Time and frequency dependent mechanical properties of LaCoO₃-based perovskites: Neutron diffraction and domain mobility

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(Received 20 April 2018; accepted 2 November 2018; published online 27 November 2018)

The study of domain wall movement and texture formation in ferroelastic LaCoO₃ perovskite under constant applied compressive stress has been performed using *in situ* neutron diffraction. It was established that under constant applied compressive stress the domain walls show mobility that may lead both to the shrinkage (creep strain) and to the expansion (negative creep strain) of LaCoO₃ perovskite. The domain wall movement and texture formation can be explained by the availability, mobility, and interaction of twins, stacking faults, antiphase boundaries, dislocations, and point defects, such as oxygen vacancies and their complexes as well as impurity atoms. The equation of motion was used to describe the possible mechanisms of domain wall movement under applied stress, and it was determined that the available solutions of this equation allow both for the shrinkage (creep strain) and for the expansion (negative creep strain) of LaCoO₃ perovskite to occur. Published by AIP Publishing. <https://doi.org/10.1063/1.5037051>

I. INTRODUCTION

Ferroelasticity of nonpolar mixed ionic electronic conducting LaCoO₃ based perovskites and its underlying mechanisms have been studied intensively in the last two decades.^{1–7} As in other ferroelastics,⁸ the ferroelastic behavior of LaCoO₃ based ceramics is determined by two major factors: the existing lattice distortion that appears due to second order *Pnmm* cubic paraelastic to $R\bar{3}c$ rhombohedral ferroelastic phase transition occurring upon cooling of cobaltites after their high temperature treatment and that this lattice distortion can be reoriented by an external mechanical stress. The spontaneous strain that appears as a result of the lattice distortion is accommodated by the formation of ferroelastic domain/twin structures in the ferroelastic phase. These domains/twins are a dominant type of different microstructural defects, such as grain boundaries, stacking faults, antiphase boundaries, dislocations, or point defects that, in fact, govern the mechanical response of $R\bar{3}c$ rhombohedral ferroelastic phase of LaCoO₃ based perovskites by providing stress accommodating mechanisms during deformation.⁹ Therefore, it is not only the availability of the domain/twin defects in the microstructure, but also the mobility of these domain walls and other defects that determine both the ferroelastic response and the size of the stress-strain hysteresis loop during perovskites deformation.¹⁰

The availability and mobility of defects in ferroelastic perovskites and the mechanisms explaining their appearances have been studied by numerous techniques.^{4–7} The direct visual characterization and the studies of the mobility of twins, stacking faults, dislocations, and other related defects in LaCoO₃ based perovskites both at room and at high temperatures were studied by high resolution TEM^{2,11–13} and under applied compressive stresses by SEM,^{14,15} where domains and their movements were directly visualized, in many cases even during *in situ* experiments. Another set of straightforward and revealing techniques used to study domain mobility and reorientation under applied compressive stress in LaCoO₃ based perovskites, very often presented as domain switching, was *in situ* X-ray or neutron diffraction techniques. The high resolution synchrotron diffraction study of domain switching and texture formation in La_{0.8}Ca_{0.2}CoO₃ perovskite under *in situ* compressive loading was performed.¹⁶ A similar study of pure LaCoO₃ perovskite ceramic was reported,^{17–19} where it was established that during loading the texture was formed leading to elastic anisotropy in the material. As the texture is inevitably connected to the growth of domains with preferred crystallographic orientation and the corresponding increase in the volume fraction of certain domains, it is possible to estimate the anisotropy and elastic properties of LaCoO₃ in different crystallographic directions if the relevant elastic properties are known.¹⁸ The partially and fully recoverable domain reorientation and texturing resulted in the appearance of hysteresis during loading and unloading cycles, leading to irreversible permanent macroscopic strain upon unloading in the case of the partially recoverable domain switching. It was

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indeed found that *in situ* characterization techniques, such as X-ray and neutron diffraction, are invaluable to determine domain switching and texture formation and to clarify the defects movement mechanisms causing elastic anisotropy of ferroelastic perovskites.

While *in situ* X-ray and neutron diffraction was used to clarify crystallographic changes and study the dynamics of the domain/twin walls movement in LaCoO_3 based perovskites during deformation by applied external stress,^{16,18,19} these studies were, however, performed only in cases where cyclic loading was applied in the manner that the uniaxial compressive stress was either constantly increasing or decreasing, but was not held constant. No *in situ* analysis was ever performed to clarify the crystallographic changes, defects' movement, or texture formation during room temperature creep experiments, as performed in Refs. 20–22. However, such *in situ* X-ray or neutron diffraction studies performed during a constant applied stress would definitely shed light on possible mechanisms that underlie the appearance of both creep and negative creep strains, which was reported for the first time to appear during creep deformation of LaCoO_3 .²⁰

Therefore, the goals of this paper are (1) to report the crystallographic behavior and texture formation in LaCoO_3 under applied constant compressive loading studied by *in situ* neutron diffraction, (2) to better understand the mechanisms of formation, growth, and movements of domains with certain crystallographic orientations, and how these domains affect the time-dependent room temperature deformation under the constant applied compressive stress in LaCoO_3 , (3) to discuss both availability of twin walls and their interaction with other lattice defects, especially point defects, such as oxygen vacancies, that leads to decreased/increased mobility of the domain walls, resulting in increased/decreased energy dissipation or damping during mechanical deformation, and (4) to provide explanations on the appearance and stress dependence of expansion, or negative creep strain, in LaCoO_3 during loading under a constant applied compressive stress, as reported in Ref. 20.

