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Ferroelasticity and hysteresis in $LaCoO_3$ based perovskites

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Abstract

Perovskite-type ABO_3 (where A = La, Ca; B = Co) ceramics are very promising materials for oxygen separation membrane and solid oxide fuel cells applications. However, their mechanical behavior has not yet been adequately studied. We studied the mechanical performance of perovskite ceramics using a combination of microindentation, compression, and bending. Our work demonstrated ferroelastic hysteretic behavior during indentation and compression loading in $LaCoO_3$ based perovskites. This behavior can be caused by domain reorientation and/or phase transformation. Domain switching under the compression loading in $LaCoO_3$ based perovskites has been demonstrated by XRD. Nonlinearity during fracture toughness measurements was observed in the dense $La_{0.8}Ca_{0.2}CoO_3$ perovskite. Such nonlinearity can be assigned to the domain switching or the phase transformation during crack propagation. This might be a reason of a higher fracture toughness of this material compared to non-ferroelastic composition. © 2002 Acta Materialia Inc. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Ferroelasticity; Stress–strain relationship; Toughening; Hysteresis; $LaCoO_3$ based ceramics

1. Introduction

Perovskite-type ABO_3 (where A = La, Sr, Ca; B = Co, Fe) ceramics are considered as very promising materials for high temperature oxygen separation membrane applications [1]. The applications envisioned range from small-scale oxygen pumps in medicine to large-scale usage in combustion processes such as coal liquefaction.

The ideal material for a novel membrane reactor must exhibit high oxygen flux rate, sufficient mechanical strength and maintain chemical stability under the reaction conditions [2]. However, when the membrane tube is operated as an oxygen separator, a high oxygen pressure is maintained outside the tube and a low oxygen pressure is maintained inside the tube. Upon heating, the tube begins to lose the oxygen that was previously incorporated in the fabrication process. The material on the inner wall loses more oxygen than that on the outer wall. As a result, a stable oxygen gradient is generated between the outer and inner walls. The material volume on the low-oxygen-pressure side will expand by an additional 2–3% over that on the other side [1]. The lattice mismatch between the materials on the inner and outer

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walls will generate stresses that may cause the tubes to fracture. Aside from the differential expansion, the problem of kinetic de-mixing exists when an initially homogeneous oxide is subjected to either thermal or chemical potential gradients [3,4]. The phase separation is attributed to the kinetic decomposition of the membrane material and arises from the non-negligible cation mobilities at the operating temperatures [5]. It can lead to a loss of membrane performance and to mechanical failure. These phenomena deserve more attention in order to be able to control the deterioration of membrane materials. Considering the brittleness of these materials, the possibility that the membrane tube will fracture under reactor conditions is of serious concern.

Although recent reports have described various perovskite-type materials that could be used in partial-oxidation ceramics membrane reactors, little work have focused on the problems associated with the mechanical reliability of the materials. Also, nearly all of the research activities on the development of mixed conductor perovskites have been dedicated to the optimization of electrochemical and thermal properties [6,7]. However, whether these materials will eventually be of practical interest is largely determined by their mechanical properties. So far the mechanical properties of transition metal oxide perovskites have not received much attention, despite the fact that the application of these materials in high temperature electrochemical cells demands at least an intermediate mechanical strength and high creep resistance. Only a few characteristics, such as bending strength and Young's modulus can be found for selected perovskites [8–11]. The mechanical properties of $LaCoO_3$, $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.8}Ca_{0.2}CoO_3$ perovskites have been studied in [12]. In this work, the strength, calculated using an elastic beam equation, was found to be 53 MPa for 83% dense $LaCoO_3$, 76 MPa for 90% dense $La_{0.8}Sr_{0.2}CoO_3$, and 151 MPa for fully dense $La_{0.8}Ca_{0.2}CoO_3$ ceramics. The fracture toughness, measured by indentation, was found to be 0.73 MPa $m^{1/2}$ for 90% dense $La_{0.8}Sr_{0.2}CoO_3$ and 0.98 MPa $m^{1/2}$ for fully dense $La_{0.8}Ca_{0.2}CoO_3$ ceramics. A nonlinear deformation has been observed during the flexure strength measurements on all three $LaCoO_3$ based perovskites.

