Influence of high-oxygen pressure on the thermoelectric properties of cobalt base perovskites

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Introduction

The identification of efficient materials for thermoelectric processes in which waste heat is converted into electrical energy is a real scientific challenge. As an alternative to conventional semiconductors based on bismuth and tellurium, oxides with a perovskite-type structure and having highly correlated electronic properties have recently been proposed, as they are characterized by greater chemical stability and less toxicity [1].
Two model compositions were selected as the object of study: one-substituted with Ni perovskite $LaCo_{0.9}Ni_{0.1}O_3$ and double-substituted with Ni and Fe perovskite $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$. Characteristically, they show better thermoelectric properties than unsubstituted lanthanum cobaltite [2]. The oxygen pressure was 200 bar and it has a direct effect on the peroxite superoxygen content.

The aim of this contribution is to study of the influence of high oxygen pressure on the thermoelectric properties of cobalt-based perovskites.

Method of preparation

Freeze-dried citrates

Single substituted

Citric acid (CA) (1M) + $La(NO_3).6H_2O$ (1M) +(1-x)$CoCO_3$ +(x) $NiCO_3$, where the La:(Co,Ni):CA ratio is 1:1:10

La-(Co+Ni) transparent citrate solution (0.25 M La, Co), x=0.1

Freeze-drying La (Co+Ni) -citrate precursors

Double substituted

Citric acid (CA) (1M) + $La(NO_3).6H_2O$ (1M) +(1-x)$CoCO_3$ +(x) $Fe(NO_3)_3.9H_2O$ +(x) $NiCO_3$ where the La:Co,(Fe+Ni):CA ratio is 1:1:10

La-(Co+Fe+Ni) transparent citrate solution (0.25 M La, Co), x=0.1

Freeze-drying La (Co+Ni, Fe)-citrate precursors

- Thermal decomposition at 400 °C for 3h
- Annealing at 900 °C for 40h

$LaCo_{1-x}Ni_xO_3$ — Press at 5 tons for 2 min

$LaCo_{1-x}Ni_xFe_xO_3$ — Press at 5 tons for 2 min

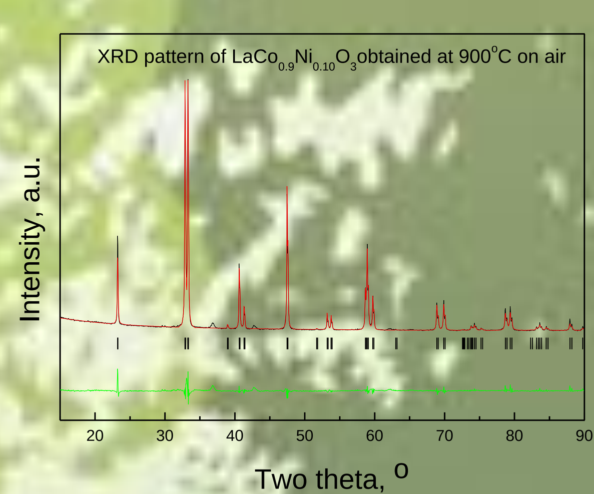
Annealing at 900 °C for 40h

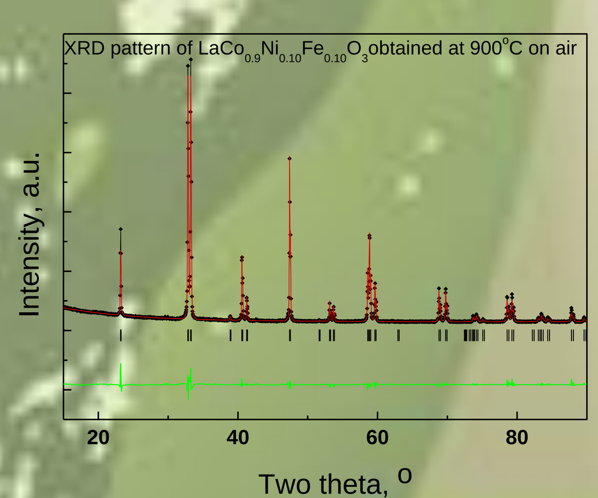
High-oxygen pressure (up to 30 Mpa at 900 °C. The samples were annealed at 900 °C in 200 bar oxygen.

Structural characterization of $LaCo_{0.9}Ni_{0.1}O_3$ and $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$

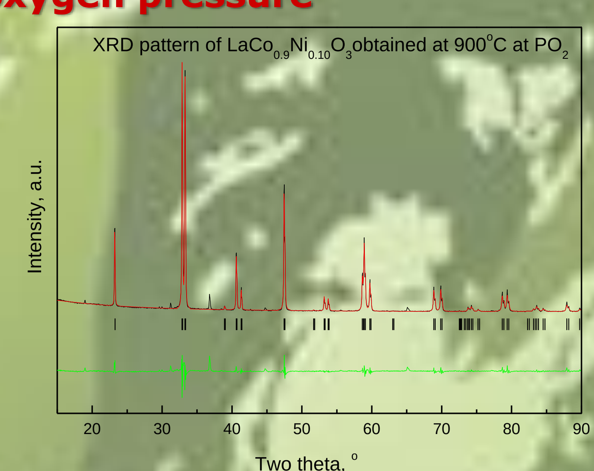
XRD patterns of $LaCo_{0.9}Ni_{0.1}O_3$ (left), $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$ (right). The samples are annealed at 900 °C for 40h