II. EXPERIMENTAL

The LaCoO_3 samples used in the current research were produced by Praxair Surface Technologies, Specialty Ceramics, and their characteristics were published.^{2,19,21,23} The LaCoO_3 samples used in *in situ* neutron diffraction experiments had dimensions of 6 mm in diameter and 12 mm in length and were machined by PremaTech Ceramics (MA, USA).

A schematic of the experimental setup used for uniaxial compression at the VULCAN diffractometer at the Spallation Neutron Source (SNS) is shown in Fig. 1(a). With a white incident beam spectrum, diffraction peaks over a 0.5 to 2.5 Å bandwidth of d -spacing are measured simultaneously by running the double-disk chopper at 30 Hz speed with a nominal 800 kW neutron source power level. The -90° (Bank 1) and $+90^\circ$ (Bank 2) detectors record the neutrons diffracted by any (hkl) crystal plane with the plane normal parallel and perpendicular to the loading direction, respectively.^{24,25} If there is no texture, the data collected from both banks can be

FIG. 1. VULCAN diffractometer setup for *in situ* neutron diffraction measurement during uniaxial compression of LaCoO_3 perovskite.^{18,19} (a) A schematic of neutron diffraction experiment. The longitudinal planes undergo compressive deformation, and the transverse planes undergo tensile deformation. (b) A photograph of the experimental setup where the LaCoO_3 cylindrical specimen is located between two compression platens. The extensometer is attached to measure the macroscopic strain with three thermocouples are also attached to continuously monitor the temperature of the sample's surface, the water cooled platens surface, and the air in the vicinity of the experiment. (c) The temperature measurements during the experiment showing the temperatures of the sample, the water-cooled platten, and the air in the vicinity of the sample.

summed. Otherwise, the data from different banks can be used to identify the texture formation or grain orientation anisotropy. The neutron diffraction measurements were performed in the high-intensity (HI) mode with an instrument resolution of

0.45%. An incident slit of 5 mm width and 3 mm height with a pair of 5 mm collimators was used together, resulting in a 75 mm^3 gauge volume.

The samples were loaded between two parallel compression platens, and an extensometer with a nominal gauge length of 9 mm was used to measure the macroscopic strain. In order to prevent a possible transfer of thermal energy from the machine to the sample, water recirculation was employed within the compression platens to ensure that the platens maintained a constant plant water temperature during the tests. Three Type K thermocouples were employed to measure temperature at three locations: (i) one thermocouple was attached to the sample's surface to record its temperature during the compression experiments; (ii) another thermocouple was attached to the platen's surface to monitor the temperature of the water cooled platens; and (iii) the last thermocouple was designated to measure the temperature of the environment near the sample, to record any change in air temperature, if any. The sample was preloaded in compression with an attached extensometer and three thermocouples as shown in Fig. 1(b).

At SNS, each collected neutron carries a time stamp by the event-based data acquisition mode,²⁶ and the *in situ* neutron diffraction data were collected continuously while loads are applied. During the creep test, the *in situ* neutron diffraction experiment was performed on LaCoO_3 cylinder sample during compression test at a constant stress of 70 MPa. The loading of the sample was performed in the load control mode with a loading rate of 3900 MPa/min until 70 MPa, and then the load was kept constant. The 70 MPa stress was chosen as it is a coercive stress for ferroelastic LaCoO_3 perovskite.²¹ The loadframe and neutron data slicing, synchronization and single peak fitting were performed using the VDRIVE software.²⁷ The collection of the data lasted for 4.17 h and 5 min data slicing was chosen based on the diffraction statistics, so a total of 50 diffraction patterns were sliced from the set of collected experimental data on creep results. After diffraction patterns were collected, both bond lengths and angles were obtained using Rietveld refinement technique. In addition, for comparison of the volume fraction of different domains as a function of ferroelastic strain obtained at a constant 70 MPa compression, the results of the gradual loading experiment that was performed in the load control mode with a loading rate of 1.3 MPa/min until 200 MPa followed by an increase of the loading rate to 7 MPa/min until 900 MPa published¹⁹ were also used in this study.

III. RESULTS

A. Creep strain

The *in situ* neutron diffraction experiments were performed on LaCoO_3 perovskite loaded in compression with a 70 MPa constant compressive stress for 4.17 h. While in previously described experiments, the temperatures of the samples, compressive platens, and the surrounding environment were not exactly controlled or recorded;²⁰ in the *in situ* neutron diffraction experiments, the compression platens were kept at the constant $18.9 \pm 0.07^\circ\text{C}$ temperature by the circulating cooling water, and the sample's temperature recorded was

