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Direct observation of ferroelastic domain effects in LSCF perovskites

B.X. Huang, R.W. Steinbrech, J. Malzbender *

Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, IEK-2, 52425 Jülich, Germany

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ABSTRACT

Polycrystalline $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) shows in bending tests a non-linear deformation behavior at room temperature and a linear one at elevated temperatures (≥800 °C). The non-linearity originates from ferroelastic domain switching in grains with rhombohedral symmetry. Ferroelastic domains cannot form in the cubic structure that exists at elevated temperatures. The critical stress of domain switching determined on the basis of bending tests from the onset of non-linear load-deflection behavior decreases from ~30 MPa at room temperature to ~5 MPa at 700 °C. Electron microscopic methods have been used to gain insight in formation, switching effects and stability of the domains under mechanical and thermal loading conditions. Direct SEM observations of the same surface area before and after compressive loading are used to verify the influence of the stress on the domain switching. Complementary TEM in-situ observations that verified the disappearance of domains at higher temperatures are discussed in terms of phase stability and oxygen partial pressure.

1. Introduction

LSCF is a promising material for the application as cathode in solid oxide fuel cells and oxygen transport ceramics in membrane based separation units [1,2]. Both applications require mixed ionic-electronic conductivity [3–5]. Especially the transport related functional properties of perovskites of the type ABO_3 with rare earth metal ions on A sites and transition metal ions in B sites have been extensively investigated [3]. These perovskites have typically a cubic phase at the envisaged operation temperatures [6]. However, structural changes to a lower symmetry at intermediate temperatures have been reported [7] and along with these transitions ferroelastic domains might form to minimize the strain energy. In LSCF such domains have been observed in grains of rhombohedral symmetry, whereas the high temperature stable cubic symmetry doesn't permit the formation of domains [8]. Moreover, the otherwise brittle LSCF perovskite displays inelastic deformation behavior during bending tests, an effect attributed to domain switching as verified for other ferroelastic materials [9].

In general, different kinds of domain formation and switching can be induced by mechanical stresses, electrical or magnetic fields [10,11]. As a result of competitive nucleation grains might contain more than a single domain array and frequently domains in energetically equivalent crystallographic orientations occur. Also growth of new domains by movement of domain walls into already existing domains has been observed [11]. The domains may have either 90° or 180° orientation with respect to initial direction [12–14].

Sintered polycrystalline ceramics are usually composed of randomly oriented grains. Since there will be a preferred orientation with respect to the lattice, different surface traces of domains can be observed, which makes the determination of orientations difficult. Also note that the domain switching in a grain could be influenced by porosity surrounding the grains and neighboring grains with different crystallographic orientation [15].

Analysis and simulation of stress states is normally based on the macroscopic mechanical properties of a material. Stress states have to be compared to the strength; crack growth is usually analyzed based on the materials toughness. Basic parameters that will be used in an assessment of the materials stability require also an understanding of the limits of their use. LSCF shows non-linear mechanical behavior at low temperatures, where the highest stresses due to thermal expansion mismatches will exist in a complex membrane assembly. Hence, besides the question what parameters are representative for a particular application related condition, it is especially important to understand the limits and origin of this non-linear behavior. Strain energy is dissipated by the domain effects, hence domain formation can affect the apparent strength and might also influence crack propagation and therefore the apparent fracture toughness of a material [13,16,17]. An understanding of the domain switching mechanisms under external stresses (or electrical fields) is not only of scientific but also technological importance [18].

Direct observation is a promising means to gain insight into the micro-structural aspects of domain stability and switching. In recent years the influence of electrical fields [19] on switching of ferroelectric domains has been investigated in great detail [12,20,21], whereas ferroelastic effects have received less attention [16,22,23]. In fact, direct observation of domain switching under mechanical loading was reported only for $LaCoO_3$ [24].

The domains in LSCF form spontaneously due to the cubic - rhombohedral transition on cooling from 800–700 °C [8]. The

* Corresponding author. Tel.: +49 246 161 6964; fax: +49 246 161 3699.
E-mail address: j.malzbender@fz-juelich.de (J. Malzbender).

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gradual distortion of the rhombohedral from the cubic symmetry which increases with deviation from this transition regime [25,26] will generate additional internal stresses that might be enhanced by the different grain orientations in the polycrystalline material. Local stresses can partly be relaxed in the rhombohedral grains by domain formation.

The present work demonstrates aspects of the ferroelastic behavior in LSCF for a polycrystalline material with all grains in rhombohedral symmetry. The micro-structural domain mechanisms are monitored by electron microscopy. The influence of mechanical loads and temperature, both important for the application of this perovskite are addressed. In particular load–displacement behavior and critical stresses were assessed on the basis of ring-on-ring bending tests, whereas the domain switching and observation was characterized only at room temperature in a compressive loading mode with associated SEM imaging.

2. Experiments

Polycrystalline LSCF was produced by Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1), Forschungszentrum Jülich GmbH. The material was prepared from powders, which were synthesized by a spray-drying technique using aqueous solutions of appropriate quantities of nitrate salts [27]. The powders were uni-axially pressed to a disc-shaped geometry with a pressure of 120 MPa and subsequently sintered at 1200 °C for 3 h. Heating and cooling rate were 5 K/min and 0.5 K/min, respectively. Due to the slow cooling rate all grains had undergone the transition from cubic to rhombohedral symmetry. Thus pronounced domain formation and macroscopic ferroelasticity was expected [8]. The Archimedes density of the as-received samples was determined to be 5.81 g/cm^3 with porosity of 6 %. The grain size was determined from SEM pictures of the polished surface with aid of the software ANALYIS in terms of the equivalent circular diameter yielding an average value of 0.6 ± 0.2 μm.

