Arch. Metall. Mater., Vol. 61 (2016), No 3, p. 1733–1738

DOI: 10.1515/amm-2016-0272

XIU SHENG WU*, JU FANG CAO*, ZHI JUN CHEN**, WEI LIU**,#

LOW-FREQUENCY MECHANICAL SPECTROSCOPY OF LANTHANUM COBALTITE BASED MIXED CONDUCTING OXIDES

The low-frequency mechanical spectra of lanthanum cobaltite based mixed conducting oxides have been measured using a computer-controlled inverted torsion pendulum. The results indicate that the internal friction spectra and shear modulus depend on the Sr doping contents (x). For undoped samples, no internal friction peak is observed. However, for $La_{0.8}Sr_{0.2}CoO_{3-\delta}$, three internal friction peaks (P2, P3 and P4) are observed. In addition to these peaks, two more peaks (P0 and P1) are observed in $La_{0.6}Sr_{0.4}CoO_{3-\delta}$. The P0 and P1 peaks show characteristics of a phase transition, while the P2, P3 and P4 peaks are of relaxation-type. Our analysis suggests that the P0 peak is due to a phase separation and the P1 peak is related to the ferromagnetic–paramagnetic phase transition. The P2, P3 and P4 peaks are associated with the motion of domain walls. The formation of this kind of domain structure is a consequence of a transformation from the paraelastic cubic phase to the ferroelastic rhombohedral phase. With partial substitution of Fe for Co, only one peak is observed, which is discussed as a result of different microstructure.

Keywords: Mixed conducting oxides, mechanical properties, domain structure, phase transition, mechanical spectroscopy, internal friction

1. Introduction

The lanthanum cobaltite based perovskites have attracted much attention for their many important properties, such as high electrical and ionic conductivity [1,2], colossal magnetoresistance (CMR) [3,4] and spin-state transition [5]. Owing to their mixed conducting characteristics, these oxides are promising for the applications of high temperature oxygen separation membranes and cathodes in solid oxide fuel cells (SOFCs) [2,6]. When partially substituting A site lanthanum cations by other metal cations with lower valences such as Sr^{2+}, the formation of oxygen vacancies and a change in the valence state of the B ions usually occur in order to maintain the charge neutrality [1]. Despite the number of publications on the oxygen permeability of the lanthanum cobaltite based perovskites, just a few concerned the mechanical properties of these materials. Recently, a few publications on the ferroelasticity and elastic hysteresis of these materials have appeared [7-14]. Generally, ferroelastic domain switching and phase transformation could be responsible for the non-elastic deformation [10]. Orlovskaya [10] recorded the dynamics of domains by an in-situ high temperature TEM study: the de-twinning during heating and the reappearance of domains during cooling. By using in-situ synchrotron X-ray diffraction, Vullum demonstrated that in $La_{0.8}Ca_{0.2}CoO_3$ ceramics the reorientation of ferroelastic domains were due to the uniaxial stress [12]. In the rhombohedral $La_{0.6}Sr_{0.4}FeO_3$ perovskite, a similar non-elastic deformation behavior in compression was observed, however, no domain/twin structure was found [15].

When the lanthanum cobaltite based ceramics are used as cathodes and membranes, cracking caused by thermal cycling through the structural transformations could seriously damage the membranes. A basic understanding of the origin of ferroelastic properties is not currently available for the lanthanum cobaltite and other mixed conductors. The internal friction technique [16-21] has been proved as a very sensitive tool to investigate microscopic relaxation processes and phase transitions in perovskites [22-26]. In this study, we present the results of mechanical loss (internal friction) measurements on $La_{1-x}Sr_xCo(Fe)O_{3-\delta}$ $(0\leq x \leq 0.6)$ ceramics. In addition, resistivity and magnetization measurements are carried out to clarify the nature of internal friction peaks.