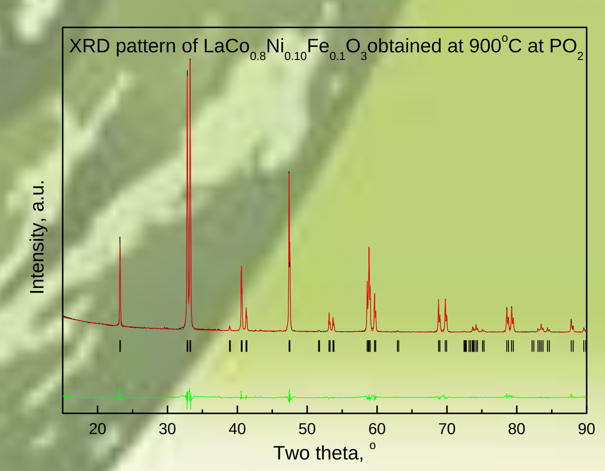
✓ Air





✓ High-oxygen pressure





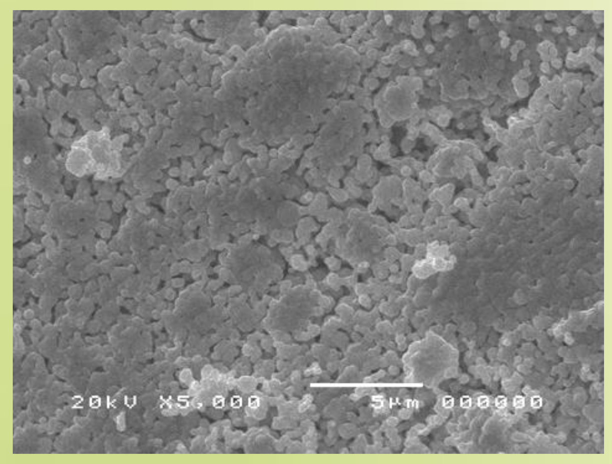
- The perovskite structure remains the same after the oxygen treatment under high-pressure.
- Avaiability of defects void to harshly change of electrical resistivity which is important for examination of thermoelectric properties.
- The perovskite structure gives opportunity to create oxygen vacations which influence the thermoelectric properties of oxides. Samples have to be poor on oxygen so they can give better thermoelectric properties.

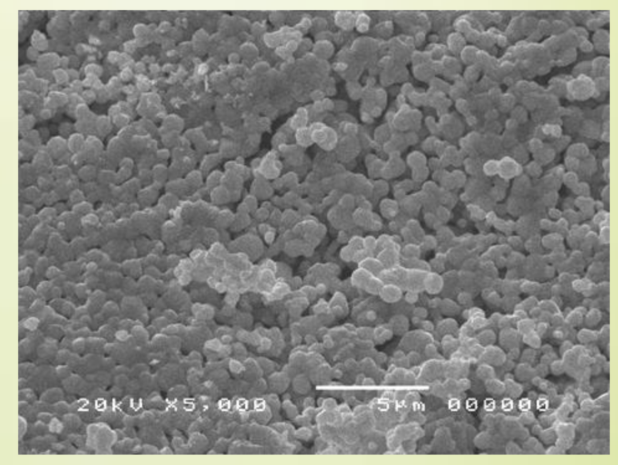
[1]. W. Tingjun, G. Peng, Development of Perovskite-Type Materials for Thermoelectric Application, Materials 11 (6) (2018) 999.
[2]. V. Vulchev, L. Vassilev, S. Harizanova, M. Khristov, E. Zhecheva and R. Stoyanova, Improving of the Thermoelectric Efficiency of $LaCoO_3$ by Double Substitution with Nickel and Iron, J. Phys. Chem. C 116 (2012) 13507.

Acknowledgment

The structural and morphological properties are determined on equipment included in the scientific infrastructure INFRAMAT (D01-155/28.08.2018 and D01-284/18.12.2019), while the electrical properties are measured on equipment included in NSI "Energy Storage and Hydrogen Energy "NSI ESHER, (D01-160/28.08.2018).