Pure $LaCoO_3$ is a rhombohedral perovskite and it remains rhombohedral up to temperatures close to its melting point (1740°) [13,14]. However, it shows a Mott insulator-metal transition with increasing temperature [15,16]. The rhombohedral distortion of $LaCoO_3$ based perovskites decreases with increasing temperature and A site cation concentration [17,18]. The hole-doping induced change is equivalent to the temperature-induced change. At ambient temperature pure $LaCoO_3$ is a semiconductor, but becomes a metallic oxide when lanthanum is substituted for alkali earth cations [6,18]. Despite a huge number of publications concerning the spin-state [19,20], electrical and magnetic transitions [6,21,22], and the oxygen permeability of $LaCoO_3$ based perovskites [23,24], to our knowledge, the ferroelasticity of these materials have not been reported.

What makes a $LaCoO_3$ based crystal ferroelastic? There are two factors [25]: (a) The phase transition between the paraelastic and ferroelastic phase which creates a lattice distortion; (b) This lattice distortion can be reoriented by external stress. Also, the walls separating the domains have to be in a mobile state and should be able move under the effect of an external mechanical stress. Therefore in order to understand the ferroelasticity in $LaCoO_3$ based ceramics one needs to study both the paraelastic to ferroelastic transition and the effect of external stress on elastic switching in the ferroelastic low temperature phase. We investigated the mechanical behavior of $LaCoO_3$ based perovskites under contact loading, compression and bending in order to better understand the ferroelastic behavior of these materials.

2. Materials and experimental

The procedure for samples preparation used for indentation and fracture toughness measurements has been described elsewhere [12]. Samples used for compression tests were similar in all aspects to the other samples. All samples were stoichiometric single phase materials without any secondary phases. The grain size of perovskites was in the range of 2–5 μm. The porosity of pure $LaCoO_3$ perovksite was about 10%, and $La_{0.8}Ca_{0.2}CoO_3$ perovskite material was almost fully dense (0.2% porosity).

Perovkite samples were indented by a diamond cone (90° angle, commercial stylus, Lunzer, USA) using an Instron 5569 universal testing machine. Two loading cells (2.5 N and 10 kN) were used for loading up to 1.2 N and 30 N. Samples were indented at a 0.01 mm/min loading rate, after this unloading was initiated at the same rate as the loading. Because the equipment used in this research was not particularly designed for the depth sensing indentation, the results of indentation tests were used for identification of hysteretic behavior and estimation of material ductility, but not for quantitative analysis.

Compression tests were performed in a servohydraulic test machine (Instron 8500) using 3×3×6mm perovskite samples. The compression axis was along the longest dimension of the sample. The loading cell used in compression tests was 2 kN. The loading rate was close to the loading rate used in indentation experiments.

The fracture toughness was measured using Single Edge V Notch Beam (SEVNB) method [26]. The size of the specimens was 6×4×45mm with a height being 6 mm. The straight notch (depth 1.2 mm) was cut into the center of specimen's tensile surface, after that V-notch was prepared by razor blade polishing with 4 μm and 1 μm diamond paste. The radius of root notch was between 3–6 μm.

X-ray diffraction analysis (XRD) (Siemens diffractometer, CuK_{α} radiation) was performed to characterize the texture and phase composition of perovskites and SEM was used to study the fracture surfaces of materials.

3. Results

3.1. Contact loading

Contact loading by diamond indenters is a good method for investigating the plasticity as well as indentation response of brittle materials [27,28]. It also provides information on structural changes (e.g. "pop-in" and "pop-out" events) that produce hysteresis behavior upon loading [29,30].

During contact loading with a conical indenter, pure $LaCoO_3$, and Ca substituted $LaCoO_3$ materials behaved in different ways. Pure $LaCoO_3$ did not show any plastic response during loading up to 1.2 N with only an elastic component of deformation [Fig. 1(a)]. Ca substituted $LaCoO_3$ materials showed some inelastic deformation and ferroelastic hysteresis loop was observed during the loading–unloading cycle of $La_{0.8}Ca_{0.2}CoO_3$ [Fig. 1(b)].