2. Experimental

$La_{1-x}Sr_xCo(Fe)O_{3-\delta}$ $(0\leq x \leq 0.6)$ powders were prepared via a citrate route. Two aqueous solutions of iron nitrate and cobalt nitrate were firstly prepared and analyzed by titrations to determine the concentration of Fe and Co ions. Then appropriate amounts of La_2O_3 (99.9%) and $SrCO_3$ (>99.0%), both of which were completely dissolved in diluted nitric acid, were mixed with iron nitrate and cobalt nitrate solutions. After a clear solution was formed, citric acid was added at a molar ratio of citric acid: metal ions = 1.5:1.0, followed by adjusting

---

* ANHUI KEY LABORATORY OF ADVANCED BUILDING MATERIALS, SCHOOL OF MATERIALS AND CHEMICAL ENGINEERING, ANHUI JIANZHU UNIVERSITY, HEFEI, ANHUI 230601, CHINA

** LABORATORY OF ADVANCED FUNCTIONAL MATERIALS AND DEVICES, DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING, UNIVERSITY OF SCIENCE AND TECHNOLOGY OF CHINA, HEFEI, ANHUI 230022, CHINA

Corresponding author: awliu@ustc.edu.cn

the pH value to 2-3. The solution was subsequently stirred and evaporated at 80°C until a formation of polymeric precursor occurred, which was burned in air to remove the organic contents. The resulting ash was ground to fine powder and calcined at 1050°C in air for 5 h. The powder was uniaxially pressed into bars at 150MPa, subsequently isostatically pressed at 300MPa and sintered in air at 1250°C for 10 h to obtain the bar-shaped samples (35.0×4.0×1.2 mm^3).

The phase composition of the calcined powder was analyzed by XRD (Philips X'Pert Pro Super, CuK). The electrical resistivity was measured by standard four-probe technique. The zero-field-cooled (ZFC) magnetization was measured in an external magnetic field of 100Oe using a commercial quantum device (superconducting quantum interference device; Quantum Design MPMSXL). The internal friction, Q^{-1}, and shear modulus, M, were measured in a computer-controlled automatic inverted torsion pendulum using forced oscillations with the maximum torsion strain amplitude kept at 1.5×10^{-5} in the temperature range from 120 to 650K.

3. Results and discussion

XRD experimental results reveal that all the samples were crystallized in single phase and exhibit a rhombohedrally distorted perovskite structure with $R\bar{3}c$ symmetry. Figures 1-3 show the temperature dependence of internal friction, Q^{-1}, and shear modulus, M, in the samples of $LaCoO_3$, $La_{0.8}Sr_{0.2}Co_{3-\delta}$ and $La_{0.6}Sr_{0.4}Co_{3-\delta}$, respectively. It is evident that the temperature dependent internal friction and shear modulus vary with the Sr doping contents (x). For the $LaCoO_3$, no obvious internal friction peak is observed, but for the Sr doped sample, three low-frequency internal friction peaks (marked P2, P3 and P4) are observed. These peaks are of relaxation type, with peak maxima shifting to higher temperatures for higher frequencies. For the $La_{0.6}Sr_{0.4}Co_{3-\delta}$, two other small peaks are found (marked P0 and P1), which are located at around 180K and 255K (Fig. 3). These two peaks do not shift with frequency, suggesting they are caused by phase transitions. To our knowledge, no structure phase transition occurs in this temperature range. Thus there may be other reasons for these two peaks. In order to identify the origins of P0 and P1 peaks, the measurements of the magnetic and electric transport properties of the $La_{0.6}Sr_{0.4}Co_{3-\delta}$ sample were carried out (Fig. 4). As the temperature increases, the ZFC magnetization rises steadily below 250 K and then drops sharply at around 250 K, consistently with a ferromagnetic - paramagnetic phase transition. This is in agreement with the published results [4]. The electric resistivity shows a monotonic increase with a change of slope at the Curie temperature Tc, which is considered as a result of spin-disorder scattering. Combining the results of magnetization and resistivity, shown in Fig. 4, we suggest that the P1 peak at 255 K may be related with a magnetic transition, while the P0 peak may originate from other mechanisms. It is well known that there is a competition of FM dominated superexchange interaction between Co^{3+} and Co^{3+} and AF dominated double exchange interaction between Co^{3+} and Co^{4+} in the $La_{1-x}Sr_xCoO_3$ system. Thus, the frustration may exist in the FM region even at temperatures close to Tc so that the whole system is not in a true ferromagnetic state. In fact, a coexistence of a hole-rich ferromagnetic phase and a hole-poor cluster glasslike phase have been suggested below Tc by NMR and ac magnetic studies [27,28]. Considering these results, it is tentatively suggested that the whole system is inhomogeneous at the temperature below Tc and there are some hole-poor clusters. These clusters grew with the decrease in temperature, resulting a cluster glasslike phase at about 180K. That is to say, the sample may undergo a phase separation at this temperature, which causes the P0 peak. An internal friction peak originated from phase separation is also reported in manganite oxides [24,26].

