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Neutron diffraction study of the perovskite-type lanthanum cobaltite $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ at 1260 °C and 394 °C

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Abstract

Crystal structure of a perovskite-type strontium- and iron-co-doped lanthanum cobaltite, $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF6482) has been studied by Rietveld analysis, maximum-entropy method (MEM) and MEM-based pattern fitting of *in situ* neutron powder diffraction data measured in air at 394 °C and 1260 °C. The LSCF6482 was trigonal $R\bar{3}c$ at 394 °C, and cubic $Pm\bar{3}m$ at 1260 °C. The refined occupancies of O atom were 1.0 and 0.904(6) at 394 °C and 1260 °C, respectively. At 1260 °C the oxygen deficiency δ in $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was estimated to be $\delta=0.288(15)$, indicating an average valence of +2.8 for the B-site $Co_{0.8}Fe_{0.2}$ cations. Refined anisotropic atomic displacement parameters and nuclear density mapping reveal that the oxide ions in LSCF6482 exhibit a large thermal motion perpendicular to the (Co,Fe)–O bond at 1260 °C, comparing at 394 °C. A curved path for oxide-ion migration between adjacent anion sites in LSCF6482 was suggested at 1260 °C, although it was not observed as a connected density in the experimental mapping.

Keywords: Crystal structure; Electrode material; Rietveld analysis; Neutron powder diffraction; Lanthanum cobaltite; Maximum-entropy method; Nuclear density distribution

1. Introduction

Perovskite-structured oxides that exhibit high ionic conductivity have attracted considerable attention due to their various applications in solid oxide fuel cells (SOFCs), batteries, catalysts and oxygen sensors. The development of improved oxide-ion and mixed conductors requires a better understanding of the diffusion paths and structural disorder of mobile oxide ions at high temperatures at which the materials work efficiently [1,2]. The Sr and Fe co-doped lanthanum cobaltites, $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ have perovskite-type structures and are ionic-electronic mixed conductors [3–12]. The $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ compounds are possible electrode materials for the doped lanthanum-gallate and ceria-based electrolytes in SOFCs. Existing phases, electrical properties and chemical diffusion of the composition $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF6482) have been studied extensively. The crystal structure of trigonal $R\bar{3}c$ $La_{1-x}Sr_xCoO_{3-\delta}$ has been the subject of a number of previous investigations [13–21]. However the crystal structure of LSCF6482 has not been known well at high temperatures. The purpose of the present study is to investigate the crystal structure and structural disorder of the cubic $Pm\bar{3}m$ perovskite-type LSCF6482 at 1260 °C. We have chosen this temperature, because the structural disorder is more prominent at higher temperatures and the specimen was prepared by sintering at this temperature. For comparison, we also investigate the crystal structure of $R\bar{3}c$ perovskite-type LSCF6482 at 394 °C.

2. Experimental

$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ specimens were prepared through solid-state reactions by the Mitsubishi Materials Co. Neutron powder diffraction data were collected in air using HERMES, a diffractometer with a 150-multi-detector system [22] at 394 °C and at 1260 °C. The HERMES diffractometer is located at the

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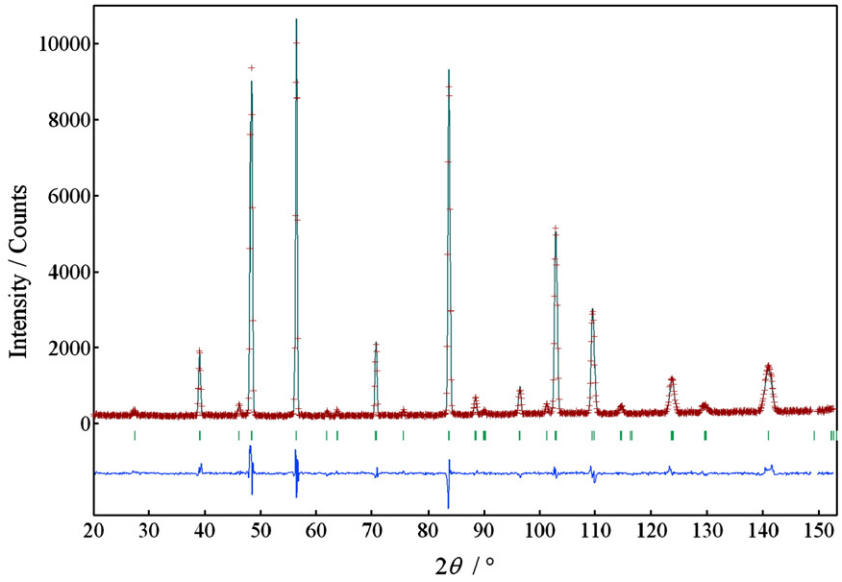

