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Ferroelastic deformation of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ under uniaxial compressive loading

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Abstract

The mechanical deformation of lanthanum strontium cobalt ferrite under uniaxial compression was investigated at various temperatures. The material revealed a rather complex mechanical behaviour related to its ferroelasticity and stress–strain curves obtained in the 1st and 2nd loading cycles were completely different. A distinctive ferroelastic creep was observed at 293 K whilst typical ferroelastic stress–strain curves were obtained in the temperature range from 473 K to 873 K. At 1073 K, high-temperature creep deformation was observed instead of the ferroelastic deformation. The apparent Young's modulus was evaluated in various ways; the modulus determined from the last unloading curve ranged between 85 and 120 GPa. The obtained critical stress monotonically decreases from about 80 MPa to zero with increasing temperature, corresponding to the behaviour of the remnant strain. The presented results indicate that the importance of an appropriate consideration of the loading history in the practical application of these ferroelastic materials.

Keywords: Ferroelasticity; Perovskites; Ceramic Membrane; Mechanical behaviour

1. Introduction

Lanthanum cobaltite perovskite (LCO) has attracted significant attention due to its potential for the use as cathode for solid oxide fuel cells (SOFCs)[1] and oxygen separation membrane for oxyfuel process.[2] Materials to be used as oxygen separation membrane are required to be a very good mixed oxygen-ion and electron conductor (MIEC). A number of studies have been devoted to an improvement of ionic conductivity or oxygen flux by doping different ions on A or B-site of LCO.[2–6] La–Sr–Co–Fe–O (LSCF), especially the composition $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, has emerged as one of most promising materials for oxygen separation membranes as well as SOFC cathodes and has hence been studied intensively.[3,6–8]

Despite numerous studies on electrochemical properties, there are few investigations on mechanical properties.[9–15] The mechanical properties such as elastic modulus and fracture properties have been investigated by means of resonance method and bending test. It has been reported that these mechanical characteristics of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ gradually decrease in air with temperature from room temperature to about 973 K and then show a significant increase between 973 K and 1073 K due to a rhombohedral–cubic phase transition.[12,14] Aiming at clarifying the application limits, creep at high temperature has been also studied.[14]

On the other hand, the lanthanum cobaltite variants are known to display ferroelastic behaviour,[9,11,15–18] which is a ferroic effect observed in the mechanical behaviour.[19] In fact, ferroelastic domain switching has been observed in situ under the application of compressive loads at room temperature.[15,16] A reported non-linear behaviours as well as hysteresis in stress–strain curves especially at low temperatures have been attributed to the ferroelasticity,[9,11,18] although an exact mathematical and physical analysis of the ferroelastic effects was not possible since some studies have used bending tests for the characterisation instead of tensile or compressive test and also the applied stress was not high enough to observe an entire response, being limited by the fracture strength of the material. Furthermore, creep effects due to the ferroelasticity, i.e., ferroelastic creep, have been reported to occur for some lanthanum

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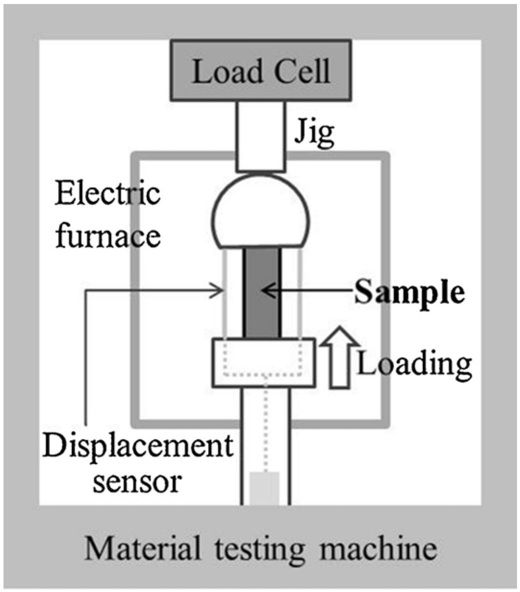

Fig. 1. Experimental setup for compressive test at elevated temperature.

cobaltite variants under uniaxial compression,[17] which are expected to lead to significant specimen deformation even at room temperature.