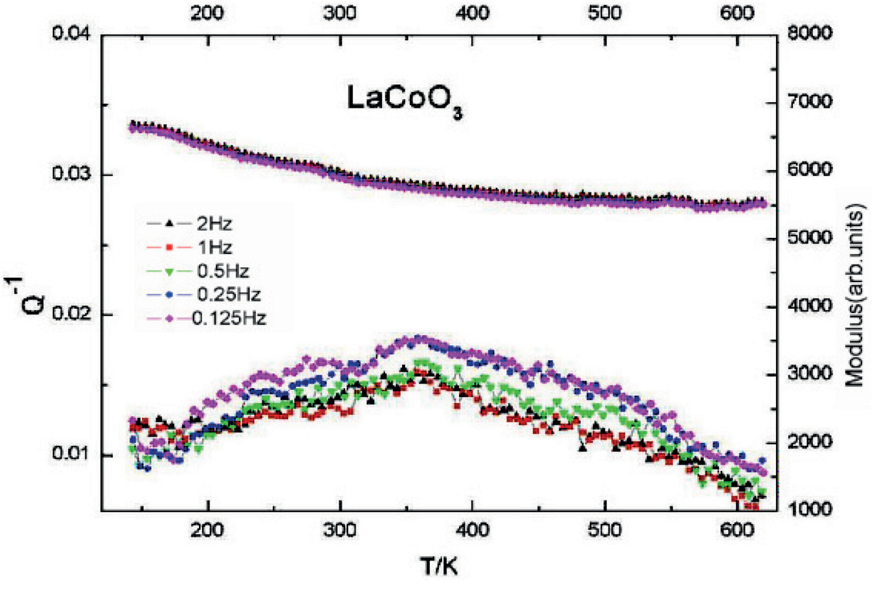

Fig. 1. Temperature dependence of the shear modulus and internal friction of $LaCoO_3$ ceramics at various frequencies: 0.125Hz, 0.25Hz, 0.5Hz, 1Hz, and 2Hz

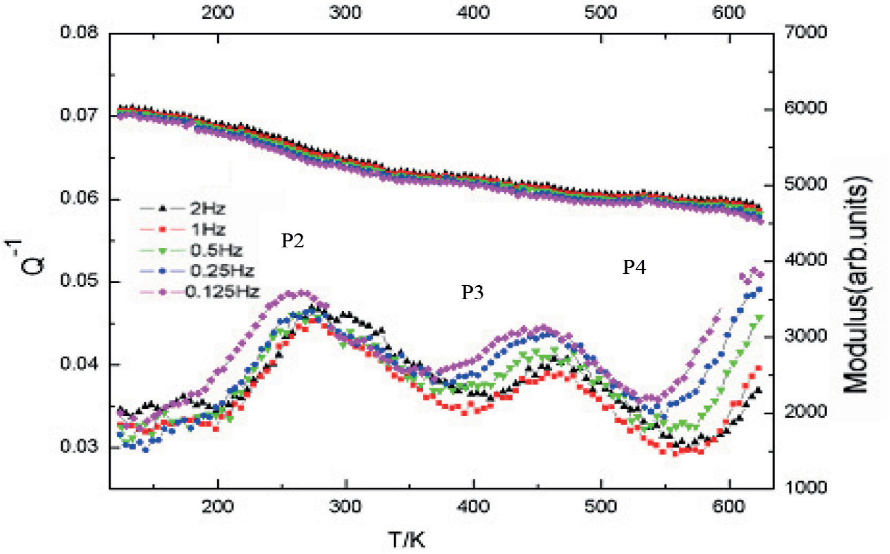

Fig. 2. Temperature dependence of the shear modulus and internal friction of La$_{0.8}$Sr$_{0.2}$CoO$_{3-\delta}$ ceramics at various frequencies:0.125Hz, 0.25Hz, 0.5Hz, 1Hz, and 2Hz