also constant at $19 \pm 0.07^\circ\text{C}$, while the air in the laboratory in the vicinity of the sample was showing $22.6 \pm 0.1^\circ\text{C}$, as measured by three independent thermocouples¹⁹ [Fig. 1(c)]. Thus, as there were no temperature variations recorded during mechanical testing of the sample, there was no possibility for the thermal expansion of the sample to occur during the 4.17 h dwell time under compression. The comparison of creep data obtained during the 4.17 h testing of LaCoO_3 under compression at 70 MPa constant applied stress as measured during *in situ* neutron diffraction experiments and during simple uniaxial compression without control of temperature is shown in Fig. 2. It is worth mentioning here that the experiment, where the neutron diffraction of the sample was collected, was performed using a very high loading rate of 3900 MPa/min where the load from 0 MPa to 70 MPa was applied in 1 s, while for the experiments without collection of structural data the loading rate of 180 MPa/min was used, which might or might not be a reason for the observed difference in the creep strain behavior of the LaCoO_3 . As one can see from Fig. 2, qualitatively the behavior of LaCoO_3 is very similar in both types of the experiments and could, in principle, be explained by the difference in the loading rates of the sample to 70 MPa, where slower or faster loading rates might play a role in how fast or slow the defects could relax upon application of the load. However, the presence of the contraction (creep) followed by expansion (negative creep) of the LaCoO_3 sample under constant compressive load was recorded in both experiments.

FIG. 2. Creep strain versus time plots of the time dependent behavior of LaCoO_3 samples compressed at 70 MPa constant applied stress as measured at Queen Mary University of London, UK [(.....) and (-----) data] and VULCAN beamline at ORNL DOE, TN [(--.-.) data]. The trend lines for each creep experiment are also shown. The insert shows the stress-strain deformation curves obtained during gradual loading till 900 MPa compressive stress of LaCoO_3 . One stress strain curve (—) was obtained at 180 MPa/min continuous loading with strain monitored by the three attached strain gauges to the surface of LaCoO_3 sample at Queen Mary University of London, UK, while another stress-strain curve (-----) was obtained at 1.3 MPa/min continuous loading with strain monitored by the attached extensometer at ORNL, TN.

FIG. 3. Neutron diffraction patterns of polycrystalline LaCoO_3 collected by Bank 1 [(a), (c), (e)] and Bank 2 [(b), (d), (f)] before the sample was loaded to a 70 MPa constant applied compressive stress [(a) and (b)], in the first 5 min [(c) and (d)] and in the last 5 min of dwell time [(e) and (f)] of 4.17 h dwell time when the LaCoO_3 sample was held under a 70 MPa constant applied compressive stress.

B. Neutron diffraction

The diffraction patterns of LaCoO_3 collected during the 4.17 h of the *in situ* neutron diffraction experiments showed that all the peaks corresponded to the rhombohedral lattice ($R\bar{3}c$ space group) and did not show any additional reflections that might indicate the appearance of secondary phases (Fig. 3). The corresponding lattice parameters, characteristic bond angles, and geometric tolerance factor for LaCoO_3 before loading and during dwell time at constant 70 MPa applied stress as measured by Bank 1 and Bank 2 on the VULCAN beamline are presented in Table I. The corresponding diffraction patterns are presented that were collected before the load was applied [Figs. 3(a) and 3(b)], during the first 5 min of 70 MPa applied stress [Figs. 3(c) and 3(d)], and during the last 5 min of 70 MPa applied stress of 4.17 h dwell time [Figs. 3(e) and 3(f)] with (hkl) interplanar

spacing exposed to compressive strain (Bank 1, parallel to the loading direction) [Figs. 3(c) and 3(e)] and (hkl) interplanar spacing under tensile strain (Bank 2, perpendicular to the loading direction) [Figs. 3(d) and 3(f)], respectively. As one can see from Figs. 3(a) and 3(b), the material is isotropic at the beginning of loading, as the diffraction patterns collected by Bank 1 and 2 are identical. Such a conclusion can be made because of a significant number of different grains (up to $3 \cdot 10^9$ grains) participated in the collection of diffraction patterns in the radial and lateral directions, therefore, the data collected by Bank 1 (loading direction) and Bank 2 (transversal direction) can be correlated. As no texture and no anisotropy were detected in LaCoO_3 before loading, the data from both banks were summed and used for the calculation of average lattice parameters and characteristic bond lengths. As it was expected from the previous experiments,¹⁹ the application of stress caused the appearance of different preferred orientations of domains under the effect of the axial compressive stress and transversal tensile strain, where peak intensities in certain doublets decreased at 70 MPa, while other peak intensities grew at the expense of others. Such a strong texture developed at 70 MPa applied compressive stress with corresponding diffraction patterns of LaCoO_3 with strongly preferred orientations at the beginning and at the end of the creep strain experiments are shown in Figs. 3(c)–3(f), respectively. No significant visible changes in the lattice structure were detected over the dwell time in LaCoO_3 and the values of characteristic Co–O and La–O bond lengths and O–Co–O, O–La–O, Co–O–Co bond angles as well as geometric tolerance factor of the rhombohedral structure remain constant within measurement errors for the whole duration of the experiment (Fig. 4). Small changes in the (208)/(220) and (202)/(006) doublet intensity ratios were detected in the neutron diffraction patterns at the beginning of the creep experiment [Figs. 3(c) and 3(d)] and at the end of the creep experiment [Figs. 3(e) and 3(f)]. The intensity ratios of (208)/(220) and (202)/(006) doublets are summarized in Table II.

