Mechanical behavior and microstructure of $La_{0.6}Sr_{0.4}FeO_3$ perovskites

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Objectives

- **Investigate the mechanical behavior of $La_{0.6}Sr_{0.4}FeO_3$ perovskites**
- **Demonstrate a ferroelastic behavior by uniaxial compression**
- **Study deformation behavior, hardness, and Young's modulus by depth sensing indentation**
- **Characterize the microstructure of $La_{0.6}Sr_{0.4}FeO_3$ perovskites by TEM**

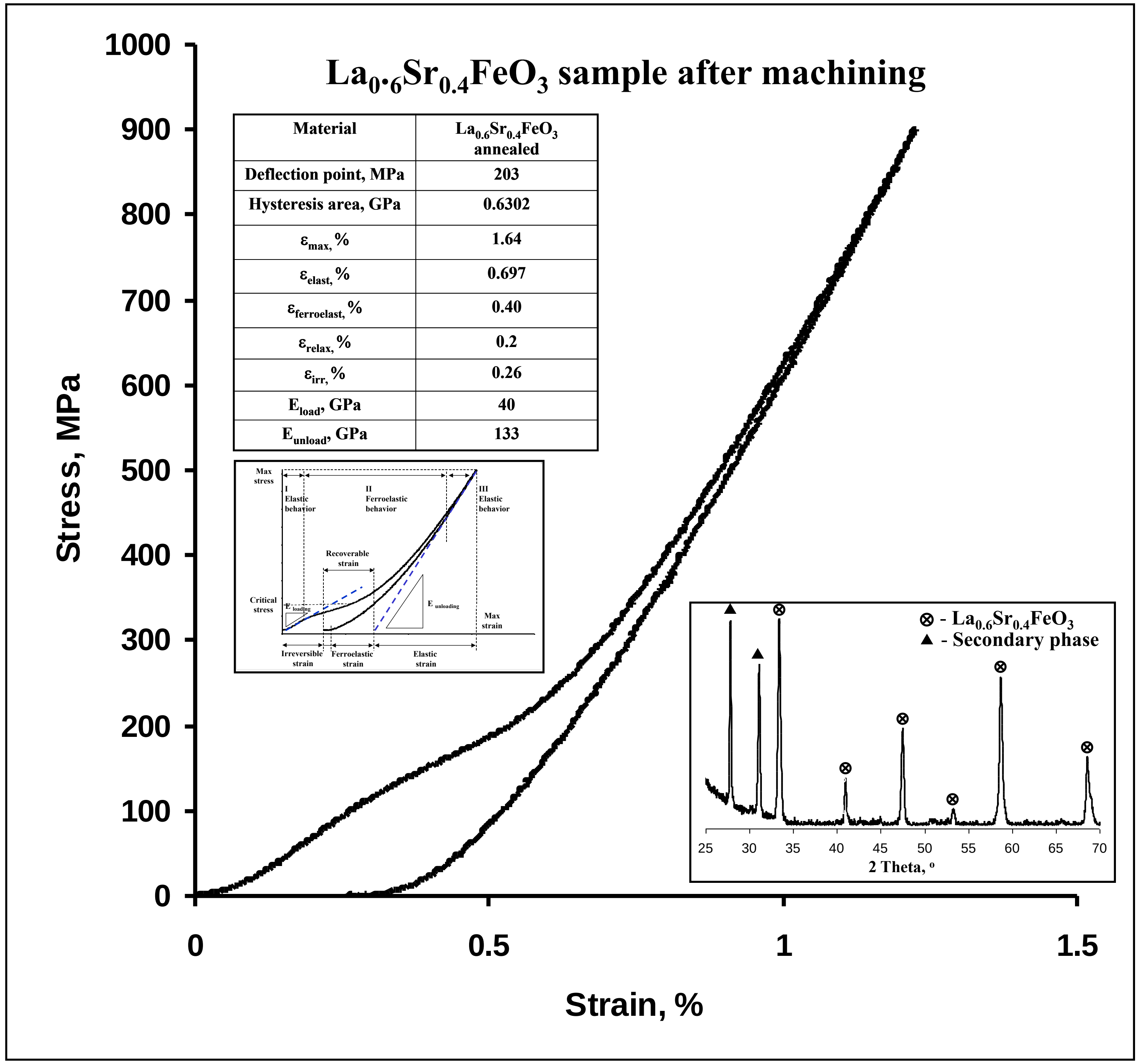
Material and Experiments

- Polycrystalline perovskite ceramics with a nominal composition $La_{0.6}Sr_{0.4}FeO_3$ was studied
- Instron universal testing machine was used to perform compression experiments
- Nanoindenter XP was used to study the mechanical response of perovskite under contact loading
- JEOL JEM-3010 microscope was used for TEM
- Environmental SEM was used to characterize Berkovich residual impressions