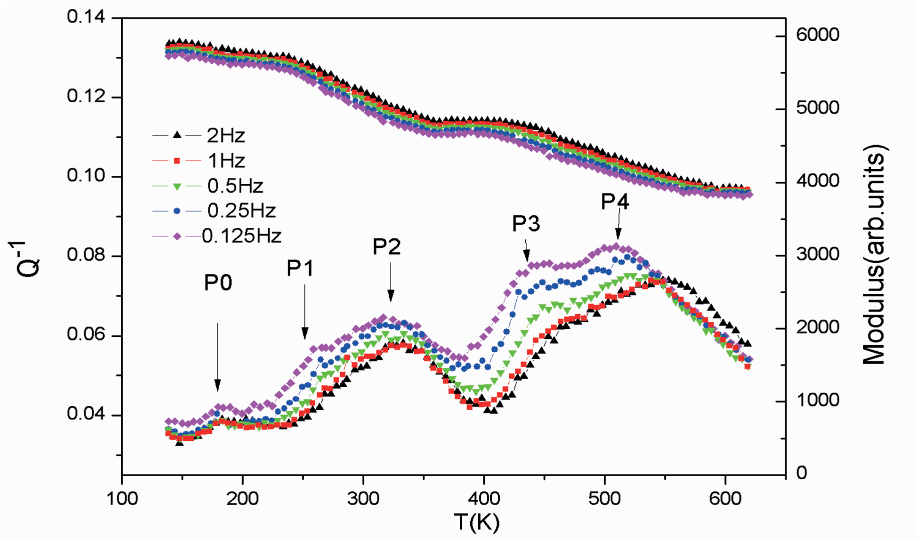

Fig. 3. Temperature dependence of the shear modulus and internal friction of La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ ceramics at various frequencies: 0.125Hz, 0.25Hz, 0.5Hz, 1Hz, and 2Hz

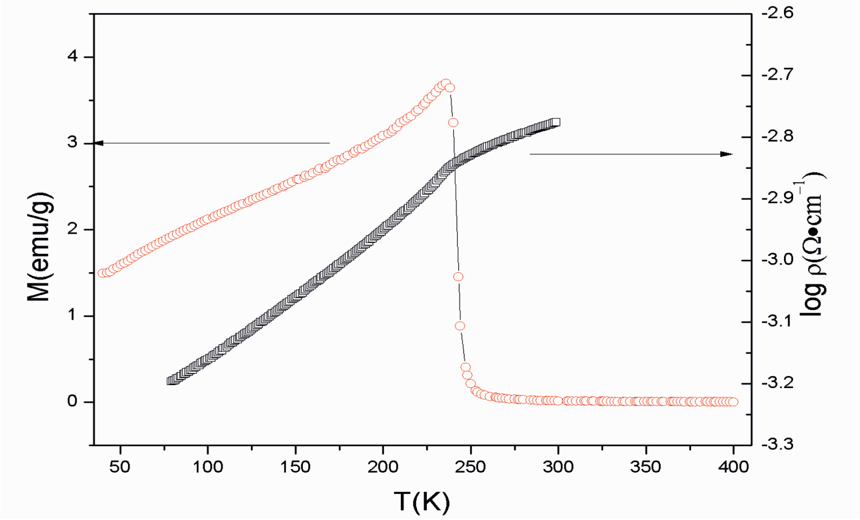

Fig. 4. The variation of the magnetization [M(T)] in a field of 100 Oe (zero-field-cooled and taken on heating) and the logarithm of the resistivity (on heating) as a function of temperature for La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$

Comparing with the P0 and P1 peaks, the other three internal friction peaks are much broader in $Q^{-1}(T)$. It has been reported that $LaCoO_3$ based perovskites exhibit non-linear stress-strain behavior and non-elastic deformation behavior [7-14]. At high temperatures, the $LaCoO_3$ based perovskites have an ideal cubic space group of $Pm\bar{3}m$, and undergo a transition from a cubic to a rhombohedral phase with a space group of $R\bar{3}c$ at a critical temperature, driven by a rotation and a compression of the CoO_6-octahedra along one of the four individual body diagonals of the cubic unit cell. Due to the choice of four equivalent triad axes about which octahedral rotation, transformation twins and domain walls can be formed, which have been confirmed by TEM [10].