When the load was increased to 30 N, pure $LaCoO_3$ showed some plastic response on the load–displacement curve, however the major part of the total deformation was still elastic ($h_{elast}\approx63.9\%$, $h_{plast}\approx36.1\%$) (Fig. 2). In comparison to porous $LaCoO_3$, Ca substituted materials showed much more plastic deformation. Two types of load–displacement curves were obtained for Ca substituted $LaCoO_3$ at 30 N maximum load [Fig. 3(a,b)]. In some cases "pop-in" events were observed during loading at about 15 N [Fig. 3(b)]. This behavior can be explained both by microcracking (fracture under indenter) or by a sudden phase transformation or domain reorientation. Since there was no "pop-out" during the unloading, these events were irreversible. $La_{0.8}Ca_{0.2}CoO_3$ exhibited a significant amount of inelastic/plastic deformation (53–60%) upon loading/unloading. At the beginning of loading

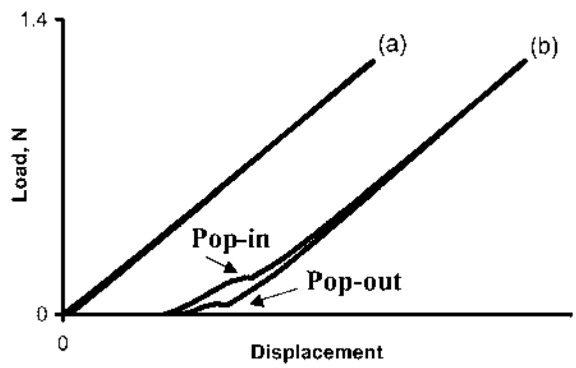

Fig. 1. Load–displacement curves of $LaCoO_3$ (a), and $La_{0.8}Ca_{0.2}CoO_3$ (b) obtained under contact loading using a conical indenter (1.2 N load). Notice the existence of a hysteresis loop in $La_{0.8}Ca_{0.2}CoO_3$ material.

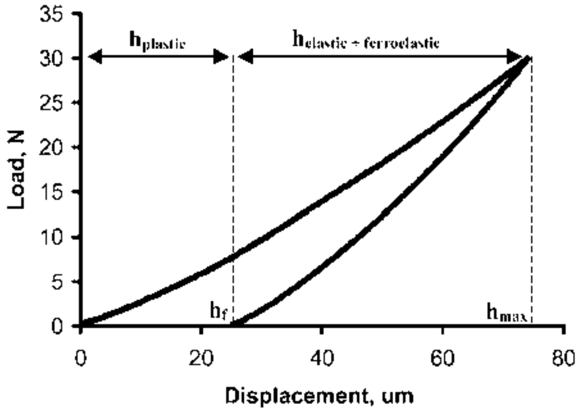

Fig. 2. Load–displacement curve of $LaCoO_3$ perovskite obtained under contact loading (30 N load).

