SOFC with different Sr content in different phases to optimize the all aspects of chemical and physical properties, such as lower TEC coexisting with higher electronic and ion conductivities and higher coefficient of surface exchange process, and if not, what the compositions, structures of multiphase and relationships between them are and how it happened.

The objectives of this work are to synthesize perovskite-type multiphase compounds by sol-gel method, and study the progress of multiphase formation and the affects. A Rietveld method is used to determine the exact coordinates of atoms, the unit cell dimensions, the atom occupation factors, isotropic temperature factors as well as the interatomic distances.

Experimental

To prepare $La_{1-x}Sr_xCo_{1-x}Fe_xO_{3-\delta}$(LSCF) powders, sol-gel method was adopted. The reactants ratio was determined according to the composition of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$. Nitrates of the constituent metals ions were separately dissolved in water. A solution of ammonia/EDTA mixed previously was then added to the mixed solution, and the final concentration of EDTA was 1.2 times that of the total metal cations. The pH value of the solution was adjusted to $8 \sim 9$ using ammonia. Secondly, the solution was heated for several hours at 350K to complete complexation until water was almostly vaporized, and the product gel we got then was torrefied to dryness in a stove at 433 K for 8h. The obtained dry mass gel precursor was divided into two groups. One group was dealt with by high-speed disintegrator (sample A) and another group was not dealt with (sample B). At last, the obtained dry mass gel precursor was added with ethanol in a mortar in air at room temperature and then powder specimens respectively were calcined at 873K, 1023 K, 1173K respectively for 2h in air atmosphere and then slowly cooled to room temperature.

X-ray powder diffraction data were collected using Siemens diffractometer with CuKα radiation at room temperature on samples treated at high temperature. The angular range was $10° \sim 90°$. A stepped scan using a step size of 0.02°and a constant counting time of 1 s per step were employed in an attempt to resolve the small structural distortions.
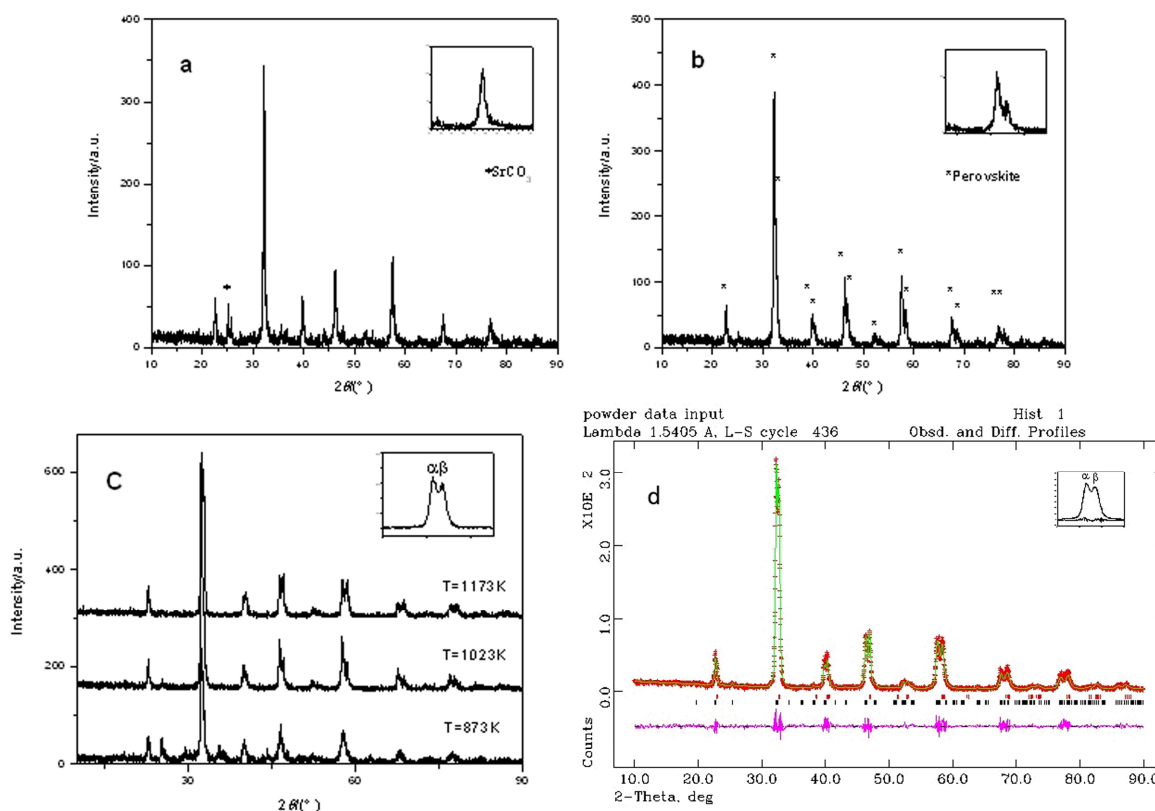
Fig. 1. XRD patterns of LSCF for (a) the sample B heated at 1023K for 2h, (b) the sample A heated at 1023K for 2h,(c) XRD patterns of the sample A heated at 873K, 1023K, and 1173K for 2h, (d)The relation between observed and calculated X-ray patterns as well as their difference for sample.