These relaxation internal friction peaks may be attributed to the motion of the domain walls. In the high-temperature cubic phase, the grain is almost free from twins. When the temperature decreases to a critical point, the system undergoes a phase transition from cubic to rhombohedral symmetry. For the $La_{0.6}Sr_{0.4}CoO_3$, this critical temperature is approximately at 673K. The phase transition is accompanied by the formation of twins and domains. The P4 peak could be attributed to the movement of domain walls, which have to withstand the frictional force exerted by lattice defects and/or the Peierls force associated with moving a wall of finite thickness through a discrete lattice. With the decrease in temperature, the mobility of domain walls decreases and domain walls eventually becomes

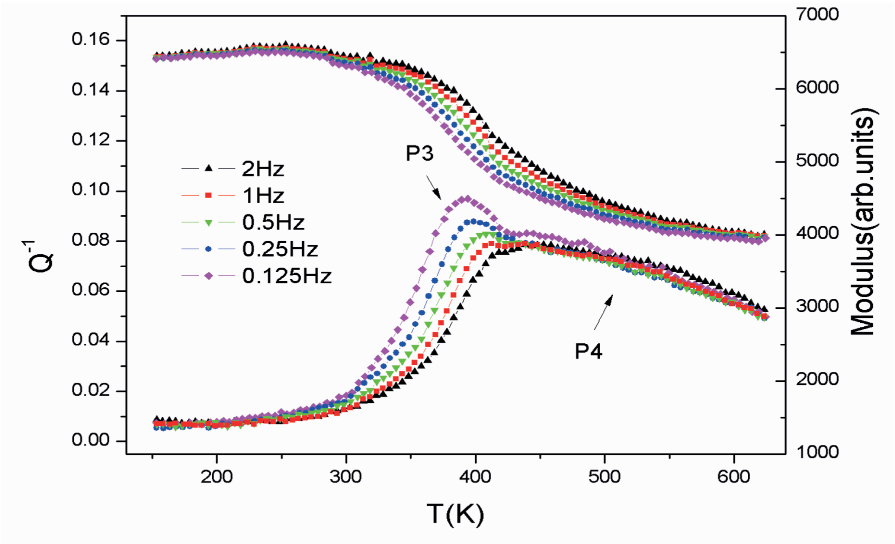

Fig. 5. Temperature dependence of the shear modulus and internal friction of $La_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ at various frequencies: 0.125Hz, 0.25Hz, 0.5Hz, 1Hz, and 2Hz