Material Processing

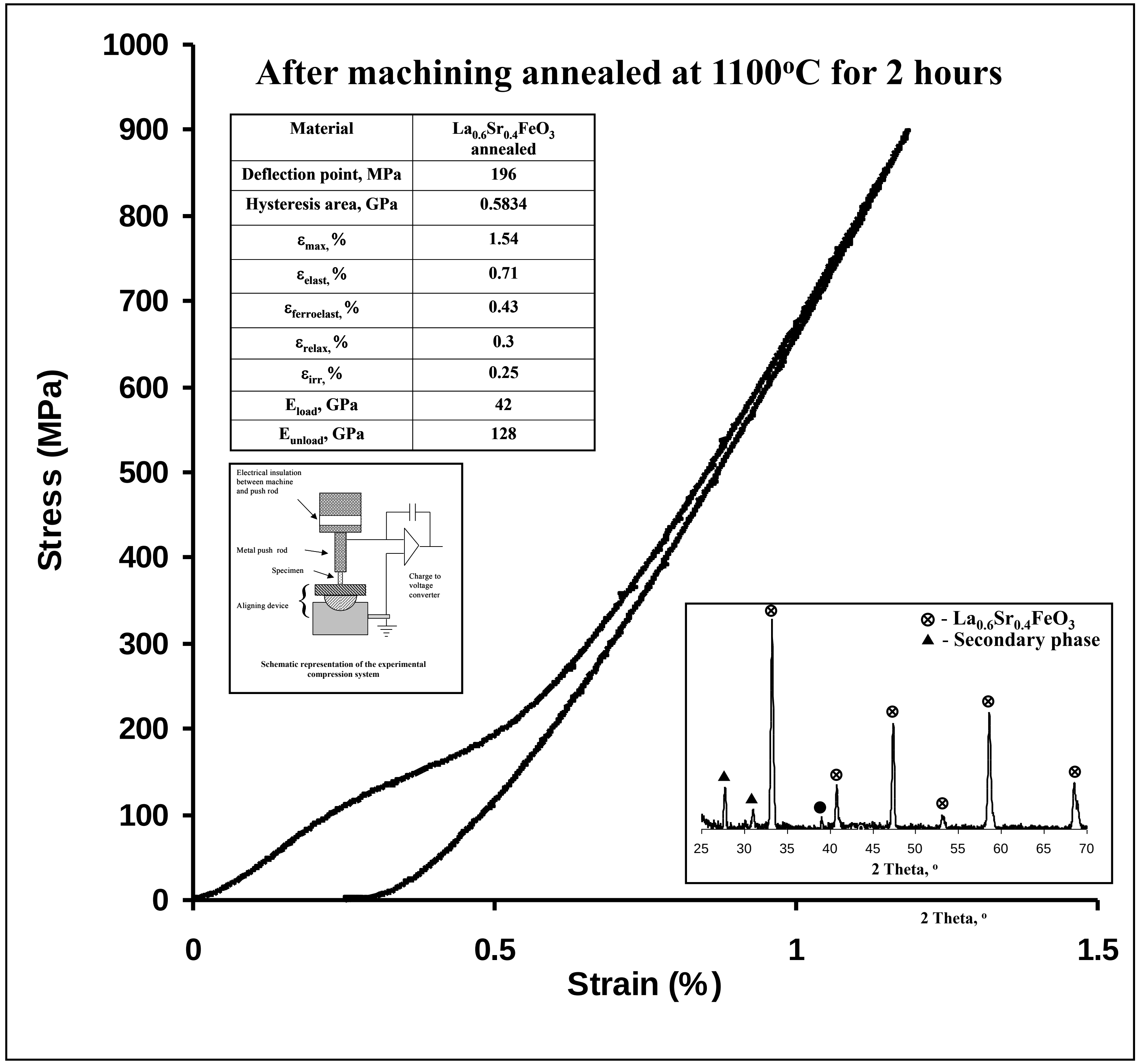
The liquid-mixing method was used to prepare $La_{0.6}Sr_{0.4}FeO_3$ fine powders. An aqueous solution of Fe nitrate was first prepared and thermogravimetrically standardized. Reagent grade lanthanum carbonate, strontium carbonate and known ratios of nitrate solutions of Fe were then mixed to form a clear solution. Citric acid and ethylene glycol were added into nitrate solution and heated slowly to form a polymeric precursor. The latter was heated to 250^{o}C to form an amorphous resin. Calcination of the pulverized resin was carried out at 800^{o}C for 8 hours. The resulting powders were isostatically pressed at 207 MPa to form powder compacts. The compacts were heated in air at 1200^{o}C to obtain sintered densities of grater than 95% of theoretical.

Ferroelastic behavior in compression



$La_{0\cdot6}Sr_{0.4}FeO_3$ sample after machining

Material	$La_{0.6}Sr_{0.4}FeO_3$ annealed
Deflection point, MPa	203
Hysteresis area, GPa	0.6302
ε_{max}, %	1.64
ε_{elast}, %	0.697
$\varepsilon_{ferroelast}$, %	0.40
ε_{relax}, %	0.2
ε_{irr}, %	0.26
E_{load}, GPa	40
E_{unload}, GPa	133



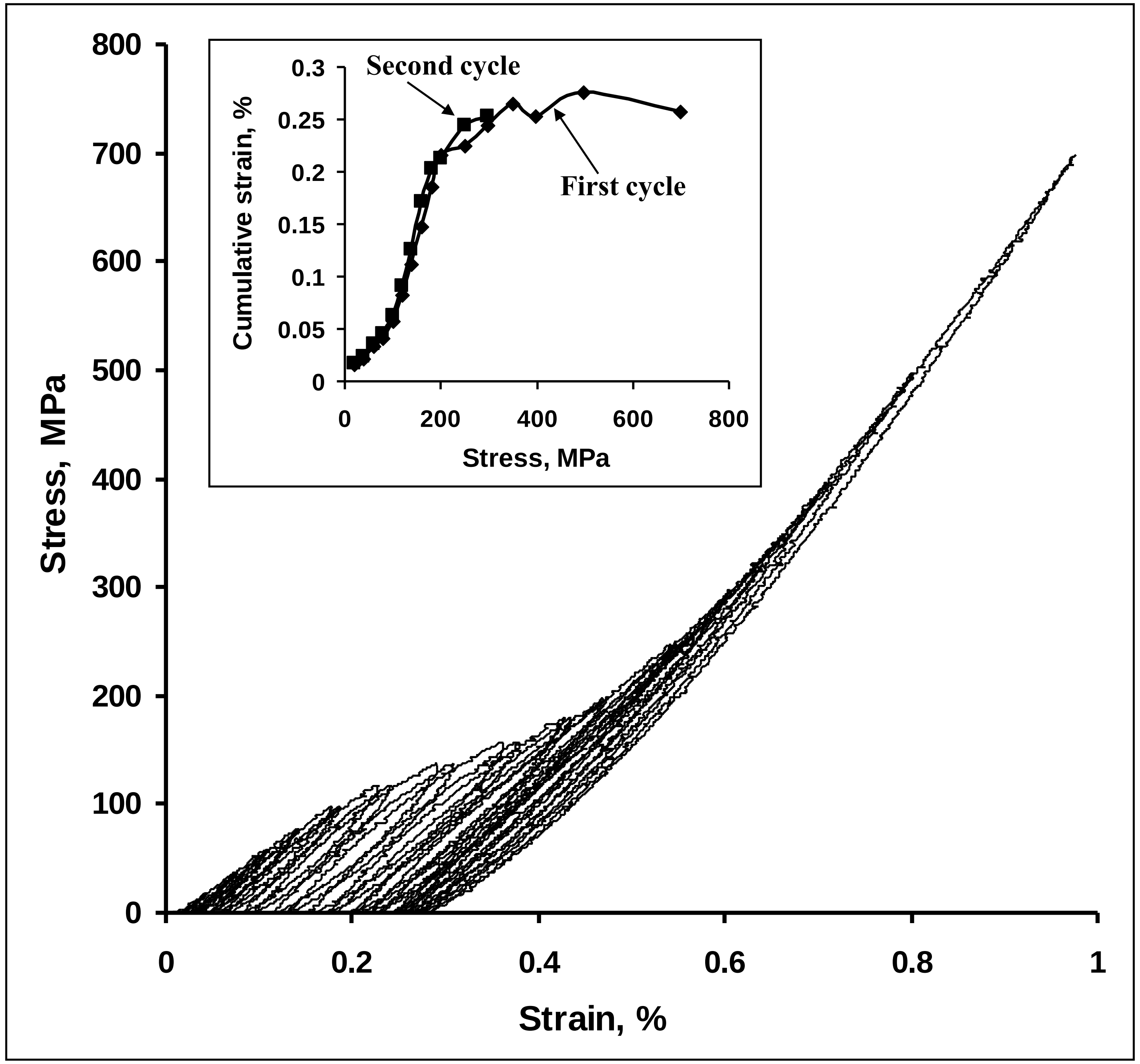
After machining annealed at 1100°C for 2 hours