The effect of domain switching on the macroscopic ferroelastic deformation behavior was characterized by ring-on-ring bending tests [28,29] of as-received LSCF discs (20 mm diameter, 1 mm thickness). Macroscopically, the energy dissipation associated with the domain switching causes inelastic deformation behavior. However, the applied stress has to exceed a critical level to induce the domain switching. The transition from linear to non-linear behavior in the loading curves can be defined as a criterion where domain switching starts. Respective stress values have been determined from the kink of the load–displacement curves of specimens tested at particular temperatures between RT and 700 °C. The average stress was used as a characteristic for the onset of ferroelastic behavior.

Some of the as-received discs were further machined into quadratic platelets (8 mm × 8 mm × 1 mm) and polished on one of the 8 mm × 8 mm surfaces for observation in a scanning electron microscope (SEM, LEO1530, Zeiss, Germany). After initial characterization a uni-axial compressive load was applied on two opposite 8 mm × 1 mm side faces of the specimens. A stress of 60 MPa could be achieved in a miniaturized testing device typically used for mechanical in-situ experiments in SEMs (Kammrath & Weiss GmbH). The changes in domain appearance and orientation (switching) were documented by SEM micrographs comparing domain features for particular grains before and after loading. In a second compressive testing step the platelets were deformed with the same maximum stress, but perpendicular to the initial loading direction. The changes in domain appearance and orientation (switching) were again documented by SEM micrographs and compared to the observations after the first loading.

Stability of LSCF domains as a function of temperature was monitored up to 700 °C by in-situ observation in a transmission electron microscope (TEM, Philips CM200) that was equipped with a heating stage. The TEM foils were prepared by a focused ion beam technique (FIB, LEO1540, Zeiss).

3. Results and discussion

Macroscopically, the ferroelastic behavior of polycrystalline LSCF with rhombohedral symmetry is reflected in non-linear load–displacement curves that were characterized here using ring-on-ring bending tests [8] (see Fig. 1(a)). The change from linear to non-linear behavior, characterized by an inflection point is assumed to indicate the integral onset of domain switching and hence a critical stress/strain. However, the critical stress of domain switching in a single crystal might be different from the averaged value for the same material in the polycrystalline form due to constraint by surrounding grains and porosity effects. Nevertheless, the temperature dependence of the determined mean critical stress is illustrated in Fig. 1(b). The values decrease from 30 MPa at RT 5 MPa at 700 °C to, which is attributed to thermal activation of dislocation sliding. Also a higher internal stress will be generated as the crystals deviate from the structure of the cubic symmetry, which would presumably lead to a higher driving force for switching at lower temperatures. A similar macromechanical behavior was reported by Christopher et al. for $LaAlO_3$ and $PrAlO_3$ [25]. In fact, a non-linear stress–strain behavior has also been reported for $La_{0.5}Sr_{0.5}Co_{0.5}Fe_{0.5}O_{3-d}$ using a similar 4-point bending test, yielding a room temperature critical stress of 80 MPa [30]. Differences in value might be related to grain size differences or different material preparation history. Although it would be interesting to determine the entire strain–stress curves of the material, this was not possible using the ring-on-ring test due to fracture at higher loads.

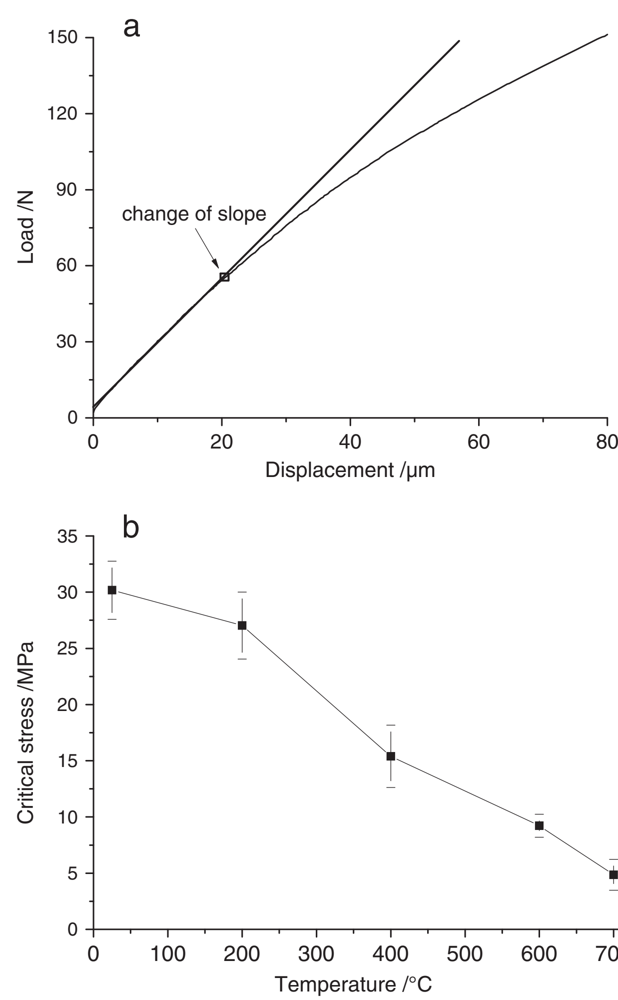

Fig. 1. Ferroelastic behavior of polycrystalline LSCF with rhombohedral submicron grains. (a) Non-linear load–displacement curve in ring-on-ring bending test at RT. Deviation from linearity reflects the onset of domain switching. (b) Temperature dependence of critical domain switching stress derived from load–displacement curves.