Resonance methods are not expected to be sensitive to the ferroelastic materials' response. Also, considering the reported non-linear stress–strain curves and the ferroelastic creep, it would not be possible to describe the macroscopic elastic behaviour of the considered lanthanum cobaltites by a single Young's modulus.

The present study presents the ferroelastic behaviour of LSCF under uniaxial compressive stress at various temperatures.

2. Experimental procedure

$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ material prepared at IEK-1, Jülich Forschungszentrum GmbH,[6] was investigated in the present experiment. The specimens, which were pressed and sintered at 1473 K for 3 h, were rectangular bars with a size of about 3 mm × 3 mm × 13 mm, a density of 5.81 g/cm (i.e., a relative density of 94%), and an average grain size of ±0.6 μm.[12] Fig. 1 schematically illustrates the experimental setup. The prepared sample was placed on an alumina ceramic table between the loading rods of a mechanical testing machine (1362, Instron) that was equipped with an electrical furnace. A semi-spherical alumina ceramics was used for an alignment and load transfer to the specimen, and a compressive preload of 3 N (i.e. a stress of ∼0.3 MPa) was applied for specimen fixation. For elevated temperatures a heating rate of 8 K/min was used, followed by a dwell period of more than 1 h before testing. The temperature was checked with a thermocouple which was located close to the specimen. In the mechanical test, the compressive load was raised to 903 N (i.e. 100 MPa) with a loading rate of 100 N/min. After some holding period at 903 N, which were normally more than 1 min, the load was decreased to 3 N using the same rate. Whilst the loading and unloading cycle was repeated twice or three times, the applied load and the deformation of the sample were measured by the load cell (3173-101, Lebow; maximum load of 1000 N) and the displacement sensor as illustrated in Fig. 1, which were both recorded using a automatised software to obtain stress–strain curves. The testing temperatures ranged from 293 K (room temperature) to 1073 K. After the tests at each temperature, i.e., after the 2nd or 3rd cycle, the specimen was heated up at 1273 K at the same rate of 8 K/min and annealed for 1 h at 1273 K and then cooled down to room temperature before next test at a particular temperature was carried out. The deformation of the displacement sensor was separately measured and subtracted from the measured displacement (compliance correction). The determined displacement has thereby an uncertainty of less than 1 μm for the short period typically representative for loading or unloading process but it increases to ±1–2 μm (strain of 0.008–0.015%) during the whole measurement period at each temperature.

It would be worth mentioning that the material cooled down from the annealing at 1273 K to room temperature with the rate of 8 K/min is known to be not completely equilibrated in rhombohedral phase but contains about 23% of cubic phase[11]; however, the material during each test can be considered to be in quasi-/equilibrium at least macroscopically since the measured stress and strain were confirmed to be completely stable before starting test at each temperature.

3. Results

Fig. 2 shows the stress–strain curves measured at each temperature, where the stress and the strain were simply calculated using the initial geometry measured at room temperature without considering either thermal and chemical expansions or non-recoverable deformation during the test. The very initial loading curve obtained at 293 K is labelled as "initial" in Fig. 2(a). After this very initial test, which may contain complex factors such as initial contact effect, the material was annealed at 1273 K and cooled down as described in the previous section, and then the 1st loading curve was obtained. It should be noted that, except for this very initial test, the 1st loading curve was always identical if the test was conducted following the annealing process at 1273 K after any loading/unloading cycle. Similarly, 1st loading curve at each elevated temperature obtained after the annealing process at 1273 K was always identical.

During the 1st loading to 100 MPa at 293 K shown in Fig. 2(a), the sample was strongly deformed and the stress–strain curve was visibly non-linear. After reaching the constant stress of 100 MPa, the strain gradually increased. The 1st unloading curve reveals a slight non-linearity. The stress–strain curves of the 2nd cycle conducted immediately after the 1st unloading shows a clear hysteresis; the curve of the 3rd cycle agrees with this cycle. The slope of the 1st unloading is steeper than the one of the 1st loading, whereas the slopes of the 2nd and 3rd cycles are generally steeper than those of the 1st cycle.

In addition, experiments with several different patterns of the loading/unloading cycle were carried out at 293 K. In case that the stress was immediately released (unloaded) after reaching