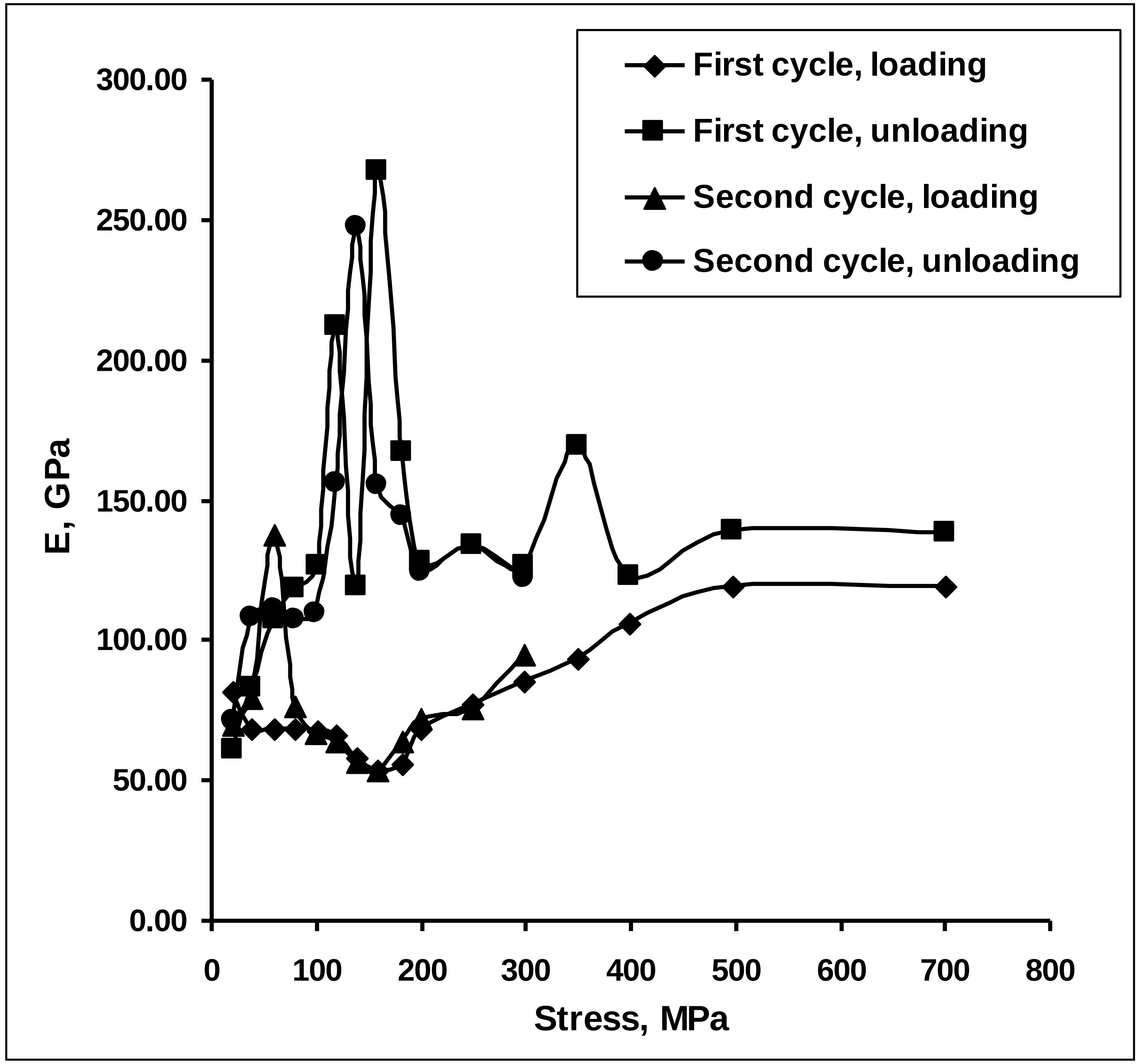
Material	$La_{0.6}Sr_{0.4}FeO_3$ annealed
Deflection point, MPa	196
Hysteresis area, GPa	0.5834
ε_{max}, %	1.54
ε_{elast}, %	0.71
$\varepsilon_{ferroelast}$, %	0.43
ε_{relax}, %	0.3
ε_{irr}, %	0.25
E_{load}, GPa	42
E_{unload}, GPa	128

Schematic representation of the experimental compression system

Nonlinear ferroelastic behavior with a high irreversible strain (ε_{irr} = 0.25% for the machined surface and 0.26% for the annealed surface) was observed after compression in dense $La_{0.8}Ca_{0.2}CoO_3$.