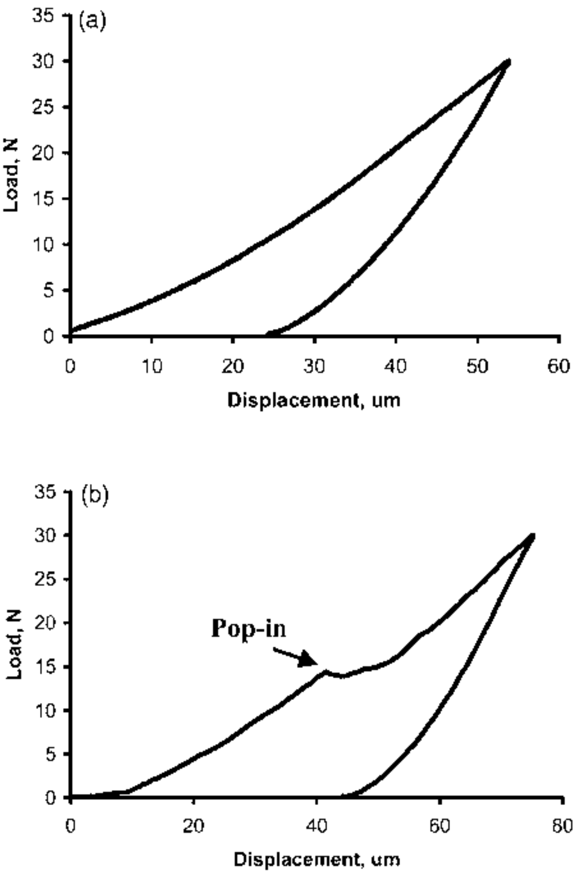

Fig. 3. (a,b) Load–displacement curves of $La_{0.8}Ca_2CoO_3$ obtained under contact loading.

(0.3–0.5 N) and at the end of unloading (0.2–0.3 N) small "pop-in" and "pop-out" events were sometimes observed [Fig. 3(b)].

The amount of elastic recovery can be characterized by the ratio of the final indentation depth h_f to the maximum indentation depth h_{max} [31] (Fig. 2). The limits for the parameter are $0 \leq h_f/h_{max} \leq 1$. In case if $h_f/h_{max} = 0$, fully elastic deformation and consequently complete recovery of the material surface after complete unloading is anticipated. The case of $h_f/h_{max} = 1$ corresponds to a rigid-plastic material, where there is no elastic recovery. The calculated values of h_f/h_{max} at 30 N maximum load for pure and Ca substituted $LaCoO_3$ are given in Table 1. In [32] the parameter of plasticity δ_H was identified as $\delta_H = 1-14.3(1-\nu-2\nu^2)H_v/E$, where $\delta_H = 1$ is the case of rigid-plastic materials, and $\delta_H = 0$ corresponds to purely elastic materials. δ_H is mainly defined by H_v/E, which characterized the indenter contact area size to the specimen compression strength under the indenter. This parameter has been calculated for pure and Ca substituted $LaCoO_3$ for the case where $\nu = 0.3$ (Table 1). Ca substituted $LaCoO_3$ become more plastically deformed under an indenter, moreover ferroelastic behavior appeared in $La_{0.8}Ca_{0.2}CoO_3$. There is a possibility that changes in the electronic structure of Ca substituted $LaCoO_3$ [6] lead to changes in the indentation response of these materials in comparison with pure $LaCoO_3$.

3.2. Compression tests

It is known that stress–strain relationships cannot be uniquely determined from the loading–unloading indentation curves [33]. However, it is important to know at which stress level the domain switching starts, what the coercive and saturation stresses in domain switching are, and at what stresses phase transformation occurs. The compression test is a simple method that provides answers to these questions.

Dense $La_{0.8}Ca_{0.2}CoO_3$ perovskite exhibits significant nonlinear ferroelastic behavior with a high irreversible strain ($\epsilon_{irr} = 0.38\%$) after compression. As one can see from Fig. 4, the smooth gradual switching process occurs under com-

Table 1
Characterization of plasticity of $LaCoO_3$ based ceramics from indentation tests

Composition	Load (N)	h_f/h_{max}		H/E	δ_H
		With "pop-in"	Without "pop-in"		
$LaCoO_3$	30	–	0.361	0.0858	0.362
$La_{0.8}Ca_{0.2}CoO_3$	30	0.591	0.528	0.0532	0.6044