In the previous work,^{18,19} the evolution of the peak intensities in the LaCoO_3 was presented as a function of

TABLE I. Lattice parameters, characteristic bond lengths and bond angles, as well as geometric tolerance factor for LaCoO_3 measured for the material (a) before it was loaded to 70 MPa constant compressive stress; (b) during the first 5 min of the experiment when the 70 MPa constant compressive stress was applied; (c) during the last 5 min of the experiment when the 70 MPa constant compressive stress was held. The total experiment duration was 4.17 h, when the LaCoO_3 sample was kept under 70 MPa constant compressive stress, during which time the neutron diffraction patterns of the material were continuously collected. The data presented were measured by Bank 1 and Bank 2 at the VULCAN beamline at Oak Ridge National Laboratory, TN.

	Bank 1			Bank 2		
	Before loading	The beginning at 70 MPa	The end at 70 MPa	Before loading	The beginning at 70 MPa	The end at 70 MPa
Lattice parameter a , Å	5.44	5.439	5.44	5.44	5.443	5.443
Lattice parameter c , Å	13.09	13.087	13.089	13.09	13.095	13.095
Co–O bond length, Å	1.931	1.93	1.931	1.932	1.932	1.932
O–Co–O bond angle, deg	91.226	91.217	91.223	91.23	91.229	91.22
Co–O–Co bond angle, deg	163.92	164.025	163.911	163.776	163.808	163.967
La–O bond length, Å	2.703	2.701	2.701	2.703	2.703	2.703
O–La–O bond angle, deg	61.436	61.426	61.433	61.445	61.441	61.429
Geometric tolerance factor	0.989	0.989	0.989	0.989	0.989	0.989

FIG. 4. Changes in the Co–O bond length (a); O–Co–O bond angle (b); Co–O–Co bond angle (c); La–O bond length (d); O–La–O bond angle (e), and Geometric Tolerance Factor (GTF) (f) structural parameters presented as a function of time in LaCoO₃ that was held under 70 MPa constant applied compressive stress for 4.17 h as measured by Bank 1 and Bank 2 of VULCAN beamline at ORNL, TN.

applied stress. In this current work, the evolution of the peak intensities in the LaCoO₃ sample was analyzed as a function of ferroelastic strain ϵ_{fer} . The ferroelastic strain ϵ_{fer} was calculated as a difference $\epsilon_{fer} = \epsilon - \epsilon_{el}$ between the total strain ϵ and its elastic portion ϵ_{el} for the given run i . These peak intensities are directly correlated to the volume fractions of the related crystallographically oriented domains expressed by the equation

$$f_{hkl}^{(i)} = \frac{I_{hkl}^{D1,2}(\sigma^{(i)})/I_{hkl}^{D1,2}(\sigma^{(1)})}{\sum_{hkl} I_{hkl}^{D1,2}(\sigma^{(i)})/I_{hkl}^{D1,2}(\sigma^{(1)})}, \quad (1)$$

TABLE II. The intensity ratio of (208)/(220) and (202)/(006) doublets of LaCoO₃, showing the domain walls movement and texture formation during 4.17 h of the creep experiments, as collected by Bank 1 and Bank 2 before loading, in the first 5 min and in the last 5 min of the experiments when the LaCoO₃ sample was held at 70 MPa constant applied compressive stress.

		Before loading	The beginning at 70 MPa	The end at 70 MPa
I_{208}/I_{220}	Bank 1	1.312	2.402	2.255
	Bank 2	1.312	0.926	0.869
I_{202}/I_{006}	Bank 1	2.287	1.056	1.156
	Bank 2	2.287	4.27	3.705

where $I_{hkl}^{D1,2}(\sigma^{(i)})$ is the intensity of the (hkl) diffraction peaks collected by Bank 1 or Bank 2 for the run i , $I_{hkl}^{D1,2}(\sigma^{(1)})$ is the intensity for the first run where the load was not applied yet. Six (hkl) peaks—(006), (018), (208), (024), (202), and (220)—were chosen for the analysis of the texture development and domain wall movement in LaCoO₃ both during monotonic stress increased from 0 MPa to 240 MPa compression based on the experimental data obtained^{18,19} [Figs. 5(a) and 5(b)] and during the 4.17 h of creep experiment where the applied stress was kept constant at 70 MPa [Figs. 5(c) and 5(d)]. The elastic macrostrain ϵ_{el} was assumed to be equal to the average lattice strain measured by diffraction. While the average lattice strain assumes using all possible crystallographic directions, however, in practice, only selected crystallographic orientations can be used to obtain a good representation of all possible crystallographic directions.^{18,28,29} The number of peaks used to calculate the average lattice strain can be as low as five, where results from use of five (hkl) peaks are indistinguishable compared with the results from using seven peaks or more.²⁹ Therefore, only six peaks of LaCoO₃ were included in the average lattice strain analysis.