Ferroelastic behavior in cycling compression





The ferroelastic behavior and stress-strain hysteresis was observed in cycling compression. The Young's modulus calculated from the beginning of loading and unloading curves also shows the hysteretic behavior with significant differences in the 100-200MPa stress region.

Our work demonstrates ferroelastic hysteretic behavior in $La_{0.6}Sr_{0.4}FeO_3$ polycrystalline perovskite during compression. However, the origin of stress/strain hysteresis in this material is not clearly understood at the moment. The two factors are typically contribute to ferroelastic behavior: a) a phase transition between the paraelastic and ferroelastic phase during cooling that create lattice distortion; b) this lattice distortion can be reoriented by external stress. Though the crystallographic symmetry of this material was determined to be rhombohedral (space group $R\bar{3}c$), the rhombohedral distortion is very small. No splitting of the {110} and {104} doublets could be detected with XRD. This is in a perfect agreement with TEM results, where the majority of $La_{0.6}Sr_{0.4}FeO_3$ grains are single domains with no twins present. Therefore, twinning/detwinning during compression cannot contribute to the stress/strain hysteresis loops.

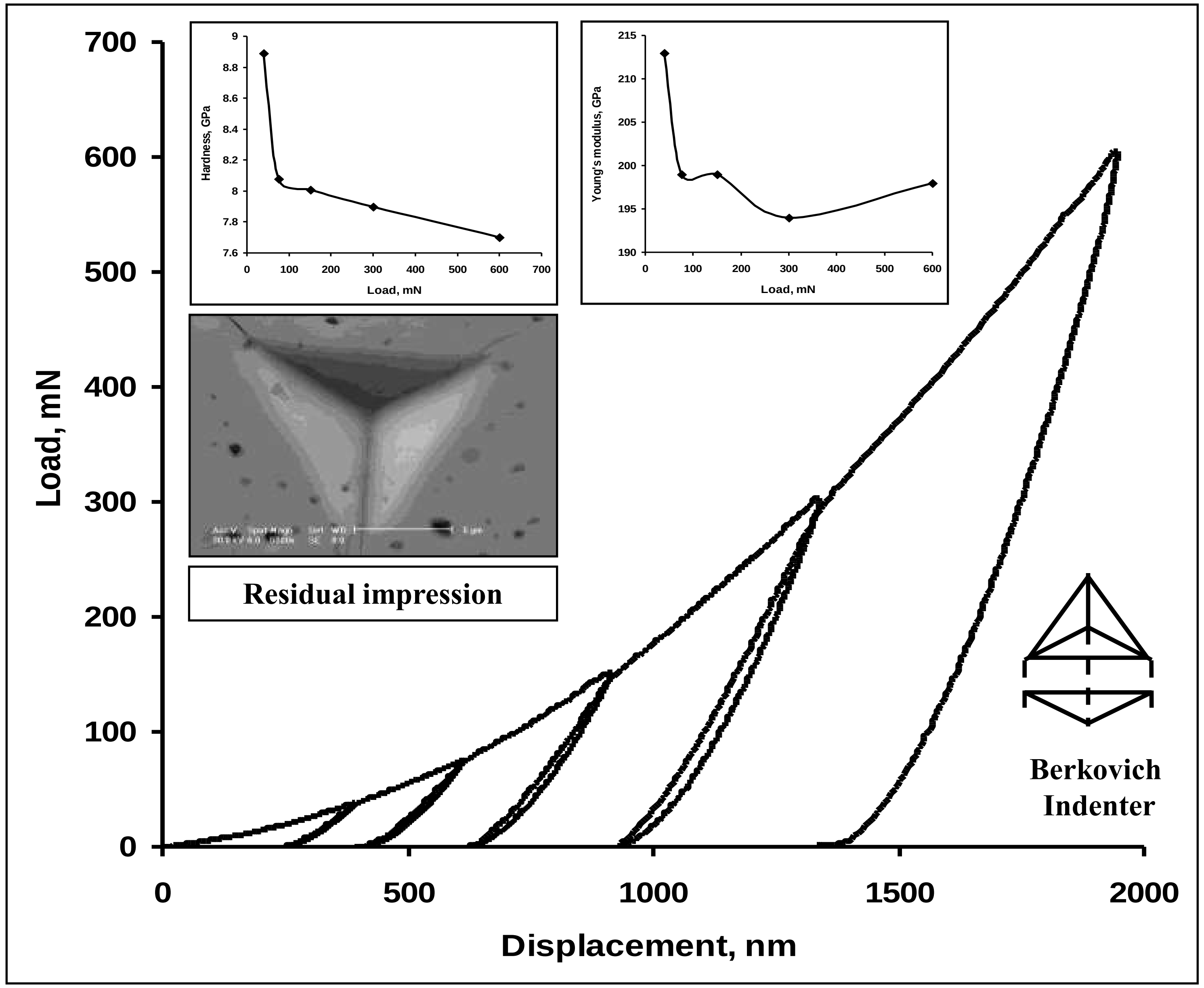
Here we propose that several other mechanisms could potentially be responsible for the $La_{0.6}Sr_{0.4}FeO_3$ ferroelastic behavior:

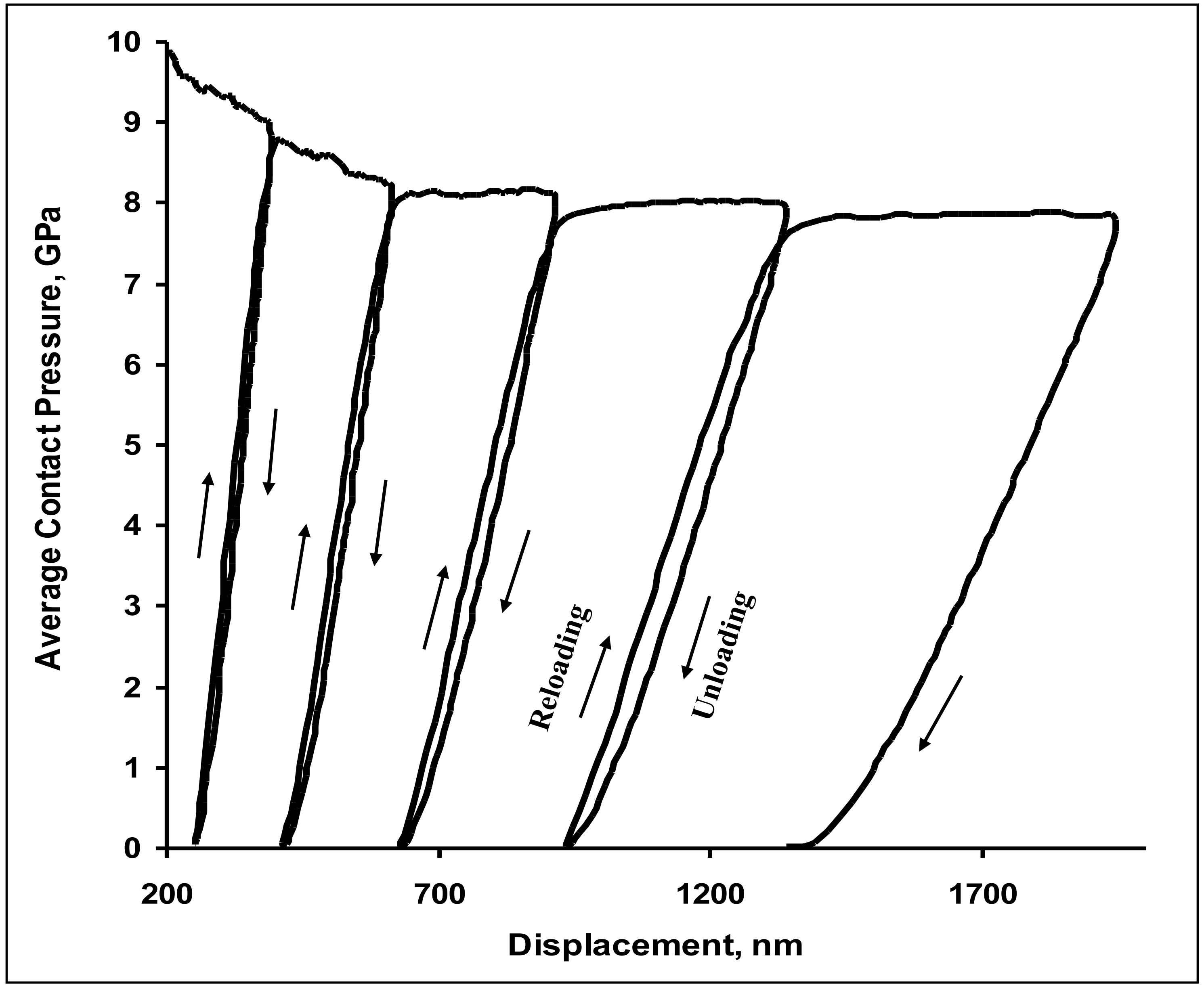
1) *In-situ* phase transition during loading;

2) Dislocation movement;

3) Grain rotation during compression;

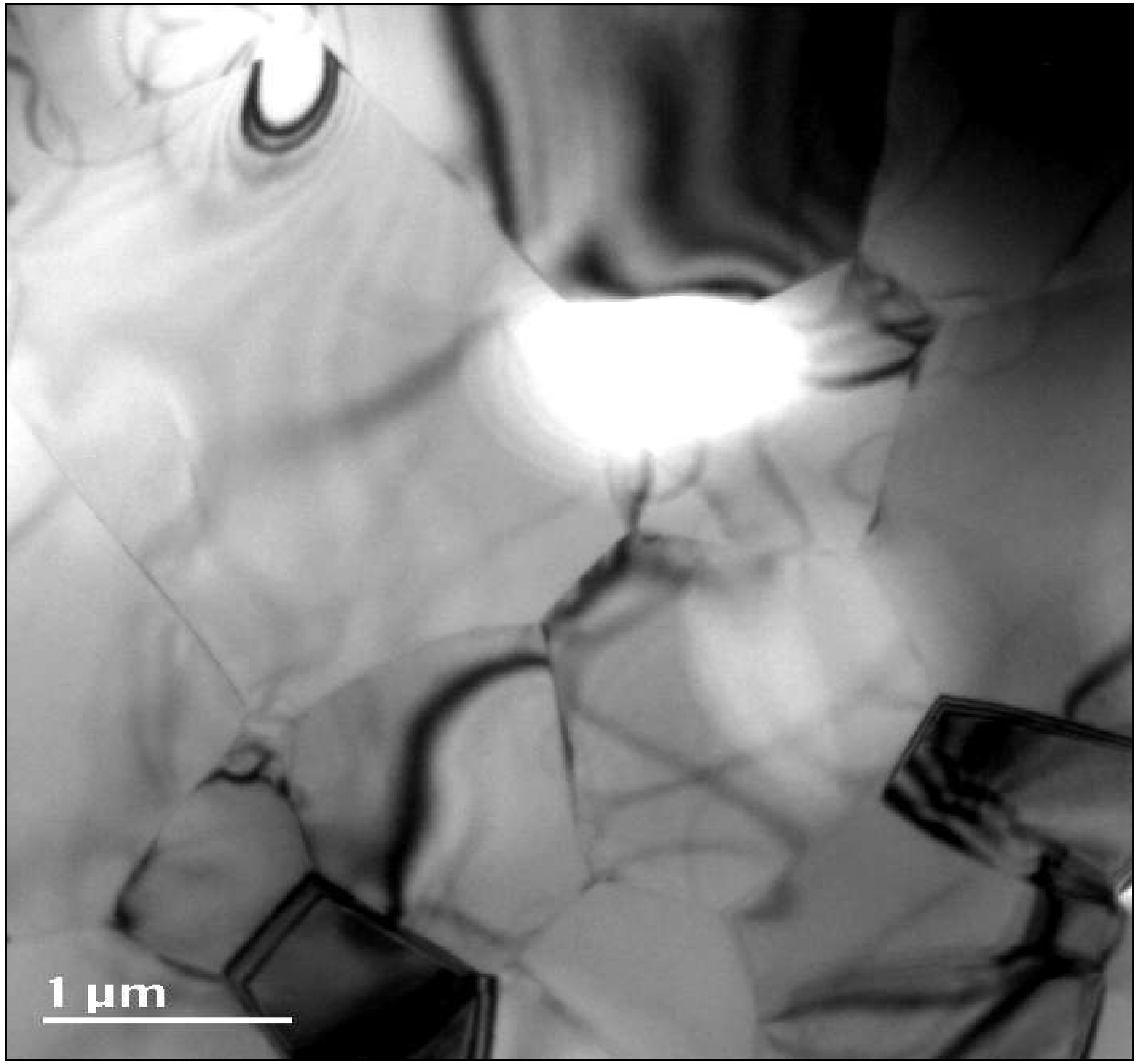
Cycling contact loading of $La_{0.6}Sr_{0.4}FeO_3$