Fig. 1. Rietveld fitting results for the neutron-diffraction data of trigonal $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ measured at 394 °C. The red plus symbols and the green line denote the observed and calculated intensities, respectively. Short verticals indicate the positions of possible Bragg reflections of trigonal $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$. The difference between the observed and calculated profiles is plotted at the bottom. The wavelength of the incident neutrons is 1.8207 Å.

T1-3 port of the JRR-3M research reactor of the Japan Atomic Energy Agency at Tokai, Japan [22]. The powder patterns were measured in the range from $2\theta = 5°$ to 155°. The wavelength of the incident neutrons was 1.8207 Å. The sample temperature was kept constant during the data collection at high temperatures using a furnace with $MoSi_2$ heaters [23].

The diffraction data were analyzed by a combination of Rietveld analysis, the maximum-entropy method (MEM) and MEM-based pattern fitting (MPF) [1,2,24]. Computer programs RIETAN-2000 [25], PRIMA [24] and VESTA [26] were utilized for the Rietveld and MPF analyses, MEM calculations and visualization of crystal structure and the nuclear-density distribution, respectively. The coherent scattering lengths (b_c) adopted for Rietveld refinement were 8.24 fm for La, 7.02 fm for Sr, 2.49 fm for Co, 9.45 fm for Fe and 5.803 fm for O. Thermogravimetry coupled with differential thermal analysis (TG-DTA-2020SA-TK18, Bruker AXS) was performed in air with the heating rate of 10 °C/min to investigate the weight loss of LSCF6482.

3. Results and discussion

Neutron-diffraction data for LSCF6482 at 394 °C indicated that the specimen consisted of a single phase of the trigonal $R\bar{3}c$ LSCF6482 (Fig. 1). All the peaks in the neutron diffraction pattern of LSCF6482 at 1260 °C were indexed by the cubic

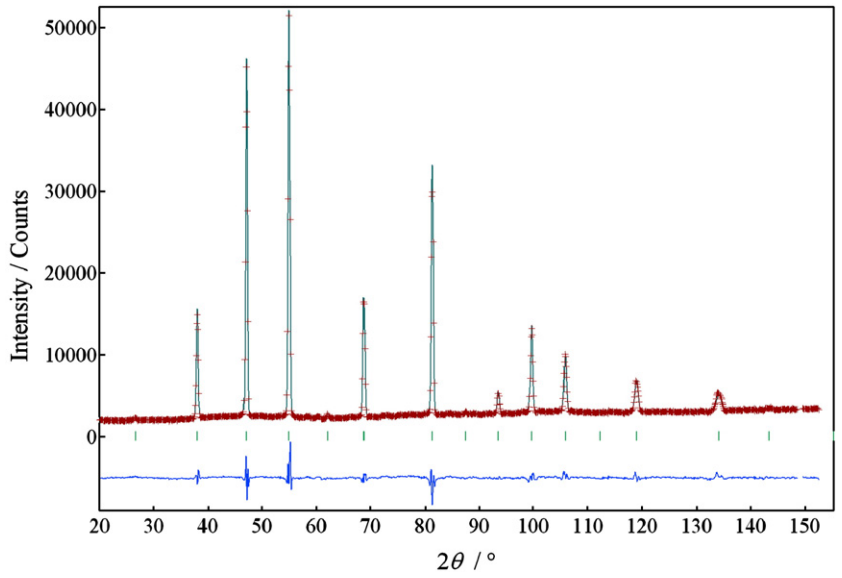

Fig. 2. Rietveld fitting results for the neutron-diffraction data of cubic $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ measured at 1260 °C. The red plus symbols and the green line denote the observed and calculated intensities, respectively. Short verticals indicate the positions of possible Bragg reflections of cubic $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$. The difference between the observed and calculated profiles is plotted at the bottom. The wavelength of the incident neutrons is 1.8207 Å.