Mechanical behavior of $La_{1-x}Ca_xCoO_3$ perovskites as a function of Ca doping

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Introduction

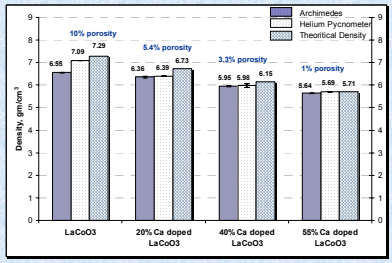
$LaCoO_3$ based perovskites are important materials for advanced energy applications. Their mechanical performance is very essential for the development of stable and reliable energy devices, such as SOFCs, oxygen separation membranes, sensors and catalysts.

The mechanical properties such as Young's modulus, strength, fracture toughness, coefficient of thermal expansion, loss modulus, and deformation behavior have been studied in this work. The materials used in the work were pure $LaCoO_3$, and 20, 40 and 55% Ca doped $LaCoO_3$.

Materials

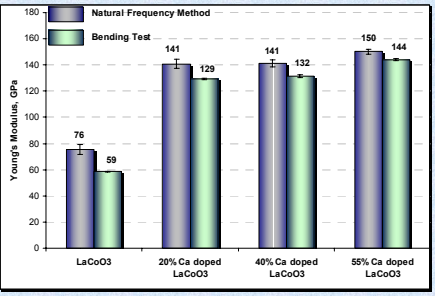
Four compositions of polycrystalline ceramics were sintered at Praxair Surface Technologies, Specialty Ceramics, Praxair Inc., USA.

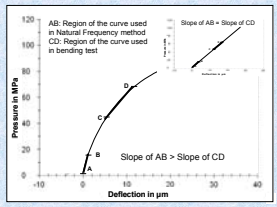
The X-ray analysis has shown that pure and 20% Ca doped $LaCoO_3$ compositions are phase pure rhombohedral perovskites. Small amounts of secondary phases have been detected in 40 and 55% Ca doped $LaCoO_3$ compositions.



The porosity of pure $LaCoO_3$ has been measured to be around 10%. The Ca doped cobaltites have been sintered to much higher densities of 95-98% of theoretical density.

Young's modulus



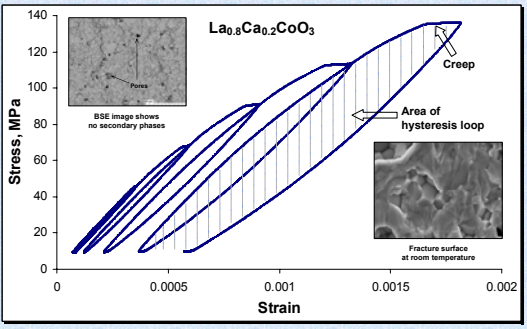


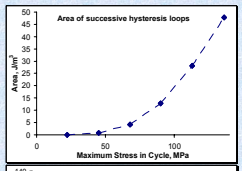
Schematic curve for cobaltites (non elastic).
Insert: Schematic curve for an elastic material

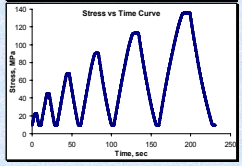
Young's modulus of $LaCoO_3$ based perovskites were measured by two different methods—Natural frequency and Bending tests. The difference between the values obtained by the two methods can be explained by the non-elastic behavior of cobaltites during loading.

In the natural frequency method, the load applied on the sample is very small (region AB in Figure). However, in the bending test, due to experimental limitations, considerably higher values of load (region CD in Figure) are used to measure the Young's modulus. Since the cobaltites exhibit non-elastic behavior during loading, the slope of CD is much lower, and as a result, Young's modulus calculated by bending test method is lower. In case of an elastic material, we would get same values for modulus in both methods.

Hysteresis in 20% Ca doped $LaCoO_3$





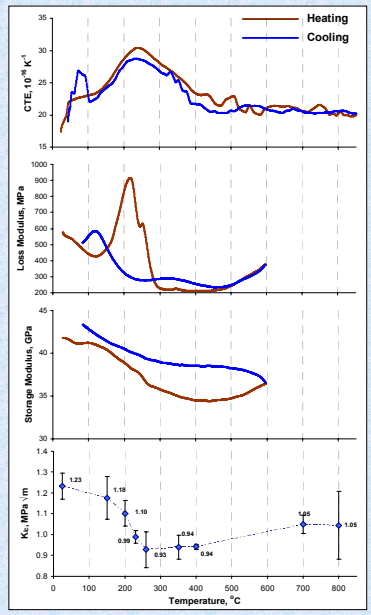


The distinctively pronounced non elastic behavior was exhibited by 20% Ca doped $LaCoO_3$ using incremental loading in four-point bending. These hysteresis loops can be explained by the movement of twin domain boundaries that exist in the rhombohedral $LaCoO_3$ based ceramics. Such mechanically activated displacement of domain walls leads to the dissipation of energy during cycling which is reflected in the stress-strain hysteresis.

