

Anelastic properties of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ at high temperatures

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Abstract

The dynamic amplitude dependence of the Young's modulus and the internal friction of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF6428) at high temperatures were evaluated by resonance measurements. At the temperatures from room temperature to 473 K and above 1073 K, the Young's modulus of LSCF6428 was independent of the dynamic amplitude, while it gradually decreased with increasing the dynamic amplitude in the temperature range from 573 to 973 K. The above dependence was successfully explained by considering the ferroelastic behavior of LSCF6428.

1. Introduction

Mechanical failures in the components of solid oxide fuel cells (SOFCs) are one of the serious issues to be solved for their full scale commercialization ^[1]. In order to successfully suppress the mechanical failures, mechanical properties of the component materials should be precisely understood especially under operating conditions.

$\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) is widely used as a cathode for SOFCs because of its high mixed electronic-ionic conductivity and fast oxygen surface exchange ^[2]. Although its electrical properties, oxygen nonstoichiometry and lattice size have been intensively

studied ^[3-6], there are few studies about the mechanical properties of LSCF especially under SOFC operating conditions. For the above background, our group investigated the elastic modulus of LSCF at high temperatures under controlled atmospheres ^[7]. It was found that the elastic modulus of LSCF significantly decreases with increasing temperature in the temperature range where LSCF has a rhombohedral phase ^[7]. It is also known that the internal friction of $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ showed comparatively larger values and had several peaks at those temperatures ^[8]. From these results, it is suggested that the rhombohedral LSCF is not ideally elastic and the decrease in the elastic modulus of LSCF is related with nonelastic effects. Furthermore, the rhombohedral LSCF is known to show ferroelastic behavior ^[9-11]. The rhombohedral crystal structure of LSCF is formed by the compression of the ideal cubic structure along the $\langle 111 \rangle$ directions of a cubic unit cell. Therefore, the rhombohedral crystal can have 4 kinds of domains which have a rhombohedral distortion along with $[111]$, $[\bar{1}\bar{1}\bar{1}]$, $[\bar{1}11]$ and $[1\bar{1}\bar{1}]$ directions ^[12, 13]. Some of domains are switched to one of the other domains when the stress applied to the rhombohedral LSCF is above a certain value, the critical stress. Such a domain switching leads to nonelastic deformation. Thus, it is expected that the rhombohedral LSCF is nonelastic and the apparent elastic modulus of rhombohedral LSCF depends on the applied stress when the applied stress is above the

critical stress. In this study, in order to understand the effect of the ferroelasticity on the elastic modulus of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF6428), the Young's modulus of LSCF6428 was investigated as a function of the dynamic amplitude by using the resonance method.

2. Experimental

A detailed procedure for the sample preparation is described elsewhere ^[7]. The resonance measurements were performed by using an elastic modulus meter (EGII-HT, Nihon Technoplus Co., Ltd.) operating in cantilever bending geometry. One end of a rectangular-shaped sample is rigidly fixed. A flexural oscillation is applied to another end of the sample by an electromagnetic actuator. The force applied to the sample was controlled by changing output voltage of the electromagnetic actuator. The resonance frequency of the sample was detected by an eddy current sensor. The eddy current sensor was calibrated by using a spectral-interference laser displacement meter (SI-F10, Keyence Corporation) to attain the absolute value of the dynamic amplitude of the

resonance oscillation. The Young's modulus, E , was evaluated from the resonance frequency and the sample dimension according to the following relation;

$$E = \frac{4\pi^2 L^4}{\alpha^2} \cdot \frac{\rho S}{I} \cdot f_f^2 \quad (1)$$

where f_f , L , α , ρ , S , I are the flexural resonance frequency, the length of the sample, a constant given by the boundary conditions, the density of the sample, the cross-sectional area of the sample, the second moment of the area, respectively. The internal friction, Q^{-1} , was calculated from the natural decay of the oscillation in every cycle, as follows,

$$Q^{-1} = \frac{1}{\pi(n-m)} \cdot \ln \frac{V_m}{V_n} \quad (2)$$

where V_m , V_n , are the m , n th dynamic amplitude of the oscillation, respectively. The internal friction reflects the energy dissipation in the sample.