A volume fraction of the domains with crystallographic (006), (018), (208), (024), (202), and (220) planes perpendicular to the loading direction is presented as a function of ferroelastic strain ϵ_{fer} for the experiment with a gradual increase of applied compressive stress [Figs. 5(a) and 5(b)]. As one can see from Fig. 5, significant linear changes of the volume fractions of the domains occur when the applied compressive stress gradually increased from 0 MPa to 240 MPa at 1.3 MPa/min loading rate. The similar changes of the volume fractions of the same six crystallographically oriented domains as a function of ferroelastic strain ϵ_{fer} during 4.17 h of creep experiment are shown in Figs. 5(c) and 5(d). Such comparison of the results obtained under different loading conditions—one at a gradually increasing applied compressive stress from 0 MPa to 240 MPa at 1.3 MPa/min loading rate and another one at a constant applied compressive stress of 70 MPa for 4.17 h—was necessary to perform in order to clearly distinguish the trend of the preferential growth or decrease of volume fractions of different domains. The reason why such comparison of the two experiments with dissimilar loading history became a feasible option was that the ferroelastic strain used for the comparison of data was calculated in an identical way in both experiments. As the total strain ϵ and the elastic macrostrain ϵ_{el} coinciding with average lattice strain were directly measured using extensometer and neutron diffraction,¹⁸ respectively, during the *in situ* loading experiment, it allowed for the calculation of ferroelastic strain. In both experiments presented in Fig. 5, the volume fractions of each six (006), (018), (208), (024), (202), and (220) domains were equal to 1/6 at $\sigma^{(1)} = 0$ MPa, as the LaCoO₃ perovskite is considered to be isotropic before loading, therefore $I_{hkl}^{D1,2}(\sigma^{(i)}) = I_{hkl}^{D1,2}(\sigma^{(1)})$ at $\sigma^{(1)} = 0$ MPa.

As one can see from Fig. 5, both for the gradual loading experiment and for the constant stress creep experiment the evolution of the peak intensities depends on the Miller indices of the reflection and on the ferroelastic strain experienced by the sample. The (hkl) peaks of LaCoO₃ were classified according to the orientation of corresponding crystallographic planes

FIG. 5. Volume fractions of domains with crystallographic planes (006), (018), (208), (024), (202), and (220) oriented perpendicular to the loading direction measured during gradual compression from 0 MPa to 155 MPa (a) and during 70 MPa constant compressive stress (c) and with crystallographic planes (006), (018), (208), (024), (202), and (220) oriented parallel to the loading direction measured during gradual compression from 0 MPa to 155 MPa (b) and during 70 MPa constant compressive stress (d) plotted against ferroelastic strain $\epsilon_{fer} = \epsilon - \epsilon_{el}$. The volume fractions of domains presented in (a) and (c) were calculated using the data collected by Bank 1, and the volume fractions of domains presented in (b) and (d) were calculated using the data collected by Bank 2. The volume fractions of domains during gradual loading presented in (a) and (b) were calculated from the data published.¹⁸ The straight lines represent the trend lines of the respective volume fractions plotted against ferroelastic strain for gradual loading [(a) and (b)]. The same trend lines are shown in (a) and (c) and in (b) and (d).

perpendicular to the loading direction relative to c -axis of the lattice as it was defined.¹⁶ A significant linear increase in the volume fraction of (006) and (018) domains at the expense of (202) and (220) domains that decrease, as well as an increase in (208) and a decrease in (024) domains' volume fractions, is clearly visible for the case when ferroelastic strain varies from 0 all the way to $50 \cdot 10^{-4}$ in the case of the continuous loading experiment for Bank 1 measurements, where the resulting strain is compressive [Figs. 5(a) and 5(b)]. The opposite changes are reported for the Bank 2 measurements where the resulting strain is tensile. Then, for the Bank 2 measurements, a significant increase in the volume fraction of (220) and (202) domains at the expense of (006) and (018) domains that decrease, as well as the decrease in (208) and increase in (024) domains' volume fractions, is detected with ferroelastic strain varies from 0 at zero applied compressive stress all the way to $50 \cdot 10^{-4}$ at 155 MPa applied compressive stress when the load is continuously and gradually applied. It was found during the creep experiment that at the constant applied compressive stress of 70 MPa, the changes in the ferroelastic strain were

detectable, where ϵ_{fer} varied from $20 \cdot 10^{-4}$ to $25 \cdot 10^{-4}$ [Figs. 5(c) and 5(d)], while the elastic strain remained constant. Similar to the changes in the volume fractions of different domains during gradual loading, where the opposite tendencies of increase or decrease of fractions of domains were detected using Bank 1 and Bank 2, identical trends were observed during constant 70 MPa loading creep experiments. These changes in ferroelastic strain during creep experiments were caused by the changes in the volume fraction of the domains and corresponding f_{hkl} vs ϵ_{fer} dependences as presented in Figs. 5(c) and 5(d). For comparison, the $20 \cdot 10^{-4}$ – $25 \cdot 10^{-4}$ strain range measured in creep experiments is highlighted in the f_{hkl} vs ϵ_{fer} plots obtained in gradual loading experiments as a rectangular box [Figs. 5(a) and 5(b)]. While the experimental data are presented by symbol data points in Fig. 5, the dashed lines in Figs. 5(a) and 5(b), each corresponding to different (hkl) reflections, show the linear fit of the data for gradually increasing applied compressive stress. These linear fits, shown in Figs. 5(a) and 5(b), are translated into the plots obtained during creep experiments at 70 MPa

constant applied stress, as shown in Figs. 5(c) and 5(d), and what was surprising to find was that the corresponding lines fit very well for all (*hkl*) reflections for the Bank 2 data, as well as for the (*hkl*) reflections of Bank 1 data, in which volume fractions are decreasing, such as (024), (202), and (220). Note that Bank 1 measured (*hkl*) reflection data, which correspond to increasing volume fraction, do not fit very well with the creep experiments.