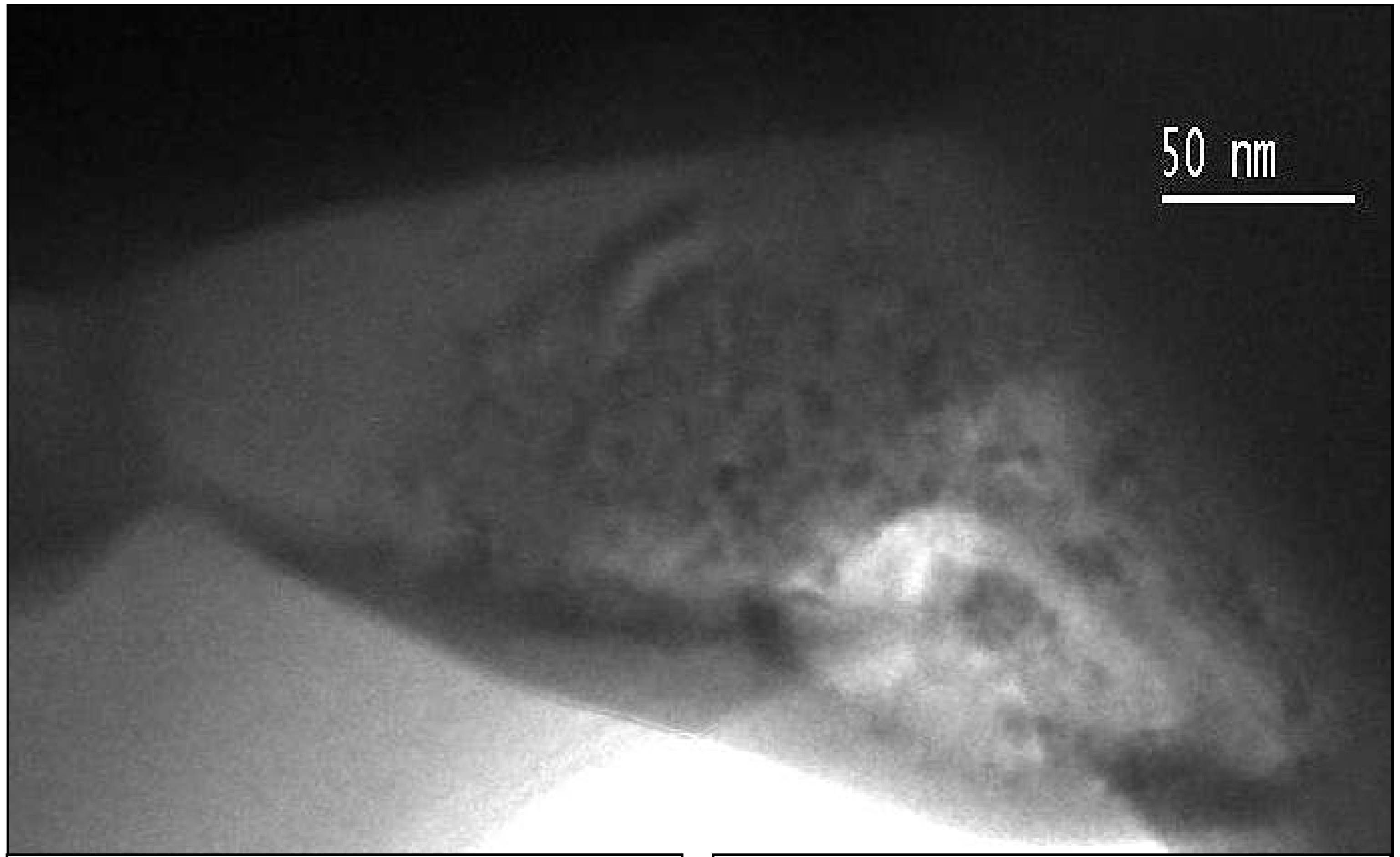


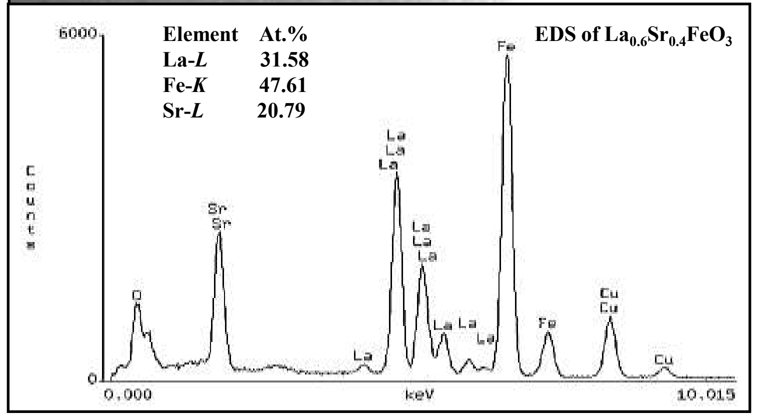
A typical load-displacement curve in cycling of the $La_{0.6}Sr_{0.4}FeO_3$ polycrystalline perovskite ceramics is shown. The Average Contact Pressure under indenter was calculated based on the power law that relates the applied load P to the elastic displacement of the indenter. The unloading and reloading parts of the deformation curve create hysteresis that can be used to characterize the mechanical performance of the