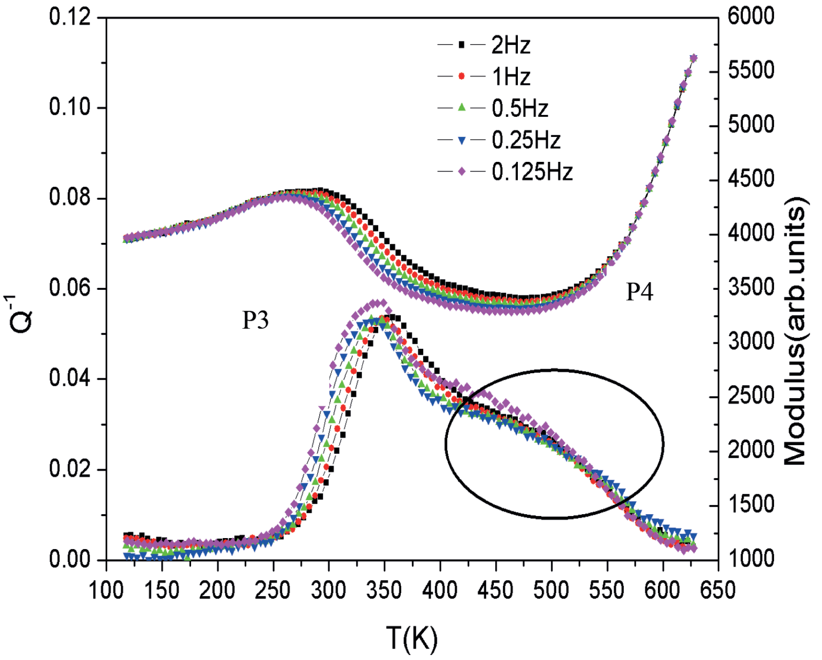

Fig. 6. Temperature dependence of the shear modulus and internal friction of $La_{0.4}Sr_{0.6}Fe_{0.5}O_{3-\delta}$ at various frequencies: 0.125Hz, 0.25Hz, 0.5Hz, 1Hz, and 2Hz

immobile. The domain walls motion is a relaxation process, and, thus, a pronounced internal friction peak P4 is observed. This phenomenon is very similar to those of $LaAlO_3$ [29] and $Ca_{1-x}Sr_xTiO_3$ [30] reported by Harrison and co-workers. For the $LaCoO_3$-based perovskites, an in-situ TEM observation was carried out by Orlovskaya. Different types of domains, such as long domains and short parallel domains oriented at 180° to each other were observed [10]. Upon heating, the 180° domains were found to be the most unstable and mobile, but other long domains were stable. Therefore, we suggest that the P2 and P3 peaks may originate from the movement of the different domain walls.

In order to improve mechanical strength and structure stability at relatively low-oxygen partial pressure, the partial substitution of the Fe for Co in the lanthanum cobaltite based ceramics was conducted. The temperature dependent internal friction and shear modulus of the $La_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ and $La_{0.4}Sr_{0.6}Fe_{0.5}O_{3-\delta}$ are shown in Figs. 5 and 6. Only one peak is observed in the Fe doped samples. At the high-temperature side of this peak, an obvious hump is observed, which suggests the existence of another peak. In comparison with Figs. 1-3, the internal friction peak shown in Figs. 5 and 6 corresponds to the P3 peak, and the hump is related to the P4 peak. The variation of modulus in Fig. 6 is larger than those in Figs. 1, 2, 3, and 5. The large increase in the shear modulus is related to a phase transition from high temperature cubic paraelastic phase to low temperature rhombohedral ferroelastic phase.

Since the ionic radius of Fe ions is larger than that of Co ions, the substitution involves a tilting of the octahedrons and increases the distortion of the perovskite cells. It is known that the formation of the transformation twins and domain originates from the choice of four equivalent triad axes that the octahedral rotation could occur. This is why the tilting of the octahedrons may have a significant effect on the formation of the domain state, leading to a different microstructure. In fact, in the $La_{0.6}Sr_{0.4}FeO_3$, no domains, twins, antiphase boundaries, stacking faults, and other planar defects were observed [15], which is different from the $LaCoO_3$ based perovskites. Thus in the Fe doped samples, different mechanical loss spectra are observed, and the P2 internal friction peak is absent. However, it should be pointed out that the effect of Fe doping on the formation of the transformation twins and domains is not fully understood as yet. Different conclusions have been drawn through different experimental conditions. Recently, the microstructural evidence of domains in rhombohedral $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ is confirmed by SEM and TEM studies [31]. More detailed studies are needed to further clarify the nature of the domain walls.

4. Summary

Five internal friction peaks are observed depending on Fe and Sr doping contents in the $La_{1-x}Sr_xCo(Fe)O_{3-\delta}$ perovskites: three relaxation peaks and two phase transition peaks. The P1 peak is correlated with paramagnetic–ferromagnetic transition; the P0 peak, located below Tc, may originate from a phase separation. At higher temperatures, the system undergoes a transition from cubic to rhombohedral phase on cooling, accompanied by the formation of transformation twins. The three relaxation peaks may be related to the viscous motion of transformation twin domain walls. The present results demonstrate that the domain motion is responsible for the non-elastic deformation of lanthanum cobaltite based mixed conducting oxides.

