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Anomalies in the thermomechanical behavior of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ ceramic oxygen conductive membranes at intermediate temperatures

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The thermomechanical properties of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) were measured using ring-on-ring tests and depth-sensitive microindentation. The cubic BSCF material exhibits an anomaly in mechanical properties between 200 and 400 °C. The observed anomaly is attributed to the transition of Co^{3+} spin states which is experimentally confirmed by susceptibility measurements. Furthermore, slip lines were observed around the impression when indentation tests were carried out above 260 °C. [DOI: 10.1063/1.3193657]

The variant $SrCo_{1-y}Fe_yO_{3-\delta}$ was one of the perovskites suggested as an oxygen transport membrane.[1–3] However, undesirable ordering of oxygen vacancies in $SrCo_{1-y}Fe_yO_{3-\delta}$ was found to reduce the oxygen flux. The partial replacement of Sr by Ba atoms is assumed to suppress this unfavorable ordering transition and thereby increases the phase stability. It also leads to a higher level of oxygen nonstoichiometry and thus increases the material permeability.[4–6] Hence, $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ is one of the most promising oxygen-permeable membrane materials.[1,4,7–9]

Oxygen stoichiometry, oxygen permeation properties, and the structural stability of BSCF have been investigated widely in recent years.[4,5,10] It has been demonstrated[4,10] that $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) retains cubic symmetry upon heating up to 1000 °C throughout an oxygen partial pressure (P_{O_2}) in the range of $10^{-5} < P_{O_2} < 10^{-1}$ atm. However, to date, little is known about the thermomechanical properties of BSCF.

In the present work fracture stress and the apparent elastic modulus, hereafter referred to as stiffness, were determined using ring-on-ring tests. In addition, the fracture toughness was derived from the length of the indentation cracks. The thermal expansion coefficient (TEC) was measured with dilatometry. The spin state was tested using magnetization measurements.

The disk-shaped BSCF samples were prepared from powders supplied by Treibacher Industries AG, Austria, which were uniaxially pressed with a pressure of 105 MPa and sintered at 1000 °C for 12 h with a heating rate of 5 K/min and subsequently cooled down with a rate of 0.5 K/min. The Archimedes density of the as-received samples was determined to be 5.37 g/cm^3 with a porosity of 4.5%. Assuming a spherical geometry, the average grain size of the equivalent diameter was 10 ± 4 μm.

The test conditions for the ring-on-ring bending experiments followed the ASTM standard C1499–05.[11] The fracture stress was derived from five experiments carried out at selected temperatures between room temperature (RT) and 800 °C. The calculation of stiffness and fracture stress from ring-on-ring tests followed an earlier report.[12] For the tests at elevated temperatures, a heating rate of 2 K/min was used, followed by a dwell time of 1 h before testing. The ring-on-ring tests were carried out with a universal mechanical testing machine (Instron1362). The loading rate was 100 N/min in all tests. The stiffness was determined from the linear part of loading curve in a stress range of 15–25 MPa.

The indentation fracture toughness was determined from the length of the indentation cracks [Fig. 2(a)].[13–15] Slip lines were detected after indentation testing at elevated temperatures using a CSM (Switzerland) system with an optical microscope and transmission electron microscope (TEM) (Philips CM200). The TEM specimens of the BSCF perovskites were prepared by focused ion beam (FIB) (LEO1540, Zeiss) cutting. The linear TEC was continuously measured using a differential dilatometer (Misura, Expert System Solutions S.r.l. Italia). Experiments with differential thermal analysis (DTA) and thermogravimetry (TG) (STA 449C Jupiter Netzsch) were carried out in air with a heating rate of 1 K/min. The magnetic characteristics and their temperature dependence were measured with a Quantum Design physical properties measurement system with heating, using a rate of 2 K/min stage to confirm the spin state of Co^{3+}.

In order to compare the thermomechanical results, the values of stiffness, fracture stress, and toughness at various temperatures are normalized with respect to the values of the as-received samples (Fig. 1). The RT values of BSCF are

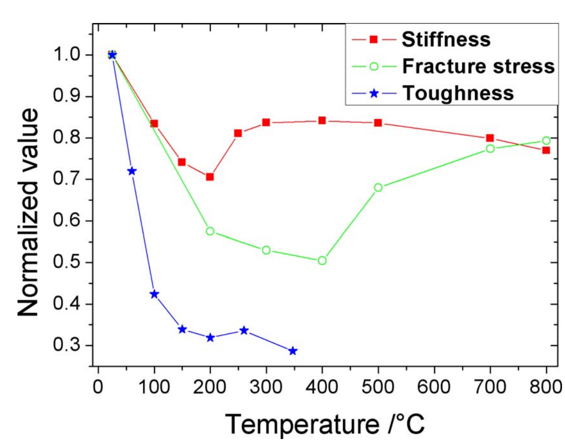

FIG. 1. (Color online) Thermomechanical properties of BSCF. Normalized values of the stiffness, fracture stress, and indentation fracture toughness are plotted (lines are guide to eyes).