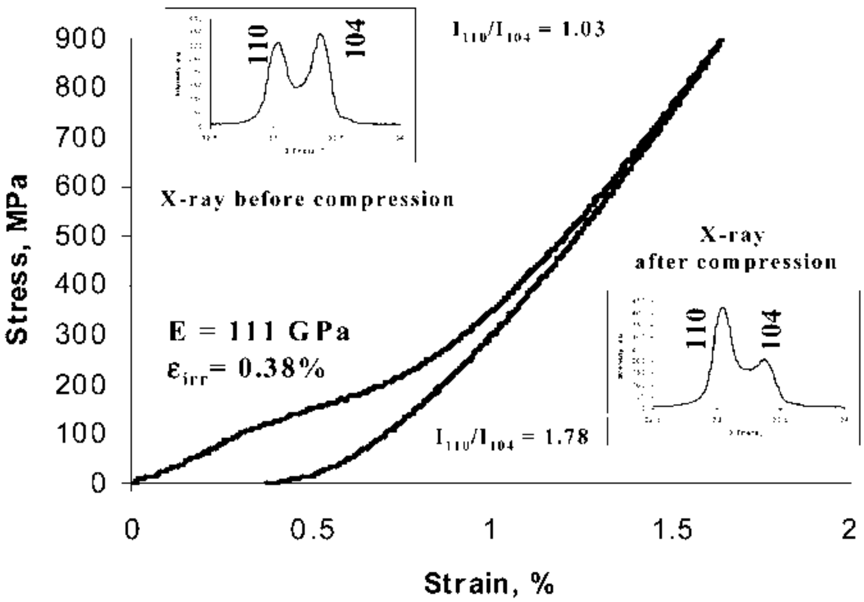

Fig. 4. Stress–strain curve of $La_{0.8}Ca_{0.2}CoO_3$ obtained under compression. Machined surface after annealing at 1100°C for 4 h. Inserts show XRD patters of the {110}/{104} doublet before and after compression.

pression. There are no sudden "pop-in" or "pop-out" events, unlike in case of indentation loading. It is a result of the random grains orientation in the material, so that there is no preferred textured structure in any direction and there is no highly localized loading. As the stress increases, initially more grains become involved in the switching process. Eventually the number of switching grains decreases until all grains with different orientations and anisotropies become reoriented [34,35]. There is a saturation point where there are no more domains in the grains to reorient.

To determine whether domain switching is produced by mechanical stressing, XRD patterns of $La_{0.8}Ca_{0.2}CoO_3$ (rhombohedral symmetry) before and after compression tests were obtained (Fig. 4, inserts). The machined $La_{0.8}Ca_{0.2}CoO_3$ bar was annealed at 1100°C for 4 h before compression. The temperature of ferroelastic to paraelastic transition (T_c) in $La_{0.8}Ca_{0.2}CoO_3$ is expected to be around 950°C [36]. Annealing at 1100°C, which is higher than T_c for this composition, produced a random orientation of the domain structure on cooling. As a result, the XRD pattern of {***110***}/{***104***} doublet after annealing reached a cumulative intensity ratio of 1.03, which corresponds to the random crystalline orientation. After the compression test, the texture ratio is $I_{\{110\}/\{104\}} = 1.78$, which reflects the reorientation of domains during compression. The intensity of

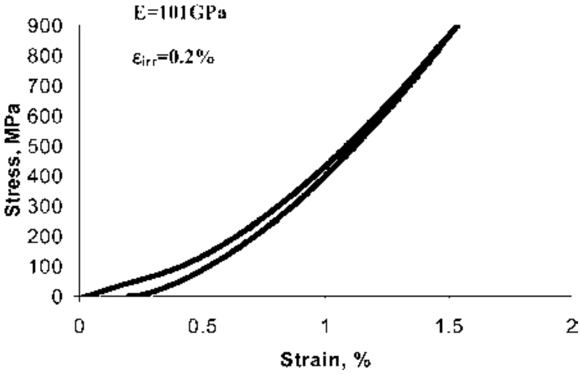

Fig. 5. Stress–strain curve of $LaCoO_3$ obtained under compression.