The dynamic amplitude dependence of Young's modulus, E , and internal friction, Q^{-1} , of LSCF6428 was studied. The $P(\text{O}_2)$ around the sample was controlled to be 1×10^{-1} bar by flowing mixture gases of O_2 and Ar, and monitored by an yttria-stabilized zirconia oxygen sensor. The measurements were repeated until the measured values of the Young's modulus and the internal friction became constant at each temperature, *i.e.*, until the sample equilibrated with the surrounding atmosphere.

3. Results and Discussion

Fig. 1(a) shows the Young's modulus of LSCF6428 as a function of the dynamic amplitude at each temperature. At temperatures below 473 K and above 1073 K, the Young's modulus of LSCF6428 was independent of the dynamic amplitude, while it gradually decreased with increasing the dynamic amplitude in the temperature range from 573 to 973 K. Fig. 1(b) shows the dynamic amplitude dependence of the internal friction of LSCF6428. The internal friction was constant below 473 K and above 1073 K but it gradually increased with increasing the dynamic amplitude between 573 and 973 K.

The stress-strain relationship of the rhombohedral LSCF6428 is reported to be a typical ferroelastic one ^[10]. Our previous study showed that the critical stress of the rhombohedral LSCF6428 monotonically decreased with increasing temperature ^[11]. At room temperature, it is about 70 MPa. It becomes less than 10MPa above 473 K. On the other hand, the stress applied to the sample during the resonance measurements is estimated to be less than 10 MPa if the sample is regarded as an elastic body. In practice, the sample is not elastic. Thus the stress applied during the resonance measurement is considered to be much smaller than 10 MPa.

Taking the above into account, the dynamic amplitude dependence of the Young's modulus and the internal friction can be explained as follows. The reason why the Young's modulus at room temperature and 473 K was independent of the dynamic amplitude is the stress applied to the sample during the resonance measurement was below the critical stress and the sample deformed elastically. Therefore, the Young's modulus was not dependent on the dynamic amplitude. As mentioned above, the critical stress decreases with increasing temperature. Thus, in the temperature range between 573 and 973 K, the domain switching can occur even if the applied stress is small. When the dynamic amplitude increases, the stress applied to the sample is considered to also increase. And the increase in the applied stress is considered to lead to the increase in the number of domain switching, which releases the applied stress. Therefore, the Young's modulus is considered to decrease with increasing the dynamic amplitude. Above 1073 K, LSCF6428 have a cubic crystal structure ^[14]. The cubic LSCF6428 can have only 1 kind of domain and no domain switching can occur when the stress is applied. Thus the cubic LSCF6428 deforms elastically and the Young's modulus was independent of the dynamic amplitude.

When the applied stress is below the critical stress or LSCF6428 is cubic, the sample deforms elastically and the energy dissipation is considered to be small. This is

likely to be the reason for the small value of the internal friction. On the other hand, in the temperature range between 573 and 973 K, the domain switching is considered to occur even if the applied stress is small. Therefore, it is considered that the internal friction has a large value since the energy dissipation is significant due to the domain switching. In addition, the energy dissipation is considered to increase with increasing the number of the domain switching. This leads to increase of the internal friction with increasing the dynamic amplitude.

As described above, the dynamic amplitude dependence of the Young's modulus and the internal friction can be explained by considering the ferroelastic behavior of LSCF6428. Therefore, it is considered that the Young's modulus of rhombohedral LSCF6428 is affected by the ferroelasticity.