IV. DISCUSSION

As measured by *in situ* neutron diffraction, there is a change in the volume fraction of the different mobile domains during creep experiment at a constant compressive stress. This change in the fractions of domains with certain crystallographic orientation relative to the loading direction is caused by the viscous ferroelastic domain walls movement in the material driven by the external mechanical field. It was proposed that five forces can be accounted for as acting on domain walls in such a case.³⁰ These forces are (a) the configuration force F_C by the external stress; (b) the attractive or repulsive force F_I responsible for the interaction between the walls; (c) the viscous force $-\Gamma\dot{x}$ acting due to the scattering of the lattice as the walls move through the grain, where Γ is the viscous constant; (d) the recovering force $-k_0x$ by the other defects, such as oxygen vacancies or dipoles, where k_0 is the force constant; and (e) the Peierls force.^{30–33} If the domain walls are to be considered as quasiparticles with an effective mass M per unit area and the Peierls force is neglected,³¹ then the following equation of the domain wall motion is proposed

$$M\ddot{x} + \Gamma\dot{x} + k_0x - F_I = F_C, \quad (2)$$

where x is the displacement of the domain wall under the applied stress; $-\Gamma\dot{x}$ is the viscous force due to the scattering of the lattice as the walls move in the crystals; $-k_0x$ is the recovering force by the defects; M is the effective mass of the domain wall per unit area; Γ is the viscous constant; k_0 is the force constant; F_I is the interaction force among the domain walls; F_C is the configuration force by the external stress.

Equation (2) states the existence of the equilibrium position for the location of the domain walls at a given external applied load. Besides, the movement of the domain walls exhibits certain inertia and they cannot reach the equilibrium position if an external applied stress is increasing from certain smaller values to a required stress level at a certain finite loading rate. Theoretically, the domain walls can reach their equilibrium position if the change in the external applied stress occurs with an infinitely low loading rate. This equilibrium state, when domain walls are at equilibrium positions at a given external applied stress, corresponds to the equilibrium ferroelastic strain ε_{eq} , where ε_{eq} is a difference between the corresponding total strain ε and elastic deformation ε_{el} . Based on this consideration, it is possible to conclude that in the situation when the external applied stress has already reached its intended value and remains constant, the domain walls are still moving toward their equilibrium positions and the ferroelastic strain ε_{fer} has still not reached its corresponding equilibrium value ε_{eq} . If the external applied stress is kept constant, the domain walls will continue

their movement toward their equilibrium positions and ε_{fer} will approach toward its equilibrium value ε_{eq} . Such conclusions are fully consistent with the results about room temperature creep of LaCoO₃-based perovskites published.²¹ Moreover, the phenomenological model developed²¹ can be used to calculate the characteristic time τ both for pure LaCoO₃ and for La_{0.8}Ca_{0.2}CoO₃ perovskites, where the characteristic time τ is an important room temperature creep parameter providing the values of the time required to reach a strain located halfway between the instantaneous and equilibrium strain at some constant stress.²¹

The characteristic time is to be used for the evaluation of how fast ferroelastic creep will occur in a ferroelastic material and it shows that the ferroelastic creep will be faster for the material with a smaller characteristic time, given that the instantaneous strain and equilibrium strain values are the same for the material under consideration. It was determined that domain walls movement, responsible for domain switching and appearance of room-temperature time dependent behavior at constant applied stress, determine the characteristic time, which depends on the switching rate or how fast the walls move. Calculations based on the developed phenomenological model²¹ estimated that the characteristic switching time is much shorter for pure LaCoO₃ in comparison with La_{0.8}Ca_{0.2}CoO₃. As τ is much smaller in LaCoO₃, it means that the domain walls are much more mobile and freer to move faster, as compared to La_{0.8}Ca_{0.2}CoO₃. The reason for such differences can be found if one estimates the availability of oxygen vacancies in the two perovskite compositions. According to thermogravimetric measurements, the LaCoO₃ is near stoichiometric,^{34,35} thus if oxygen vacancies and their complexes exist in LaCoO₃ it could be only due to minute temperature fluctuations within the material. At the same time, Ca²⁺ doping brings a significant amount of oxygen vacancies and La_{0.8}Ca_{0.2}CoO_{3- δ} becomes nonstoichiometric with the oxygen deficiency δ value reaching rather high values.³⁴ Therefore, such availability of the point defects that easily form different complexes, such as dipoles, with surrounding ions, could be a reason of the significant differences in the characteristic time τ for the domain walls movement of pure and Ca²⁺ doped LaCoO₃ reported.²¹ At the same time, the availability of these point defects and their complexes could tremendously affect both the value of the loss modulus and also the area of the hysteresis obtained during stress-strain measurements of the mechanical behavior of cobaltites in comparison, as reported.²⁰

Equation (2) could be represented by a simple mechanical model that includes a spring pendulum with a damped mechanical oscillator (Fig. 6). This equation allows different solutions for a damped mechanical oscillator and also for the movement of domain walls depending on the materials' parameters, such as temperature, stress, rhombohedral distortion of the lattice, domain wall density, availability of other defects, such as oxygen vacancies and the complexes affecting the mobility of domain walls or different impurities, the interactions both among domain walls themselves and among domain walls and other defects present in the structure. Equation (2) can provide three different solutions, when one