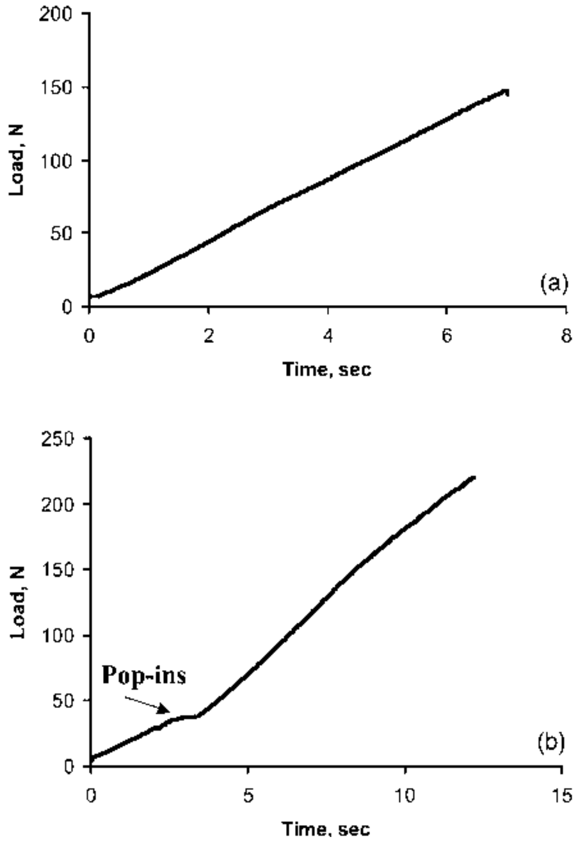

Fig. 6. Load–time curves for notched $LaCoO_3$ and $La_{0.8}Ca_{0.2}CoO_3$ samples used for K_{Ic} measurements.

the {***110***} peak increased after compression while that of {***104***} decreased substantially. No crystal symmetry changes were detected. Such changes in the intensity ratio after compression presented evidence of the existence of ferroelasticity of $LaCoO_3$ ceramics.

It is expected that pure dense $LaCoO_3$, which has a higher rhombohedral distortion than that of $La_{0.8}Ca_{0.2}CoO_3$, will exhibit a more pronounced hysteresis loop with higher switching stresses, and, as a result, a higher fracture toughness. However, in our experiments, $LaCoO_3$ had 10% of porosity. It was found that the area under the hysteresis loop under compression is strongly affected by the porosity level of the materials. For the 10% porous $LaCoO_3$ perovskite the loop can be hardly observed and the irreversible deformation is rather low ($\epsilon_{irr} = 0.2\%$) (Fig. 5). The reversible expansion of material to pores can accommodate the deformation that is accommodated by domain switching in dense materials. At the same time, pores can act as pinning points for the moving domain walls under stress, thus decreasing the inelastic hysteretic behavior of this material.

3.3. Fracture toughness

Load–time curves for notched $LaCoO_3$ and $La_{0.8}Ca_{0.2}CoO_3$ samples are shown in Fig. 6. As can be seen, the crack growth is linear for the pure $LaCoO_3$ perovskite [Fig. 6(a)] indicating absence of inelastic behavior or energy dissipation. However, for $La_{0.8}Ca_{0.2}CoO_3$ ceramics one can see "pop-in" events not far from the starting point of measurements and near the critical stress point [Fig. 6(b)]. Fracture toughness of $La_{0.8}Ca_{0.2}CoO_3$ ceramics is about twice as large as the fracture toughness of pure $LaCoO_3$ (2.25 and 1.32 MPa $m^{1/2}$, respectively). Nonlinear behavior during fracture gives a good explanation for the higher fracture toughness value of $La_{0.8}Ca_{0.2}CoO_3$ ceramics because the ferroelastic deformation reduces the stress concentration at crack tips.

The domain reorientation in the near crack stress field may provide a potential toughening mechanism, analogous to dislocation plasticity in metals [37]. The toughening mechanism as a ferroelastic domain switching has been proposed for $BaTiO_3$ [38] and $PbZr_xTi_{(1-x)}O_3$ [39] ceramics. The mechanics of toughening by domain switching have been examined by several groups [36,40–42]. It was estimated [36] that the increase in fracture toughness by domain rotation alone would be lower than 10%, therefore other processes such as phase transformation or change in stiffness can affect the fracture toughness. The ferroelastic hysteresis loop, which was observed during compression for Ca-doped materials, indicates a contribution of domain switching to the overall toughness of $La_{0.8}Ca_{0.2}CoO_3$ perovskite below T_c. However the “pop-in” event might also indicate the phase transformation occurs as a crack propagates during fracture toughness measurements.