Acknowledgement

The research was supported by the National Natural Science Foundation of China (Grant No. 11204406).

REFERENCES

[1] A.J. Burggraaf, L. Cot, Dense ceramic membranes for oxygen separation, Fundamentals of Inorganic Membrane Science and Technology, First ed., Elsevier, Amsterdam, 1996.

[2] Y. Teraka, H.M. Zhang, S. Furukawa, N. Yamazoe, Oxygen permeation through perovskite-type oxides, Chemistry Lett. **14,** 1743-1746 (1985).

[3] R. Mahendiran, A.K. Raychaudhuri, A. Chainami, D.D. Sarma, The large magnetoresistance of $La_{1-x}Sr_xCoO_3$ at low temperatures, J. Phys.: Condens. Matter. **7,** L561-L565 (1995).

[4] M.A. Senaris-Rodriguez, J.B. Goodenough, Magnetic and transport properties of the system $La_{1-x}Sr_xCoO_{3-\delta}$ ($0 < x \leq 0.50$), J. Solid State Chem. **118**, 323-336 (1995).

[5] A. Alonso, M.J. Martinez-Lopez, C. de la Calle, V. Pomjakushin, Preparation and structural study from neutron diffraction data of $RCoO_3$ (R = Pr, Tb, Dy, Ho, Er, Tm, Yb, Lu) perovskites, J. Mater. Chem. **16**, 1555-1560 (2006).

[6] C.H. Chen, H.J.M. Bouwmeester, R.H.E. van Doorn, H. Kruidhof, A.J. Burggraaf, Oxygen permeation of $La_{0.3}Sr_{0.7}CoO_{3-\delta}$, Solid State Ionics **98**, 3-13 (1997).

[7] N. Orlovskaya, K. Kleveland, T. Grande, M.-A. Einarsrud, Mechanical properties of LaCoO3 based ceramics, J. Eur. Ceram. Soc. **20**, 51-56 (2000).

[8] K. Kleveland, N. Orlovskaya, T. Grande, A.M.M. Moe, M.-A. Einarsrud, K. Breder, G. Gogotsi, Ferroelastic behavior of $LaCoO_3$-based ceramics, J. Am. Ceram. Soc. **84**, 2029-2033 (2001).

[9] N. Orlovskaya, Y. Gogotsi, M. Reece, B. Cheng, I. Gibson, Ferroelasticity and hysteresis in $LaCoO_3$ based perovskites, Acta Mater. **50**, 715-723 (2002).

[10] N. Orlovskaya, N. Browning, A. Nicholls, Ferroelasticity in mixed conducting $LaCoO_3$ based perovskites: A ferroelastic phase transition, Acta Mater. **51**, 5063-5071 (2003).

[11] N. Orlovskaya, D. Steinmetz, S. Yarmolenko, D. Pai, J. Sankar, J. Goodenough, Detection of temperature- and stress-induced modifications of $LaCoO_3$ by micro-Raman spectroscopy, Phys. Rev. B **72** 014122-1-7 (2005).

[12] P.E. Vullum, J. Mastin, J. Wright, M.-A. Einarsrud, R. Holmestad, T.R. Grande, In-situ synchrotron X-ray diffraction of ferroelastic La0.8$Ca_{0.2}CoO_3$ ceramics during uniaxial compression, Acta Mater. **54**, 2615-2624 (2006).

[13] N. Orlovskaya, M. Lugovy, S. Pathak, D. Steinmetz, J. Lloyd, L. Fegely, M. Radovic, E.A. Payzant, E. Lara-Curzio, L.F.

Allard, J. Kuebler, Thermal and mechanical properties of $LaCoO_3$ and La0.8$Ca_{0.2}CoO_3$ perovskites, J. Power Sources **182**, 230-239 (2008).

[14] M. Selten, G.A. Schneider, V. Knoblauch, R.M. McMeeking, On the evolution of the linear material properties of PZT during loading history - an experimental study, Int. J. Solids Struct. **42**, 3953-3966 (2005).