FIG. 6. A schematic representation of the simplified mechanical model that includes a spring pendulum with damping (damped mechanical oscillator) used in the explanation of the creep strain room-temperature time dependent behavior of LaCoO_3 .

solution can be found as damped oscillations about the equilibrium position [Fig. 7(a)]. If such damped oscillations are absent, then the other solutions that Eq. (2) provides would be the approach of the domain walls to the equilibrium position either from one side of their original location [Fig. 7(b)] or, if the domain walls are highly mobile, then they could jump through the equilibrium position, but then return back

FIG. 7. A schematic graphical representation for the three solutions of the domain walls motion equation. (a) Damped oscillations of domain wall about its equilibrium position; (b) domain wall approaching the equilibrium position from one side of its original location; (c) domain wall jumps through the equilibrium position followed by its return back approaching the equilibrium position from the opposite side.

approaching the equilibrium position from the opposite side [Fig. 7(c)]. The solution of Eq. (2) shown in Fig. 7(b) obviously represents the creep strain behavior, while the solution presented in Fig. 7(c) could be easily explained by negative creep. This “negative creep” situation is possible if, when the constant applied load is established, the domain walls have a velocity sufficient to make a jump through the equilibrium position. Such a situation can be realized if the domain walls in the material have rather low inertia, e.g., low effective mass M , and high mobility. Based on the data presented,^{34,35} LaCoO_3 is rather stoichiometric, which means that not only do the domain walls have minimal interactions with oxygen vacancies, but also the oxygen vacancies cannot segregate along or at the domain walls^{10,36} as there are very few of them in near stoichiometric pure LaCoO_3 . Thus, domain walls have high mobility, smaller effective mass, and low inertia in LaCoO_3 , which results in their higher velocity and shorter distance to equilibrium position at the moment of “creep”/“negative creep” process onset. The high mobility, smaller effective mass, and low inertia of domain walls in LaCoO_3 are also confirmed by much shorter characteristic time. Both “creep” and “negative creep” room-temperature time dependent behavior of LaCoO_3 based ceramics have the same driving force, i.e., the movement of domain wall to equilibrium position. The difference is only in the velocity of domain wall and its distance to equilibrium position at the moment of “creep”/“negative creep” process onset. If the domain wall has enough velocity and small distance to equilibrium position to jump over this position, there is “negative creep” behavior. Otherwise, there is “creep” behavior.

V. CONCLUSIONS

The unusual room temperature time dependent mechanical behavior of LaCoO_3 based perovskite ceramics was detected during compression experiments under the external constant applied stress of 70 MPa. Both the shrinkage (creep strain) and the expansion (negative creep strain) of the LaCoO_3 under applied compressive stress were measured as a function of time. The *in situ* neutron diffraction experiment was performed to clarify the unusual time dependent deformation and to measure the changes in LaCoO_3 structure which occur during dwell time under constant compressive stress. The movement of the domain walls leading to the texture formation was detected during 4.17 h of the experiment when the LaCoO_3 sample was compressed at 70 MPa and continuous neutron diffraction patterns were collected at the same time.

It was discussed that the available internal forces acting on ferroelastic domain walls in LaCoO_3 during application of external constant applied stress affect their viscous movement driven by the external mechanical field. The equation of the domain wall motion that accounts for all of these internal forces implies the existence of the equilibrium position of the domain walls at any given external applied stress. However, in practice, because of their inertia, the domain walls cannot reach equilibrium positions, thus creating the situation where the external applied stress is already at its desired value and remains constant, but the domain walls are still moving toward their equilibrium positions. They can theoretically

reach equilibrium positions by damped oscillating motion about the equilibrium. They can approach the equilibrium position from one side of their original location, which would correspond to the creep strain during time dependent deformation. They can also jump through the equilibrium position forward, but then return back approaching the equilibrium position from the opposite side, which would correspond to the negative creep strain in LaCoO₃ time dependent deformation. It was predicted that the domain walls in LaCoO₃ are relatively mobile with a low effective mass, due to a small number of the point defects and have a high mobility with very short characteristic time for the domain switching and domain wall movement. Thus, the negative creep strain situation is possible to occur during room-temperature time dependent deformation of LaCoO₃ at a constant applied external stress.

ACKNOWLEDGMENTS

This work was supported by the NSF Project No. CMMI-0968911 “Time Dependent Creep Deformation of Nonpolar Mixed Conducting Ferroelastic Perovskites.” Neutron scattering was carried out at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory, which is one of the user facilities sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. The authors thank Mr. H. D. Skorpenske from SNS for the technical support of the neutron experiment.

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¹N. Orlovskaya, Y. Gogotsi, M. Reece, B. Cheng, and I. Gibson, *Acta Mater.* **50**, 715 (2002).

²N. Orlovskaya, N. Browning, and A. Nicholls, *Acta Mater.* **51**, 5063 (2003).

³N. Orlovskaya, H. Anderson, M. Brodnikovskyy, M. Lugovy, and M. Reece, *J. Appl. Phys.* **100**, 026102 (2006).

⁴D. Zhou and M. Kamlah, *Acta Mater.* **54**, 1389 (2006).

⁵T. Fett and G. Thun, *J. Mater. Sci. Lett.* **17**, 1929 (1998).