The analysis of fracture surfaces reveals the transgranular fracture for pure $LaCoO_3$ ceramics for the entire fracture surface (Fig. 7). However fracture mode of the $La_{0.8}Ca_{0.2}CoO_3$ fracture surface changed from mixed transgranular and intergranular near the notch to almost completely fully transgranular at the end of fracture (Fig. 8). This behavior is typical for the fracture of notched samples where the amount of transgranular fracture increases with the distance from the notch. The extended time of slow crack growth and presence of a fairly large slow crack zone show a higher damage tolerance of this ceramics. Such behavior during fracture may explain the higher fracture toughness value of $La_{0.8}Ca_{0.2}CoO_3$ ceramics.

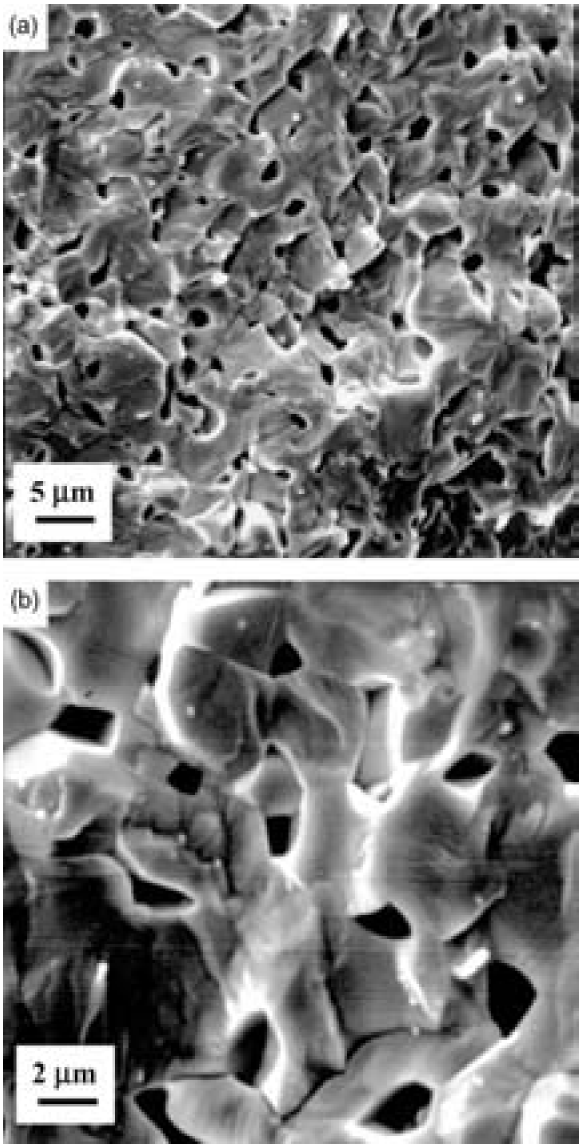

Fig. 7. Fracture surface of $LaCoO_3$ perovskite after K_{Ic} measurements.

4. Conclusions

Our results show ferroelastic hysteretic behavior of the cobaltite perovskites under loading. These ceramics show distinct “pop-in” and “pop-out” events upon loading and unloading when subjected to a contact load. The hysteresis observed during microindentation can be assigned to reversible domain reorientation or phase transformation upon loading. Ferroelastic behavior of $La_{0.8}Ca_{0.2}CoO_3$ was also observed during uniaxial compression tests. The domain switching under compressive loading was unambiguously demonstrated by XRD. Nonlinearity during fracture toughness measurements was observed in dense $La_{0.8}Ca_{0.2}CoO_3$ perovskite. Such nonlinearity can be assigned to the domain switching or the phase transformation during crack propagation. This might explain higher fracture toughness of this material.

Understanding and use of the “pseudo-ductility” of the materials that was observed in our experiments, can lead to development of damage tolerant perovskite ceramics with an improved reliability and fracture toughness.