Morphological characterization of: $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$ obtained at 900 °C

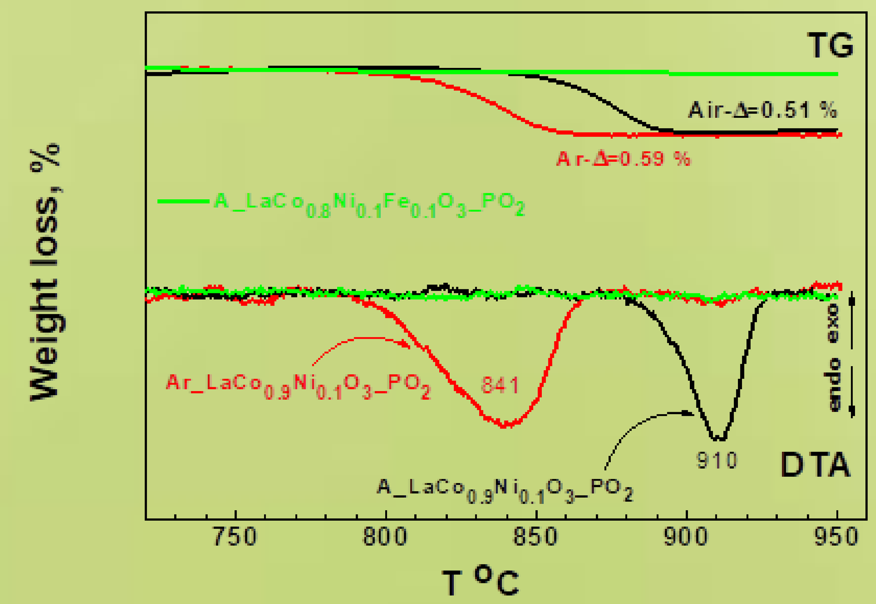




SEM images of tablets heated at 900 °C for 40 hours top view: $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$ (left) obtained at normal pressure and (right) a sample obtained under high-oxygen pressure $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$.

- As can be seen from the SEM images, the high oxygen pressure does not affect the morphology of the perovskites: it consists of well-interconnected particles with sizes ranging between 0.4 and 0.7 μm

Thermogravimetric analysis



TG and DTA curves of freeze-dried $LaCo_{0.9}Ni_{0.1}O_3$ oxides annealed at 900 °C in high-oxygen atmosphere (at black line), $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$ oxide annealed at 900 °C in high-oxygen atmosphere (at green), freeze-dried $LaCo_{0.9}Ni_{0.1}O_3$ oxides precursors annealed at 900 °C in high oxygen atmosphere decomposed under argon atmosphere (at red line). The ratio between metal ions and citric acid is 1:1:10.

- Compares TG and DTA curves of oxides $LaCo_{0.9}Ni_{0.1}O_3$, $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$ annealed under high-oxygen pressure. The first sample $LaCo_{0.9}Ni_{0.1}O_3$ decomposed in air the DAT curves display one endothermic process at 909 °C, for the same sample but decomposed in argon display endothermic process at 841 °C. TG curve for $LaCo_{0.9}Ni_{0.1}O_3$ show losses on air Δ=0.51 % and for the same sample decomposed under argon losses are Δ=0.59%. For another samples $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$ are missing the endothermic processes (green line). Double substituted samples undergoes changes after oxygen treatment can not absorb oxygen from further oxygen treatment can not absorb oxygen from further oxygen treatment. According to the thermal properties of oxides the endothermic process can be assigned to the adsorbed oxygen from high oxygen treatment.

Temperature dependence of the carrier density and carrier mobility for $LaCo_{0.9}Ni_{0.1}O_3$ and $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$

Oxygen content, mobility and density of current carriers in perovskites, obtained at normal pressure and under high oxygen pressure: $LaMO_{3+\delta}$

Sample	Oxygen content, δ ± 0.009	Mobility of current carriers, (cm^2/Vs)	Density of current carriers, (cm^{-3})	Resistivity, (Ω.cm) at 290 K
$LaCo_{0.9}Ni_{0.10}O_{3+\delta}$	0.045	4	9×10^{19}	0.038
$LaCo_{0.9}Ni_{0.10}O_{3+\delta}$ (high O_2 pressure)	0.077	50	6×10^{18}	0.041
$LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_{3+\delta}$	0.055	2	3×10^{18}	0.072
$LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_{3+\delta}$ (high O_2 pressure)	0.075	212	5×10^{17}	0.057

- When treating perovskites under high oxygen pressure, about a twofold increase in superstoichiometric oxygen was observed, and this increase did not depend on the type of replacement elements. Changes in the oxygen content are associated with a change in the transport properties of perovskites: the mobility of current carriers increases, while their density decreases. As a result, the resistance of the Perovskites changes slightly.

CONCLUSIONS

- Single substituted perovskites in $LaCo_{0.9}Ni_{0.10}O_3$ and double substituted perovskite $LaCo_{0.8}Ni_{0.1}Fe_{0.1}O_3$ obtained on air and under high oxygen vacuum yields oxides with a rhombohedrally distorted perovskite structure.
- The electrical resistivity (ρ) significantly decreases for single and double substituted perovskites obtained on air or under oxygen treatment.
- This study presents how, by varying the oxygen content in perovskite oxides, their thermoelectric properties can be controlled - an important condition for their application.

„ ЮБИЛЕЙНА НАУЧНА СЕСИЯ, ПОСВЕТЕНА НА 100-ГОДИШНИНАТА ОТ РОЖДЕНИЕТО НА АКАДЕМИК ГЕОРГИ БЛИЗНАКОВ"
18 ноември 2020г., София