4. Conclusions

The dynamic amplitude dependence of the Young's modulus and the internal friction was evaluated. At room temperature, 473 K and above 1073 K, the Young's modulus of LSCF6428 was independent of the dynamic amplitude, while it gradually decreased with increasing the dynamic amplitude in the temperature range from 573 to

973 K. The internal friction was constant at room temperature, 473 K and above 1073 K but it gradually increased with increasing the dynamic amplitude between 573 and 973 K. The above dependence can be explained by the ferroelastic behavior of LSCF6428. Therefore, it is possible that the Young's modulus of the rhombohedral LSCF6428 was affected by the ferroelasticity. Considering the above, the decrease in the Young's modulus observed at low temperatures may be associated with the ferroelasticity. These results suggest that the ferroelasticity affects the stress distribution in SOFCs especially during starting up/shutting down of SOFCs. Therefore, it is important to take the effects of the ferroelasticity into account when one uses the data of the Young's modulus to design cell/stacks of SOFCs or determine the operational margin.

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Figure captions;

Fig.1. Dynamic amplitude dependence of (a) the Young's modulus and (b) the internal friction of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF6428) in the temperature range between room temperature and 1173 K under $P(\text{O}_2)$ of 1.0×10^{-1} bar measured by using the resonance method.

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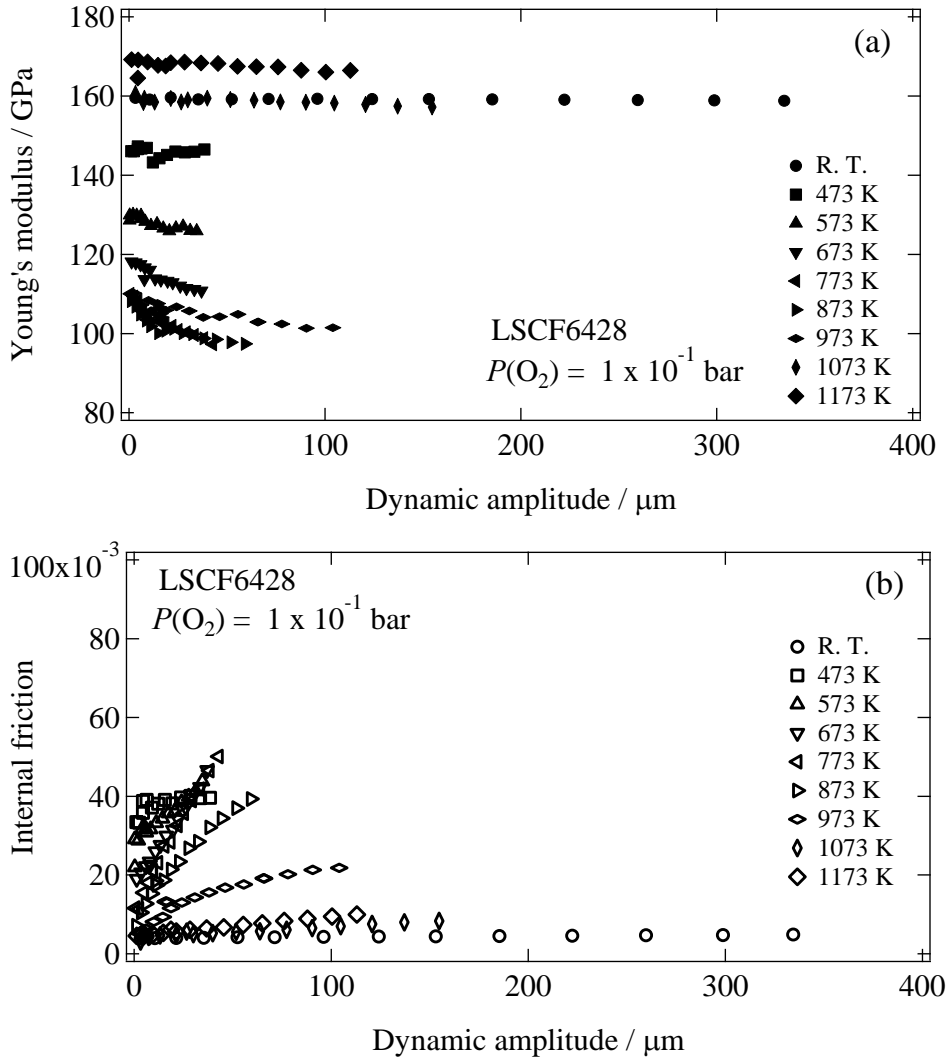


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