Acknowledgement

•The work at Drexel, Philadelphia, USA and EMPA, Dübendorf, Switzerland was supported by NSF, DMR (project #0201770).
•We would like to thank Roland Bächtold of EMPA, Dübendorf, Switzerland, for his help with the bending and K_{Ic} testing.
•The research at Oak Ridge National Laboratory was supported by NSF, DMR (project #0201770) and in part by an appointment to the Department of Energy's Faculty and Student Teams program. This research was also supported in part by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR Vehicle Technologies, as a part of the High Temperature Materials Laboratory User Program, Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract # DE-AC 05-00OR 22725. We would also like to thank John Lloyd for his help with TMA and DMA tests at ORNL.

$LaCoO_3$



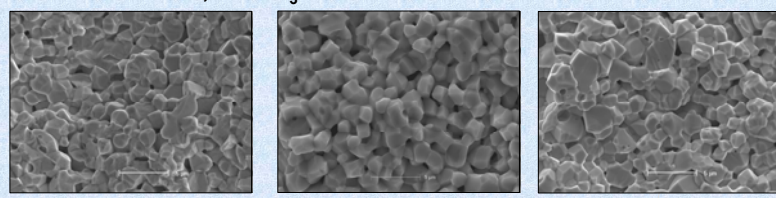
➢ Average CTE of pure $LaCoO_3$ is 22-23 x10^{-6} K^{-1} up to 1000°C. There is an increase in CTE to 30x10^{-6} K^{-1} at 230°C. This can be explained either by the intermediate to high spin state transition of Co^{3+} ion, or the monoclinic↔rhombohedral phase transition.

➢ The loss modulus exhibits two peaks at 220°C and 250°C, which coincide with an increase in CTE and hardening/softening of the storage modulus. This is due to mobility of the twin domain walls and formation of oxygen vacancies in $LaCoO_3$.

➢There is a decrease of storage modulus upon heating from 42 GPa (RT) to 37 GPa (600°C). The minimum value of storage modulus is equal to 34 GPa (450°C). The local hardening occurs at ~70°C, followed by an additional softening at 276°C.

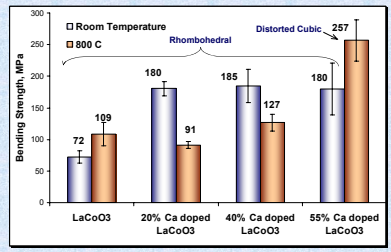
➢While an increase of K_{Ic} would be expected with increase in loss modulus, this is not observed in the 200-250°C temp range. In fact the shape of the storage modulus curve resembles the fracture toughness plot very closely. There is a minimum K_{Ic} = 0.93±0.08 MPa√m at 260°C.

Fracture Surfaces, $LaCoO_3$

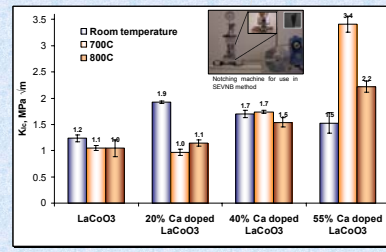


Room temperature | 230°C | 800°C

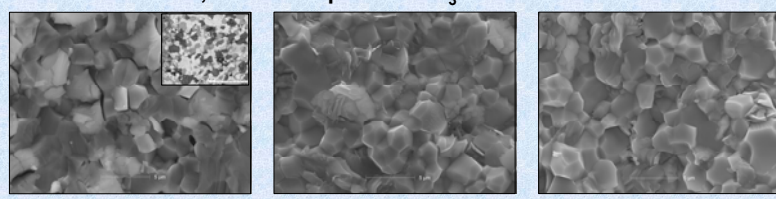
Bending Strength



Fracture Toughness



Fracture Surfaces, 55% Ca doped $LaCoO_3$



Room temperature
Insert: BSE image showing Secondary phases | 700°C | 800°C

Conclusions

➢ The mechanical properties of $LaCoO_3$ based perovskites with 0, 20, 40 and 55% Ca doping have been studied in this work. The Young's modulus, strength, fracture toughness, CTE, loss modulus and stress strain curves have been measured.

➢ A significant deviation from elastic behavior has been detected in $La_{0.8}Ca_{0.2}CoO_3$ perovskite during bending tests. Possible creep has also been observed at the maximum load during cyclic loading of the samples at room temperature.

➢The fracture toughness of pure $LaCoO_3$ decreased with increasing temperature. The decrease in K_{Ic} coincides with softening of Young's Modulus as temperature increases.

➢The high temperature mechanical behavior of the $LaCoO_3$ based perovskites depends on the amount of Ca doping. For 55% Ca doped $LaCoO_3$ composition, a significant increase in strength and fracture toughness were measured at 800°C compared to RT. Such increase can be explained by the influence of secondary phases in the composition.