perovskite. Hardness and Young's modulus were calculated from the beginning of the unloading curve in each cycle.

Microstructure structure in $La_{0.6}Sr_{0.4}FeO_3$ by TEM

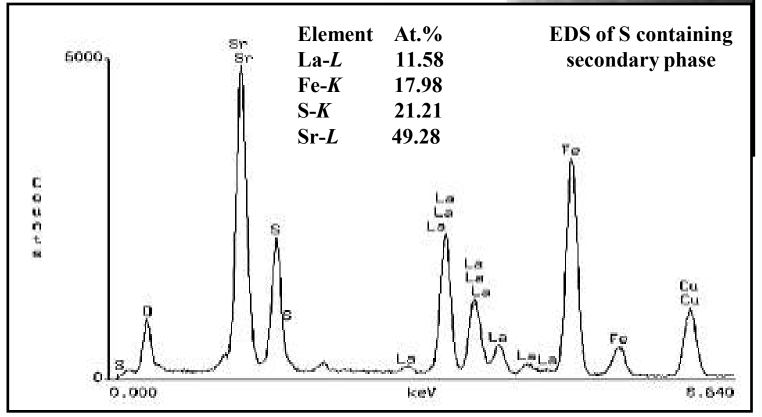


TEM micrograph showing grain structure in $La_{0.6}Sr_{0.4}FeO_3$. The grains are single domain grains with an average size of 1-3µm. Some porosity can be also observed.




EDS of $La_{0.6}Sr_{0.4}FeO_3$

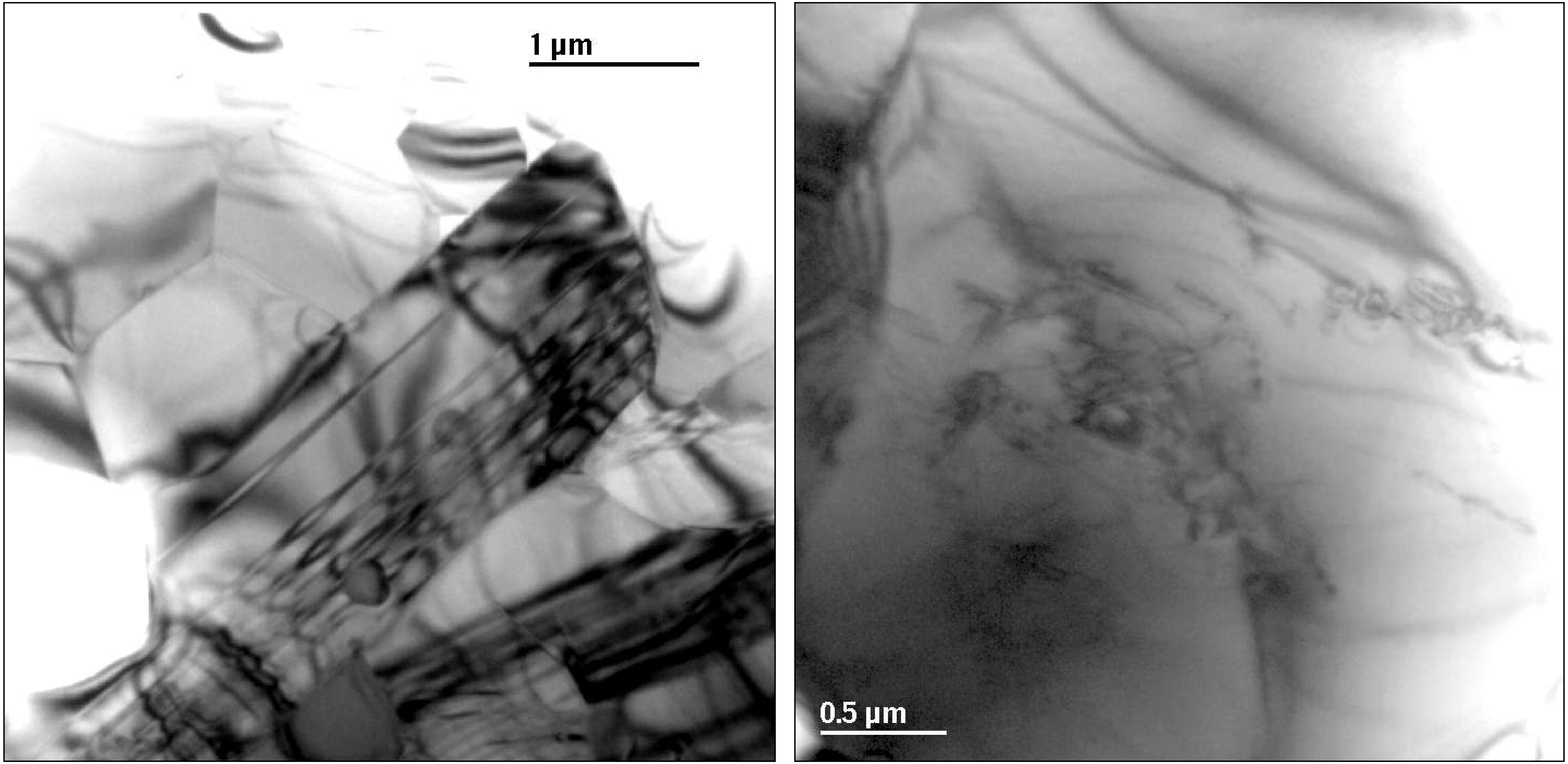
Element	At.%
La-*L*	31.58
Fe-*K*	47.61
Sr-*L*	20.79