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64 ± 3 GPa, 99 ± 10 MPa, and 1.0 ± 0.1 MPa $m^{0.5}$, for stiffness, fracture stress, and toughness, respectively.

Although the temperature variations in the fracture stress and toughness resemble the stiffness behavior of the material, and hence appear to be associated with similar effects, they are, however, even in the normalized plot of Fig. 1, not fully consistent. The stiffness decreases sharply (~29%) with increasing temperature to reach a minimum at 200 °C before increasing again till 300 °C. Above this temperature, the stiffness of BSCF behaves as expected for normal ceramics materials,[16] i.e., it decreases slightly with increasing temperature. Similar to the stiffness, the fracture stress decreases initially. However, the range of the minimum in the curve is much broader with the lowest value at ~400 °C.

The indentation fracture toughness of BSCF could only be determined for the initial temperature range due to the experimental limit in the maximum testing temperature. Since the fracture toughness should be proportional to the fracture stress,[16] the normalized curves of both parameters are expected to be identical. Although the curve shapes are similar, the toughness curve obviously deviates in amplitude from that of the fracture stress (Fig. 1). The increase in the fracture stress at higher temperatures (above 400 °C) is attributed to additional energy dissipation by plastic deformation [Fig. 2(a)].

A typical impression of an indentation obtained at ~300 °C is shown in Figs. 2(a) and 2(b). Contrary to the observations after RT indentation, elevated temperature testing reveals deformation traces in grains surrounding the impression. The deformation traces were identified as slip traces by TEM investigation [Fig. 2(c)].

It has been suggested that the association/dissociation reaction between point defects could cause mechanical anomalies in specific temperature ranges.[17–19] Indeed, a small enthalpy change was observed at about 240–250 °C with DTA, which appears to be an indication of an association/dissociation reaction. The proposed reaction is also considered to be accompanied by a volume change. The TEC of BSCF in Fig. 3 reveals a decrease with increasing temperature up to ~250 °C, and furthermore, a change from 450 to 530 °C. However, the pronounced volume change expected to take place as a result of the association/dissociation reaction is not observed in the TEC.

A stiffness anomaly, similar to the present BSCF results, was reported for $LaCoO_3$ (Refs. 20–22) and attributed to a spin transition of Co^{3+}. In an analogous argument the stiffness anomaly of BSCF at low temperatures might be attributed to a spin transition of Co^{3+} neglecting the contribution from Fe ions. The spin transition of Co^{3+} in $LaCoO_3$ has been studied extensively since the 1950s.[22–25] A low-spin Co^{3+} ($t_{2g}{}^6 e_g{}^0$, $S=0$) configuration can be thermally activated to a high-spin Co^{3+} ($t_{2g}{}^4 e_g{}^2$, S=2) state. The susceptibility (χ) of a paramagnetic material is described by the Curie–Weiss law,[26] $\chi = C/(T-\Delta)$, where T is the temperature, and C and $\Delta(<T)$ are positive material constants. χ usually decreases with temperature. However, C contains the density of the magnetic moments n_1, $C=n_1 C_1$. If the density of the high spin Co^{3+} (n_1) ions increases more rapidly, χ may actually increase with temperature.[27] Therefore, the magnetic susceptibility measurements can give a strong indication for a spin transition of Co^{3+}.