Results and Discussion

Characterization of product. Fig. 1 shows typical XRD patterns of LSCF for (a) the sampleB heated at 1023K for 2h, (b) the sample A heated at 1023K for 2h, respectively. Apparently, although peak of non-perovskite phases remain in both patterns (a) and (b), the sample B has formed single perovskite phase in spite of additional un-reacted precursors and the sample A has formed multiphase of perovskite at the same sintering temperature.

Fig. 1(c) shows XRD patterns of the sample A heated at 873K, 1023K, and 1173K for 2h. It is found that the peak intensity for non-perovskite fades with increasing temperature and the peak for non-perovskite disappears at 1173K. Only two perovekite phases of α and β were observed at 1173K and both phases have the similar characteristic peaks.

Structure refinement. Rietveld method using GSAS program was applied to the sample A heated at 1173K for 2h to determine structure and compositions of phases α and β(Fig. 1(c)). The structure of $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ can be either orthorhombic Pbnm, Cubic Pm3m, or trigonal R-3c. It is reported that the space group of $La_{1-x}Sr_xFeO_{3-\delta}$ prepared in air is Pbnm at x<0.3 and R-3c at x>0.3. Taking into account the comparability of the structure of $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ and $La_{1-x}Sr_xFeO_{3-\delta}$, we carried out the refinement in the space group Pbnm for α and R-3c for β, using the starting models of $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ and $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ respectively. Refinement included all atomic positions, cell parameters, scale factors, background and peak shapes. Fig. 1(d) illustrates observed and calculated X-ray patterns as well as their difference for the sample.

Orthorhombic phase of $La_{0.75}Sr_{0.25}Co_{0.2}Fe_{0.8}O_3$ and trigonal phase of $La_{0.46}Sr_{0.54}Co_{0.2}Fe_{0.8}O_{2.94}$. During the initial stages of the refinement, for both α and β phase, we have tried out several space groups, including cubic Pm3m, Orthorhombic Pbnm and Trigonal R-3C. The validity of these space groups was examined by refining the structures. Finally, it is with space group Pbnm and R-3C for phase α and β respectively that the modles refinement achieves minimization of the weighted profile R-factor, R= 0.1022, wR=0.1407. In addition, atomic coordinates from refinement have small changes with for different models and bond lengths obtained are appropriate for the perovskite structure. The models we carried out produce credible structure parameters. Consequently, The $La_{0.75}Sr_{0.25}Co_{0.2}Fe_{0.8}O_3$ phase shows orthorhombic symmetry with space group Pbnm and the space group of $La_{0.46}Sr_{0.54}Co_{0.2}Fe_{0.8}O_{2.94}$ is R-3c.