EDS of S containing secondary phase

Element	At.%
La-*L*	11.58
Fe-*K*	17.98
S-*K*	21.21
Sr-*L*	49.28

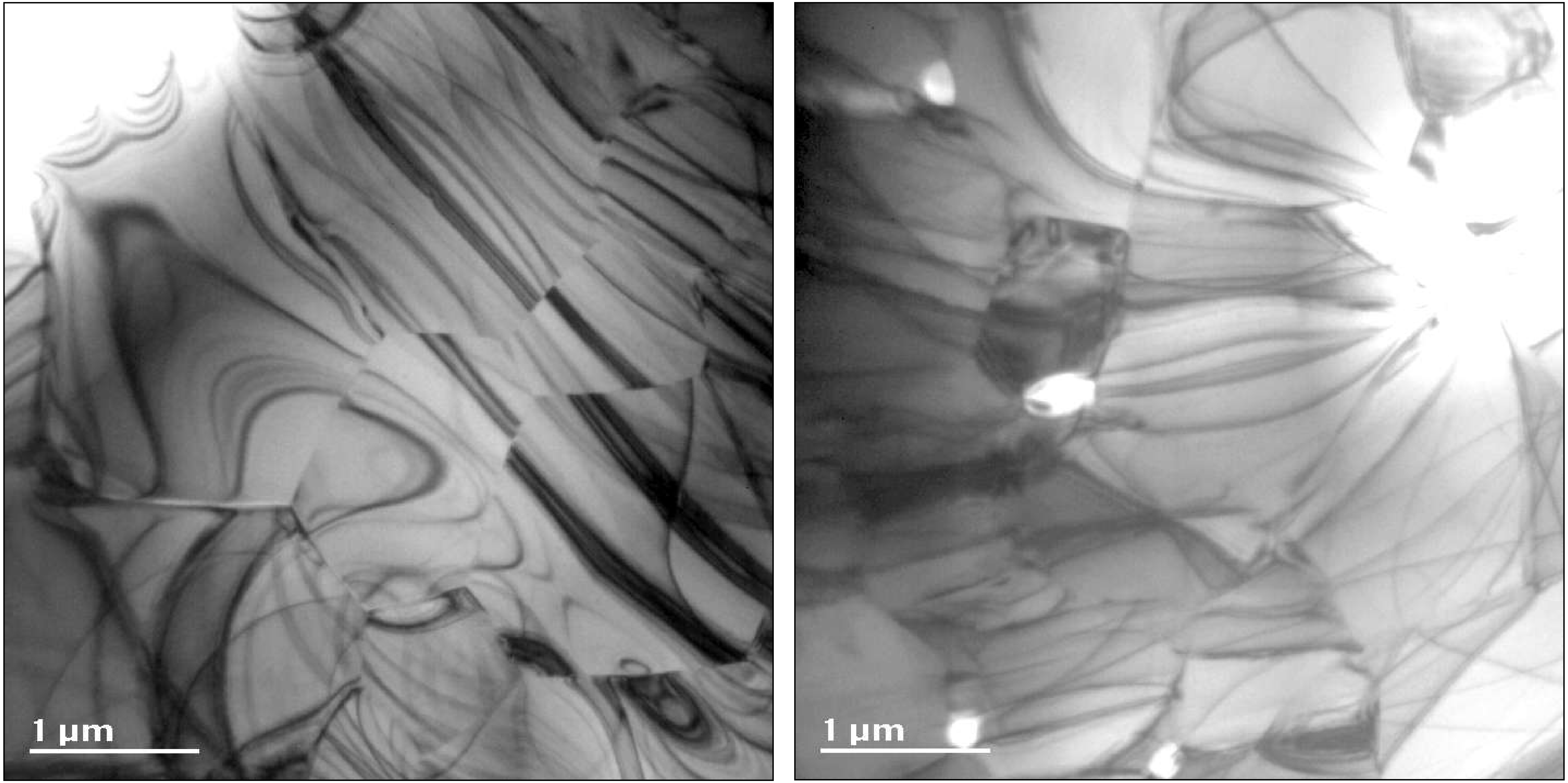
A sulfur containing secondary phase was found in some of the closed pores. The presence of such secondary phase can be explained by residues of sulfur containing salts that were used to synthesize LSF perovskite

Defects and dislocations in $La_{0.6}Sr_{0.4}FeO_3$



Some small amount of grains have twins, however, there are few of them (less then 1% of total amount of grains that were studied here) and they are rich in Fe. Another micrograph showing grains with dislocations. The dislocations movement under the applied stress could lead to the non-elastic ferroelastic behavior of LSF.

Defects in $La_{0.6}Sr_{0.4}FeO_3$



TEM micrograph showing grains with bend contours due to the local bending of the crystals.

Conclusions

- **Ferroelastic behavior and stress/strain hysteresis have been observed in $La_{0.6}Sr_{0.4}FeO_3$ perovskite.**
- **No doublet splitting in diffraction pattern of $La_{0.6}Sr_{0.4}FeO_3$ perovskite were recorded by XRD, therefore, the rhombohedral distortion in this material is very small.**
- **No twin structure was found and the majority of the grains were single domain grains, which is in good agreement with XRD.**
- ***In-situ* phase transition under compression, and/or dislocation movement, and/or grain rotation could be the mechanisms responsible for ferroelastic behavior and non-linear deformation.**
- **Significant increase in Young's modulus of the perovskite during compression could be a strong evidence for the *in-situ* phase transition occurring during material's loading.**

Acknowledgements

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