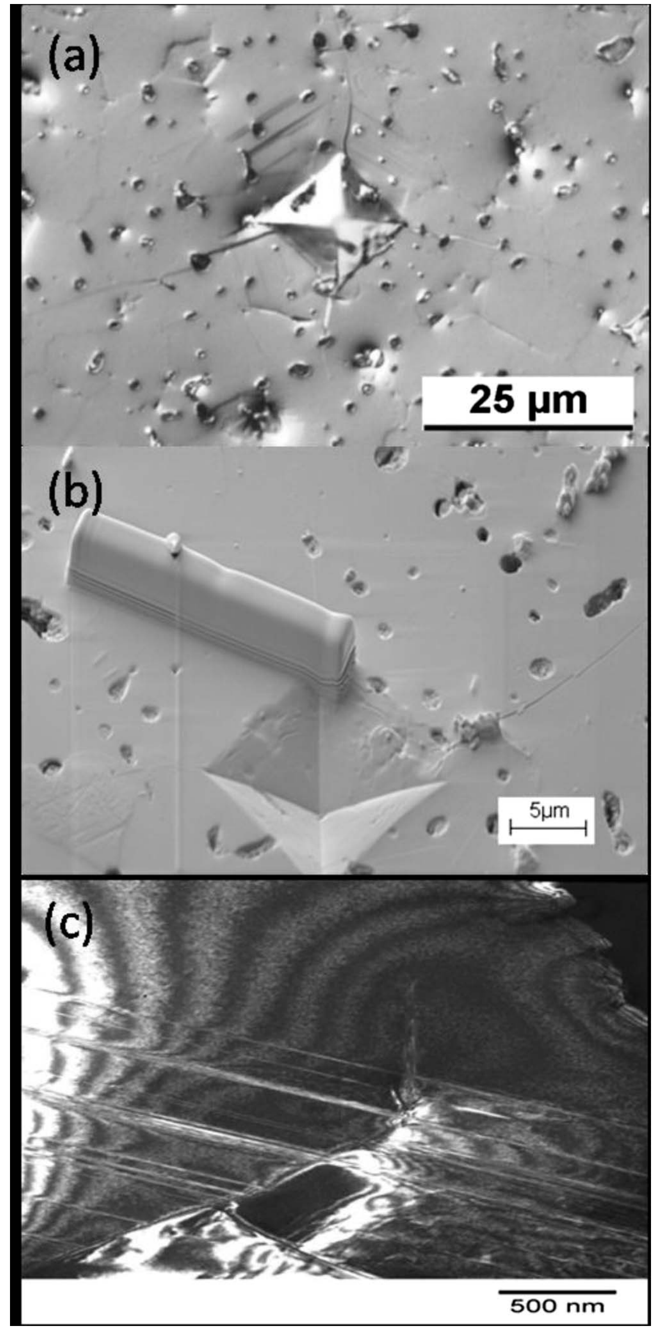

FIG. 2. (a) Shear slip lines around an indentation impression obtained at 300 °C. (b) Sample preparation for TEM with FIB. (c) Slip lines observed with TEM in dark field mode.

The susceptibility of BSCF as a function of temperature is shown in Fig. 4. The increase in χ reflects the increase in the magnetic moments in BSCF. A maximum in χ is observed at ~250 °C, which corresponds to the stiffness minimum at the same temperature.

The low spin-high spin transition is accompanied by an abnormal expansion of the Co ions besides the normal thermal expansion,[21,24] which may strongly influence the mechanical behavior of BSCF.[20] The higher value in the TEC curve at 50–250 °C can be related to such a transition, which is consistent with the susceptibility values. The susceptibility increases rapidly from approximately RT to 250 °C. The change in the TEC from 450 to 530 °C can be attributed to chemical expansion, since an oxygen loss is observed above 450 °C in TG investigations.

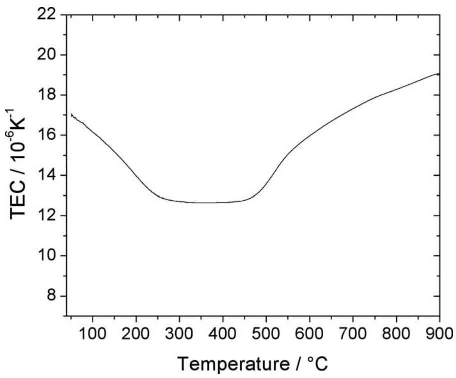

FIG. 3. Thermal expansion coefficient of BSCF.

BSCF exhibits pronounced anomalies in terms of minimum values for fracture stress and fracture toughness at intermediate temperature. The anomalies are attributed to the transition of the Co^{3+} spin state. The higher value in the TEC curve between 50 and 250 °C supports the spin transition hypothesis. The change in TEC curve from 450 to 530 °C is attributed to chemical expansion. Additionally, indentation testing above 260 °C leads to traces of plastic deformation around the impressions.

BSCF exhibits a high fracture stress and stiffness around the proposed operation temperature for gas separation, and thus appears in this respect to be suitable for membrane application. However, the observed anomalies in the mechanical properties at intermediate temperatures may cause damage of the membranes, and therefore special attention should be directed to the heating and cooling procedure applied during operation.

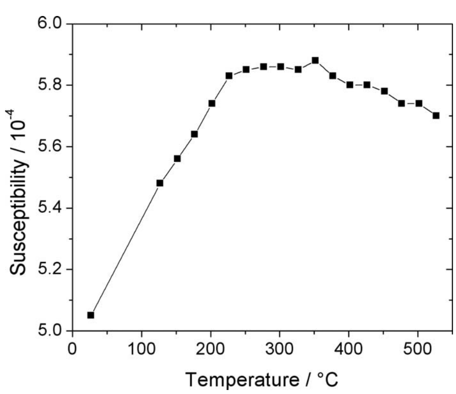

FIG. 4. Magnetic susceptibility of BSCF as a function of temperature (the line is guide to eyes).

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