⁶J. S. Forrester and E. H. Kisi, *J. Eur. Ceram. Soc.* **24**, 595 (2004).

⁷E. C. Subbarao, M. C. McQuarrie, and W. R. Buessem, *J. Appl. Phys.* **28**, 1194 (1957).

⁸K. B. Chong, F. Guiu, and M. J. Reece, *J. Appl. Phys.* **103**, 014101 (2008).

⁹G. Metrat, *Ferroelectrics* **26**, 801 (1980).

¹⁰J. F. Scott, E. K. Salje, and M. A. Carpenter, *Phys. Rev. Lett.* **109**, 187601 (2012).

¹¹J. C. Walmsley, A. Bardal, K. Kleveland, M. A. Einarsrud, and T. Grande, *J. Mater. Sci.* **35**, 4251 (2000).

¹²P. E. Vullum, R. Holmestad, H. L. Lein, J. Mastin, M. A. Einarsrud, and T. Grande, *Adv. Mater.* **19**, 4399 (2007).

¹³P. E. Vullum, H. L. Lein, M. A. Einarsrud, T. Grande, and R. Holmestad, *Philos. Mag.* **88**, 1187 (2008).

¹⁴S. Faaland, T. Grande, M. A. Einarsrud, P. E. Vullum, and R. Holmestad, *J. Am. Ceram. Soc.* **88**, 726 (2005).

¹⁵B. X. Huang, R. W. Steinbrech, and J. Malzbender, *Solid State Ion.* **228**, 32 (2012).

¹⁶P. E. Vullum, J. Mastin, J. Wright, M. A. Einarsrud, R. Holmestad, and T. Grande, *Acta Mater.* **54**, 2615 (2006).

¹⁷A. Aman, R. Jordan, Y. Chen, R. Stadelmann, M. Lugovy, N. Orlovskaya, E. A. Payzant, C. dela Cruz, M. J. Reece, T. Graule, and J. Kuebler, *J. Eur. Ceram. Soc.* **37**, 1563 (2017).

¹⁸M. Lugovy, A. Aman, Y. Chen, N. Orlovskaya, J. Kuebler, T. Graule, M. J. Reece, D. Ma, A. D. Stoica, and K. An, *J. Appl. Phys.* **116**, 013504 (2014).

¹⁹A. Aman, Y. Chen, M. Lugovy, N. Orlovskaya, M. J. Reece, D. Ma, A. D. Stoica, and K. An, *J. Appl. Phys.* **116**, 013503 (2014).

²⁰M. Lugovy, N. Orlovskaya, S. Pathak, M. Radovic, E. Lara-Curzio, D. Verbylo, J. Kuebler, T. Graule, and M. J. Reece, *J. Appl. Phys.* **124**, 205103 (2018).

²¹M. Lugovy, V. Slyunyayev, N. Orlovskaya, D. Verbylo, and M. J. Reece, *Phys. Rev. B* **78**, 024107 (2008).

²²W. Araki, T. Abe, and Y. Arai, *J. Appl. Phys.* **116**, 043513 (2014).

²³N. Orlovskaya, M. Lugovy, S. Pathak, D. Steinmetz, J. Lloyd, L. Fegely, M. Radovic, E. A. Payzant, E. Lara-Curzio, L. F. Allard, and J. Kuebler, *J. Power Sources* **182**, 230 (2008).

²⁴X. L. Wang, T. M. Holden, A. D. Stoica, K. An, H. D. Skorpenske, A. B. Jones, G. Q. Rennich, and E. B. Iverson, *Mater. Sci. Forum* **652**, 105 (2010).

²⁵K. An, H. D. Skorpenske, A. D. Stoica, D. Ma, X. L. Wang, and E. Cakmak, *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.* **42**, 95 (2011).

²⁶R. Riedel, SNS Report No. 107030200-TD005-R04, Oak Ridge National Laboratory, Oak Ridge, TN, 2007.

²⁷K. An, Oak Ridge National Laboratory Report No. ORNL-TM-2012-621, 2012.

²⁸M. R. Daymond, M. A. Bourke, and R. B. Von Dreele, *J. Appl. Phys.* **85**, 739 (1999).

²⁹M. R. Daymond, *J. Appl. Phys.* **96**, 4263 (2004).

³⁰Z. Liu, X. Chen, H. Shen, Y. Wang, H. Young, and P. C. Fung, *Phys. Status Solidi A Appl. Mat.* **116**, K199 (1989).

³¹J. A. Combs and S. Yip, *Phys. Rev. B* **28**, 6873 (1983).

³²Y. N. Huang, Y. N. Wang, and H. M. Shen, *Phys. Rev. B* **46**, 3290 (1992).

³³Y. N. Wang, Y. N. Huang, H. M. Shen, and Z. F. Zhang, *J. Phys. IV* **6**, 505 (1996).

³⁴J. Mastin, M. A. Einarsrud, and T. Grande, *Chem. Mat.* **18**, 1680 (2006).

³⁵V. Oygarden and T. Grande, *Dalton Trans.* **42**, 2704 (2013).

³⁶W. L. Warren, K. Vanheusden, D. Dimos, G. E. Pike, and B. A. Tuttle, *J. Am. Ceram. Soc.* **79**, 536 (1996).