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Non-congruence of high-temperature mechanical and structural behaviors of $LaCoO_3$ based perovskites

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ABSTRACT

This paper presents the mechanical behavior of $LaCoO_3$ and $La_{0.8}Ca_{0.2}CoO_3$ ceramics under four-point bending in which the two cobaltites are subjected to a low stress of ~8 MPa at temperatures ranging from room temperature to 1000 °C. Unexpected stiffening is observed in pure $LaCoO_3$ in the 700–900 °C temperature range, leading to a significant increase in the measured Young's modulus, whereas $La_{0.8}Ca_{0.2}CoO_3$ exhibits softening from 100 °C to 1000 °C, as expected for most materials upon heating. Neutron diffraction, X-ray diffraction and micro-Raman spectroscopy are used to study the crystal structure of the two materials in the RT–1000 °C temperature range. Despite a detailed study, there is no conclusive evidence to explain the stiffening behavior observed in pure $LaCoO_3$ as opposed to the softening behavior in $La_{0.8}Ca_{0.2}CoO_3$ at high temperatures (above 500 °C).

1. Introduction

Mixed Ionic Electronic Conducting (MIEC) $LaCoO_3$ based perovskites have been studied very extensively due to their unique and distinctive electronic, electrochemical, catalytic, and mechanical properties [1–8]. It was reported that polycrystalline $LaCoO_3$ based perovskites exhibit nonlinear ferroelastic behavior, which can be well explained by the kinetics of ferroelastic switching and corresponding changes in the cobaltite's microstructure and crystallographic orientation during loading [9]. The phenomena of domain switching and texture development were reported to be responsible for the appearance of elastic anisotropy and stress-strain hysteresis during deformation [9,10]. It was also reported that at room temperature both pure $LaCoO_3$ and Ca doped $LaCoO_3$ have $R\bar{3}c$ low symmetry rhombohedral structure with $a = 5.378$ Å and $\alpha = 60.8°$ for pure $LaCoO_3$, and $a = 5.374$ Å and $\alpha = 60.72°$ for 20% Ca doped $LaCoO_3$, which is in perfect agreement with previously reported measurements [11–13]. Upon heating, the rhombohedral distortion in the lattice gradually decreases along with an increase in the lattice parameters up to the temperature at which a phase transition takes place to the high symmetry $Pm\bar{3}m$ cubic structure. Doping $LaCoO_3$ with cations like Ca^{2+} is known to reduce the lattice distortion and lower the transition temperature [14]. The $R\bar{3}c$ to $Pm\bar{3}m$ phase transition has been reported to occur above 1200 °C for pure $LaCoO_3$ and at ~950 °C for $La_{0.8}Ca_{0.2}CoO_3$, corresponding to the fact that a greater rhombohedral distortion at room temperature results in a higher transition temperature to cubic structure [14]. It is also know that the transition from the higher symmetry paraelastic phase to the lower symmetry ferroelastic phase leads to distortion of the cubic lattice, which results in spontaneous strain, and hence the lower symmetry phase has a non-linear deformation behavior. While only $R\bar{3}c$ rhombohedral structure was found at

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room temperature using most diffraction techniques, the existence of an even lower symmetry monoclinic I2/a phase in $LaCoO_3$ based perovskite was confirmed by TEM and high-resolution synchrotron diffraction experiments. It is hard to detect the monoclinic phase in general by normal X-ray and neutron diffraction techniques due to the fact that the monoclinic distortion is very small and there are overlapping peaks [15–17]. Vullum et al. also reported the presence of a monoclinic phase in $LaCoO_3$, even though they reported the monoclinic space group as $P2_1/m$ [18,19].

It is important to mention that in our previous investigation of the thermal and mechanical properties of $LaCoO_3$ and $La_{0.8}Ca_{0.2}CoO_3$, a very unusual behavior was observed for pure lanthanum cobaltite [11]. At high temperatures (700–1000 °C), $La_{0.8}Ca_{0.2}CoO_3$ perovskite exhibits significant softening as expected and the value of Young's modulus decreases in comparison with the value at room temperature. On the other hand, pure $LaCoO_3$ exhibits an unexpected increase in Young's modulus with temperature, varying from 76 GPa at room temperature to 120 GPa at 800 °C, a 30% increase in magnitude, while the lattice continuously expands from room temperature to 1000 °C as reported in [11]. The Young's modulus of $LaCoO_3$ and $La_{0.8}Ca_{0.2}CoO_3$ perovskites was measured from the loading portions of the stress-strain deformation curves obtained during 4-point bending experiments. The stiffening of $LaCoO_3$ reported in [11] was not explained and no detailed investigation into the unusual phenomenon was performed. In a paper by Raccah and Goodenough, the high temperature phase transition in $LaCoO_3$ was reported [20], however, these results were retracted in a later publication [12], where the explanation of the phase transition in $LaCoO_3$ was replaced by the appearance of the secondary Co_3O_4 oxide spinel phase as an impurity in $LaCoO_3$, thus leading to the disruptive changes in measured lattice parameters, that were erroneously assigned to the first order phase transition in $LaCoO_3$.

