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Ceramics International 41 (2015) 2852–2862

CERAMICS INTERNATIONAL

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XRD and *in-situ* XAFS investigation on high-temperature thermal expansion of $La_{0.6}Sr_{0.4}Ti_xFe_{1-x}O_{3-\delta}$ $(0 \leq x \leq 0.3)$

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Received 8 August 2014; received in revised form 14 August 2014; accepted 17 October 2014
Available online 27 October 2014

Abstract

High temperature stability of perovskite oxide is important for the application of cathode materials in solid oxide fuel cells (SOFCs) and oxygen-permeable conductors. The thermal expansion behavior of perovskite oxides with the formula, $La_{0.6}Sr_{0.4}Ti_xFe_{1-x}O_{3-\delta}$ (LSTF, $x=0$, 0.1, 0.2, and 0.3) were measured in both air and a H_2 atmospheres and were investigated using thermogravimetry (TG), powder X-ray diffractometry, and X-ray absorption spectroscopy. The additional expansion caused by reduction of transition metals in the H_2 atmosphere was observed over 200 °C and the rate of increase in expansion became slow above 400 °C for all compositions. While LSF ($x=0$) showed large thermal expansion ratio, $\Delta L/L$, of 1.089% in the H_2 atmosphere at 400 °C, that of LSTF ($x=0.3$) was reduced to 0.548%. This difference of $\Delta L/L$ corresponded to the decrease of the oxygen anion non-stoichiometry, δ, estimated by TG analysis, from 0.20 to 0.07 with $x=0$, and 0.3, respectively. The Fe cation valence of LSTF was also studied by *in-situ* X-ray absorption near edge structure in both air and a H_2 atmosphere over the range of 25 to 800 °C, and compared to the Fe cation valances estimated from the values of δ. The valence states Fe and Ti in LSTF and the differences in the reducing kinetics for Ti substitution are discussed.

Keywords: C. Thermal expansion; $La_{0.6}Sr_{0.4}Ti_xFe_{1-x}O_{3-\delta}$; XAFS; Oxygen vacancies

1. Introduction

Perovskite oxide systems have been studied extensively for the use as high-temperature oxide electrodes for solid oxide fuel cells (SOFCs) and oxygen-permeable conductors. Their advantage stems from high degree of control of ion transport, achieved by substituting a La site (A site, larger cation in 12-fold coordination) or a transition metal (M) site (B site 6-fold coordination) of ABO_3 lattice. The La or Sr ions are chosen to obtain the appropriate ionic radii for the easy construction of the lattice. In addition, the mixed charge valences of the transition metals, especially Co, Ti, Fe, and Mn, are facilitate formation of oxygen defects [1–3].

However, in real applications, the thermal expansion behavior of perovskite oxide materials could cause a serious problem. This was illustrated by Hirano et al. [4], who found that with increasing temperature the expansion rate of $LaMnO_3$ became nonlinear or even negative. Furthermore, these materials undergo significant expansion in a reducing atmosphere, resulting in cracks, and consequently poor durability in cyclic operation.

Pei et al. [5] reported that these failures result from large volumetric changes in the crystal lattice. Cracks are caused by strain on the tubes, which are attributable to differences in the amount of thermal expansion at different oxygen partial pressures, (P_{O_2}).

$La_{1-x}Sr_xTi_{1-y}Fe_yO_{3-\delta}$ (LSTF) materials may offer a solution to the problem, as evidenced by the promising results obtained in

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http://dx.doi.org/10.1016/j.ceramint.2014.10.107
0272-8842/

recent work on LSTFs in practical applications [6,7]. For example, in our previous study [8] of $La_{0.6}Sr_{0.4}Ti_{0.1}Fe_{0.9}O_{3-\delta}$ has carried out dilatometry and *in-situ* powder X-ray diffractometry were employed at high temperature (1000 °C) and at P_{O_2} level of 0.21 and 1×10^{-20} atm to understand the chemical and crystallographic stability at the micro-level and the structural stability at the macro-level. Although the thermal expansion was relatively low, it was larger at the lower oxygen partial pressure. The change in the crystal lattice parameters analyzed by XRD Rietveld refinement revealed that the crystal lattice volume increased with an increase in temperature and a decrease in-P_{O_2}, suggesting that the introduction of an oxygen vacancy could promote the repulsion between Fe ions [8]. The relationship between the thermal expansion coefficients and the non-stoichiometry of LSTF samples in low-P_{O_2} environments was also discussed by Park and Jacobson [9].