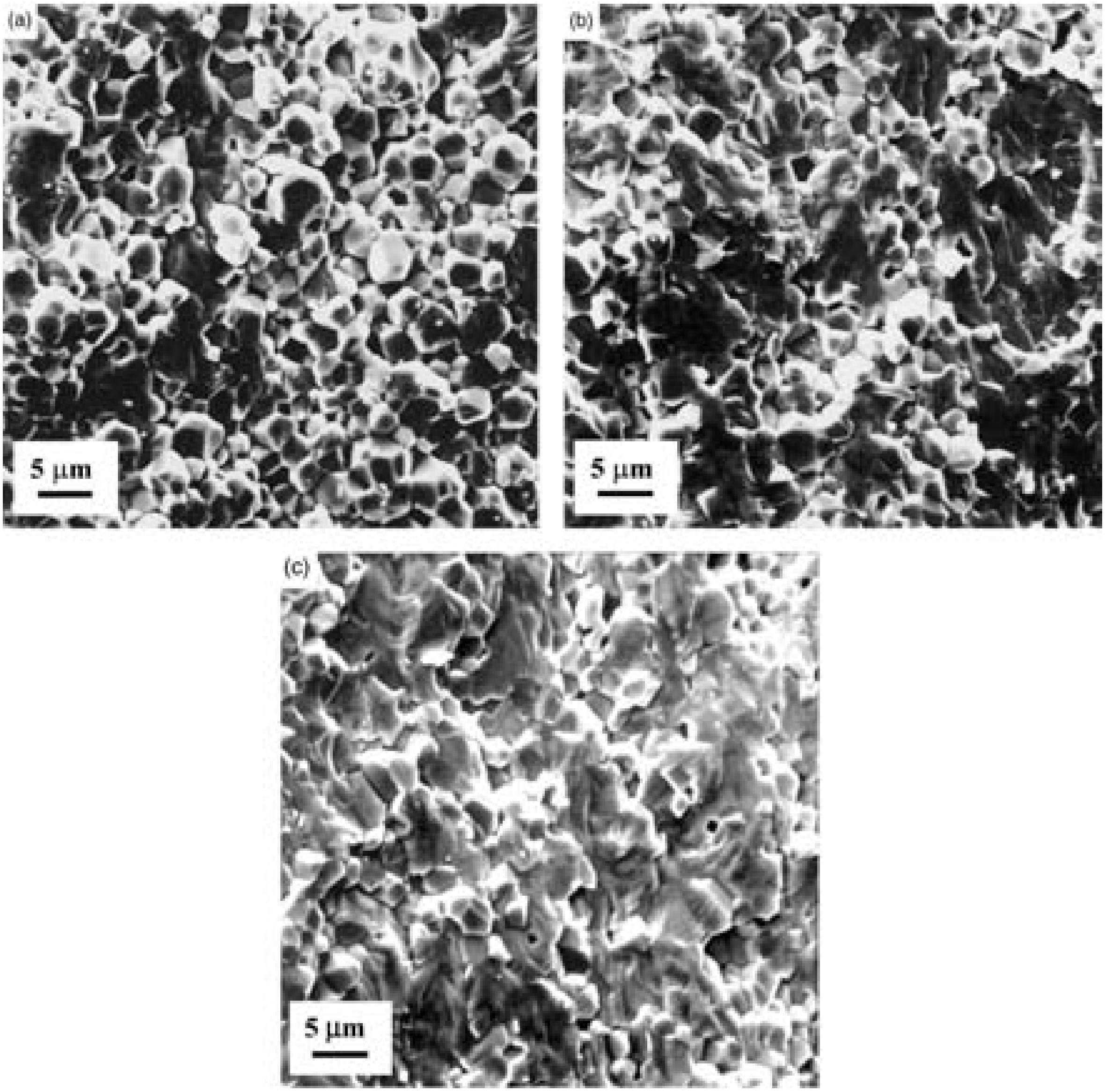

Fig. 8. Fracture surface of $La_{0.8}Ca_{0.2}CoO_3$ perovskite after K_{Ic} measurements. (a) near the notch; (b) central part; (c) near the edge.

Acknowledgements

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