A summary of the many published results that have reported the variation of Young's modulus with temperature in different MIEC perovskites, all of them being of high relevance for their use in solid oxide fuel cells, was presented in [21]. This rather comprehensive review revealed that for certain perovskite compositions under certain experimental conditions, the Young's modulus decreases in the 100–600 °C temperature range and then increases in the 700–1000 °C temperature range [22,23], while other materials with different perovskite compositions under similar or different experimental conditions showed the expected softening upon heating to 1000 °C [24,25]. A significant softening of $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ and $La_{0.8}Sr_{0.2}Fe_{0.7}Ga_{0.3}O_{3-\delta}$ in the 200–400 °C temperature range followed by an increase in the Young's modulus at 700–900 °C was reported in [23]. The phase transition occurring in the 700–900 °C temperature range was considered to be responsible for the stiffening of the material in the higher temperature range (700–900 °C) in $LaCoO_3$ based ceramics [23]. Similar softening followed by a small stiffening behavior of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ during heating to 1100 °C was attributed to the successive structural changes in this perovskite material [26]. Changes both in Young's and shear moduli reported in [26] lead to the appearance of a significant discontinuity in the Poisson's ratio of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ at 600 °C. A significant increase in measured Young's modulus of dense $La_{0.8}Sr_{0.2}MnO_3$ perovskite ceramics was reported to occur in the 600–1000 °C temperature range, while no change in Young's modulus was found for the same composition when the ceramics had low density and an open pore structure [22]. A very large increase in Young's modulus of $La_{1-x}Sr_xMnO_3$ at high temperatures was also reported [21]. The variation of Young's modulus with temperature for $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ was reported in [27], and an attempt at explaining the phenomenon by phase transition is covered in [28]. Similar stiffening of other mixed ionic electronic conducting ceramics was found in [22], where an increase

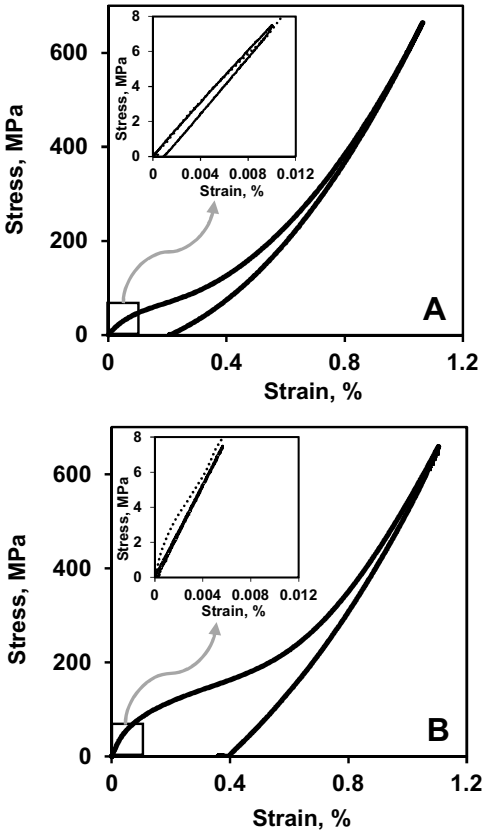

Fig. 1. Stress-strain curve during uniaxial compressive loading and unloading for (A) $LaCoO_3$ and (B) $La_{0.8}Ca_{0.2}CoO_3$. The inset portions of the curves in the two figures show the initial portion of the stress-strain curve from uniaxial compressive loading (dotted line) plotted with stress-strain curve from 4-point bending for the two compounds.

in Young's modulus of $LaMnO_3$ and $LaFeO_3$ based perovskites in the 800–1000 °C temperature range was reported, however, again, no reasonable explanations were provided to explain this behavior.

In the current paper, the significant increase in Young's modulus of $LaCoO_3$ in the 700–1000 °C temperature range is reported, as measured using stress-strain deformation plots in four-point bending and sample resonance using the impulse excitation technique. For comparison, the properties of $La_{0.8}Ca_{0.2}CoO_3$ perovskite were also measured. Since the cobaltites exhibit non-linear deformation behavior upon loading, even at very small stresses, the Young's modulus cannot simply be directly determined from stress-strain data. Therefore, in the case of the four-point bending measurements the term "Young's modulus" will be replaced by the term "effective Young's modulus" in the paper. A detailed study of the crystal structure of the two cobaltite compositions were performed using powder X-ray diffraction and neutron diffraction.

2. Experimental

The $LaCoO_3$ and $La_{0.8}Ca_{0.2}CoO_3$ samples were sintered by Praxair Surface Technologies, Specialty Ceramics, USA; and machined by PremaTech Ceramics, USA. Three separate sample geometries were prepared – bars with dimensions 3 mm × 4 mm × 50 mm for four-point bending experiments, bars with dimensions 50 mm × 14 mm × 14 mm for impulse excitation measurements, and cylindrical pellets with 6 mm diameter and 12 mm length for compression testing.

The four-point bending tests of $LaCoO_3$ and $La_{0.8}Ca_{0.2}CoO_3$ samples were carried out at Empa, Swiss Federal Laboratories for

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