Bond lengths. It is known ABO_3 perovskite is made up of sheets of (BO_6) octahedral sharing corners. The present refinement reveals that A cation in ABO_3 is surrounded by 12 neighboring O atoms at distances ranging from 2.41 to 3.23 Å for $La_{0.75}Sr_{0.25}Co_{0.2}Fe_{0.8}O_3$ and 2.67 to 2.81 Å for $La_{0.46}Sr_{0.54}Co_{0.2}Fe_{0.8}O_{2.94}$. Within the octahedra, B cation is also surrounded by 6 atoms. Bond lengths and selected bond angles of multiphase are shown in Table 1. In comparison, at least four of the twelve A-O bonds and four of the six B-O bonds of $La_{0.75}Sr_{0.25}Co_{0.2}Fe_{0.8}O_3$ are longer than those of $La_{0.46}Sr_{0.54}Co_{0.2}Fe_{0.8}O_{2.94}$ in spite of the replacement by Sr(1.26 Å) having a larger ionic radius than La(1.16 Å).

Table1. Bond length and bond angel of multiphase

Phase	α		β
Space group	Pbnm		R-3c
A-O1 × 1	3.0239(8)	A-O1 × 3	2.8135(6)
O1 × 1	2.5756(7)	O1 × 3	2.6677(6)
O1 × 1	3.0643(8)	O1 × 6	2.7297(6)
O1 × 1	2.4625(7)		
O2 × 2	2.7208(4)		
O2 × 2	2.4094(4)		
O2 × 2	2.7760(5)		
O2 × 2	3.2320(5)		
B-O1 × 2	1.9951(5)	B-O1 × 6	1.93509(34)
O2 × 2	2.0778(4)		
O2 × 2	1.9086(4)		
∠B-O1-B	159.055(7)		175.6820(5)
∠B-O2-B	157.3562(35)		
		Tolerance factor	
AO(12)/ √2BO	0.9873		0.9996
Tolerance factors are given by the observed bond length, not from $t=(r_A+r_O)/2(r_B+r_O)$			

The bond angle ∠B-O1-B is the tilting angle of the octahedron relative to (001) plane and ∠B-O2-B is the rotation angle around the c axis in phase. ∠B-O1-B of α is 159.06°, ∠B-O2-B 157.36° and ∠B-O-B of β is ,175.68°. All three bond angles are smaller than 180, and this indicates that both the structures of α and β can be transformed under certain conditions until all both the tilting angle ∠B-O1-B and the rotation angle ∠B-O2-B become 180. For example, orthorhombic Pbnm and trigonal R-3c are transformed to tetragonal I4/mcm or Cubic Pm3m. Especially for phase α, the structure transition maybe results from the tilting angle ∠B-O1-B□of the octahedra relative to the (001) plane and the rotation ∠B-O2-B around the c axis. In addition, Uiso of O2 is larger than that of O1, which probably indicates a greater degree of rotation of the BO_6 octahedra in comparison with the tilting motion or may be correlated with the O occupancy factor. Although ∠B-O-B of β is 175.68°, larger than that of α, lattice parameters a=b=5.48Å of β is still slightly smaller than a=5.508Å, b=5.548Å of α. This feature is consistent with the fact that increasing Sr content can produce more B^{4+} which results in decreases of A-O and B-O distances for β phase.

Conclusions

In order to optimize of chemical and physical properties, multiphase LSCF has been synthesized by sol-gel method. The sample dealed with by high-speed disintegrator helped formation of multiphase, but the phases compositions and fractions were altered with increasing sintering temperature. Rietveld method can be used to do the structure refinements of multiphase. Two phases of LSCF coexisted in the products in our experiments with different structures, one orthorhombic Pbnm and another trigonal R-3c. The structures tolerance factor (Table 1.) given by observed bond lengths of phase β is 0.9996 larger than α 0.9873, which means $La_{0.46}Sr_{0.54}Co_{0.2}Fe_{0.8}O_{2.94}$ is more stable than $La_{0.75}Sr_{0.25}Co_{0.2}Fe_{0.8}O_3$.

Acknowledgements

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