The ability to withstand high temperature and low-P_{O_2}, levels is critical in ion transport membranes. Moreover, the choice of the transition metal ion and the relative amount seem to have an important effect on the durability in cyclic operation at high temperatures, so that an understanding of the bonding characteristics of the transition metal to oxygen (M–O) is essential in the design of these oxide systems. Synchrotron X-ray absorption spectroscopy (XAS) is a very useful tool to investigate the local structural and electron properties of transition metals in perovskite oxides. This technique offers the possibility for *in-situ* measurement. However, there were few reports for $La_{0.6}Sr_{0.4}Ti_xFe_{1-x}O_{3-\delta}$ series using XAS.

In this study, the effect of Ti content on thermal expansion behavior of $La_{0.6}Sr_{0.4}Ti_xFe_{1-x}O_{3-\delta}$ (x=0, 0.1, 0.2, and 0.3) was investigated by dilatometry in both air and a strong reducing atmosphere, H_2 1 atm. The oxygen non-stoichiometry, δ, and the

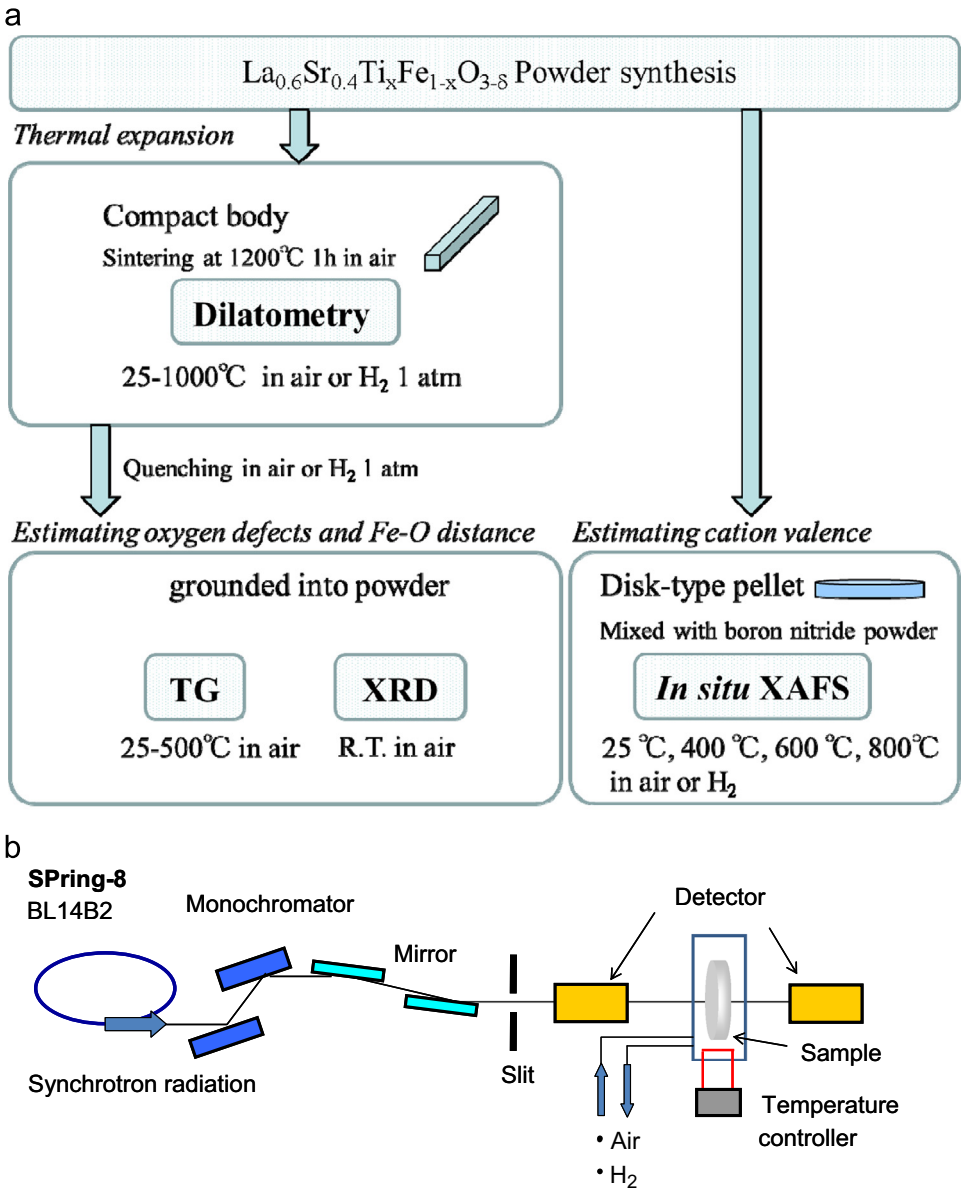

Fig. 1. Experimental procedure of (a) dilatometry, TG analysis, and (b) experimental set up for *in-situ* XAFS.