[15] N. Orlovskaya, H. Anderson, M. Brodnikovskyy, M. Lugovy, M.J. Reece, Inelastic deformation behavior of $La_{0.6}Sr_{0.4}FeO_3$ perovskite, J. App. Phys. **100**, 026102 (2006).

[16] A.S. Nowick, B.S. Berry, Anelastic Relaxation in Crystalline Solids, Academic Press, New York, 1972.

[17] R. De Batist, Internal Friction of Structural Defects in Crystalline Solids, North-Holland, Amsterdam, 1972.

[18] L.B. Magalas, Mechanical spectroscopy – Fundamentals, Sol. St. Phen. **89**, 1-22 (2003).

[19] S. Etienne, S. Elkoun, L. David, L.B. Magalas, Mechanical spectroscopy and other relaxation spectroscopies, Sol. St. Phen. **89**, 31-66 (2003).

[20] R. Schaller, G. Fantozzi, G. Gremaud (Eds.), Mechanical Spectroscopy Q-1 2001, Materials Science Forum 366-368 (2001).

[21] L.B. Magalas, Mechanical spectroscopy, internal friction and ultrasonic attenuation. Collection of works, Mater. Sci. Eng. A **521-522**, 405-415 (2009).

[22] W.L. Warren, K. Vanheusden. D. Dimos, G.E. Pike, B.A. Tuttle, Oxygen vacancy motion in perovskite oxides, J. Am. Cerm. Soc. **79**, 536-538 (1996).

[23] Q.F. Fang, X.P Wang, Mechanical and dielectric relaxation studies on the mechanism of oxygen ion diffusion in $La_2Mo_2O_9$, Phys. Rev. B **65**, 064304 (2002).

[24] Y.Q. Ma, W.H. Song, R.L. Zhang, J.M. Dai, J. Yang, J.J. Du, Y.P. Sun, C.Z. Bi, Y.J. Ge, X.G. Qiu, Internal friction evidence of the intrinsic inhomogeneity in $La_{0.67}Ca_{0.33}MnO_3$ at low temperatures, Phys. Rev. B **69**, 134404 (2004).

[25] X.S. Wu, Y.B. Zuo, J.H. Li, C.S. Chen, W. Liu, Low-frequency internal friction study of phase transitions in $La_{1/3}Sr_{2/3}FeO_{3-\delta}$ ceramics, J. Alloys Compd. **462**, 432-435 (2008).

[26] W.J. Lu, Y.P. Sun, B.C. Zhao, X.B. Zhu, W.H. Song, Inhomogeneous strain and phase coexistence in $Bi_{0.4}Ca_{0.6}MnO_3$, Phys. Rev. **B 73**, 214409 (2006).

[27] D.N.H. Nam, K. Jonason, P. Nordblad, N.V. Khiem, N.X. Phuc, Coexistence of ferromagnetic and glassy behavior in the $La_{0.5}Sr_{0.5}CoO_3$ perovskite compound, Phys. Rev. **B 59**, 4189 (1999).

[28] P.L. Kuhns, M.J.R. Hoch, W.G. Moulton, A.P. Reyes, J. Wu, C. Leighton, Magnetic phase separation in $La_{1-x}Sr_xCoO_3$ by ^{59}Co nuclear magnetic resonance, Phys. Rev. Lett. **91**, 127202-1–127202-4 (2003).

[29] R.J. Harrison, S.A.T. Redfern, The influence of transformation twins on the seismic-frequency elastic and anelastic properties of perovskite: dynamical mechanical analysis of single crystal $LaAlO_3$, Phys. Earth Planet. Int. **134**, 253-272 (2002).

[30] R.J. Harrison, S.A.T. Redfern, J. Street, The effect of transformation twins on the seismic-frequency mechanical properties of polycrystalline $Ca_{1-x}Sr_xTiO_3$ perovskite, American Mineralogist **88**, 574-582 (2003).

[31] B.X. Huang, J. Malzbender, R.W. Steinbrech, E. Wessel, H.J. Penkalla, L. Singheiser, Mechanical aspects of ferro-elastic behavior and phase composition of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, J. Membr. Sci. **349**, 183-188 (2010).