

SYNTHESIS, STRUCTURE AND CONDUCTIVITY OF LAYERED PEROVSKITES

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By using the nitrate-citrate method we have been able to synthesize layered perovskites from the Ruddlesden-Popper (R-P) phases $(LaSr)_{n+1}Fe_nO_{3n+1}$, where $n = 1, 2, 3$. In this paper we present the results about their thermal evolution during the wet-chemical synthesis, structural and microstructural characterization by means of thermogravimetry/differential thermal analysis, X-ray diffraction and scanning electron microscopy. By measuring the total conductivity, using 4-probe DC method an attempt to correlate structure and conductivity of layered perovskites has been made. We established that at temperature over 140°C electrical conductivity of triple layer $LaSr_3Fe_3O_{10}$ perovskite is significantly higher compared with these of single and double layer compounds. The materials possess potentially applicable mixed electron-ion conductivity and catalytic activity, as well.

INTRODUCTION

The layered perovskites are potentially applicable materials because of their various technologically-important properties as ionic conductivity [1, 2], dielectricity [3], superconductivity [4], luminescence [5], photocatalytic [6], magnetism [7], and giant magnetoresistivity [8]. In the rational search for new materials with improved properties the ability to replace an inter-layer cation with a larger cation of the same charge would be a useful tool for studying the structure-property relationships in a series of compounds that have subtle structure differences [9].

The Ruddlesden-Popper (R-P) phases [4] with a general formula $A_{n+1}B_nO_{3n+1}$, where A = alkali metal, alkaline earth or lanthanide, B = octahedrally coordinated cation. The value n determines the thickness of the perovskite slab and gives the number of BO_6 octahedra corner sharing the c axis. For example, the conventional perovskite ABO_3 is the end member of the R-P series for $n = \infty$ and the A_2BO_4 compound for $n = 1$ of this series is known as K_2NiF_4 - type structure.

There are many scientific studies on layered perovskites with mixed conductivity as La_2NiO_4 [10, 11], La_2CuO_4 [12], $Ln_{1-x}Sr_{1+x}CoO_4$ [13].

To prepare layered perovskites it has been applied the methods, such as solid-state reaction and wet chemical methods. T. Nishi et al. [14] reported preparation of $LaSrFeO_4$ and $LaSr_3Fe_3O_{10-\delta}$ by solid-state reaction at 1500°C for 12 h. The same method has been applied for

obtaining of $(La, Sr)_{n+1}V_nO_{3n+1}$ ($n = 1, 2, 3$) [15]. For synthesis of selected layered perovskites we have applied a nitrate - citrate method, which has been used for synthesis of perovskite-related materials as Ln_2MO_4 ($Ln = La, Pr, Nd$; $M = Ni, Cu$) [16].

The aim of this paper is to present synthesis of layered perovskites from the series $(LaSr)_{n+1}Fe_nO_{3n+1}$, where $n = 1, 2, 3$ by the nitrate-citrate method, structural characterization and their electrical conductivity.

EXPERIMENTAL

Synthesis of $LaSrFeO_4$, $La_2SrFe_2O_7$ and $LaSr_3Fe_3O_{10}$ was carried out by a nitrate-citrate method. Highly pure La_2O_3 , $Sr(NO_3)_2$ and $Fe(NO_3)_3 \cdot 9H_2O$ were used as starting materials. The starting oxides and nitrates in respective stoichiometrical ratio were dissolved in aqueous solution of nitric acid at heating and stirring. After complete dissolution citric acid in molar ratio 3.3:1 in relation to metal ions was added. The obtained clear solution was concentrated and dried at 200°C. After drying, the self-combustion of the dry residue gave powdered precursors. A thermal treatment at temperatures from 700 to 1100°C for 2 hours and simultaneous thermogravimetry/differential thermal analysis (TG/DTA) was performed to observe the thermal decomposition of pre-

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cursors. The TG/DTA measurements were made using Q-1500-D derivatograph at heating rate of 10°C/min in the temperature range from 15 to 1000°C in air atmosphere. The obtained ceramic powders were characterized by XRD. The X-ray diffraction analysis was performed using a DRON-3 diffractometer (Cu-K α radiation) for the identification of the phase composition of the prepared powders and sintered samples. The phase identification was evaluated by "Powder Cell 2.2" software. The ceramic powders were pressed to bars and sintered at 1250°C for 5 h and at 1400°C for 1 h in order to measure the electrical conductivity of materials by DC 4-terminal method. The microstructure of sintered samples was observed by scanning electron microscopy (SEM) using JEOL-JSM-35CF microscope.

RESULTS AND DISCUSSION

Figure 1 presents the TG and DTA curves of the gels with nominal compositions LaSrFeO₄, La₂SrFe₂O₇ and LaSr₃Fe₃O₁₀ after drying at 200°C/2 h. The TG/DTA measurements were made using Q-1500-D derivatograph at heating rate of 10°C/min in the temperature range from 15 to 1000°C. It is observed that the initial loss of weight up to 180°C is due to removal of the water. After 250°C we observed several exothermal effects combined with significant loss of weight, which is due to a stepwise burning out of the organic matter and the strongest effect can be determined between 450°C and 650°C. Figure 1b shows the appearance of endothermal effects at 640°C and 770°C, probably due to the formation of perovskite phase. Above 800°C no thermal effects in the samples were observed.

Figure 2 shows the diffraction patterns of the powder samples LaSrFeO₄, calcined at 700°C, 800°C, 900°C and 1000°C for 2 h. It is observed that the formation of LaSrFeO₄ phase begins at 900°C and after treatment at 1000°C for 2 h there are not additional phases in the sample. X-ray diffraction patterns of La₂SrFe₂O₇ samples calcined at 700°C, 800°C, 900°C, 1000°C and 1100°C for 2 h, at 1250°C for 5 h and at 1400°C for 1 h are presented on figure 3. The analysis of the patterns shows that up to 1100°C in the sample, a formation of the single layer LaSrFeO₄ perovskite occurs and at 1250°C begins the formation of the double layer La₂SrFe₂O₇ perovskite phase. In the sample sintered at 1400°C for 1 h the presence of around 80% of La₂SrFe₂O₇ phase with admixtures of LaSrFeO₄ and perovskite phases is established. We assume that a thermal treatment at higher temperature or at longer time is necessary to obtain a single phase sample. Figure 4 shows X-ray diffraction patterns of LaSr₃Fe₃O₁₀ precursor powders calcined at 700°C, 800°C, 900°C, 1000°C and 1100°C for 2 h. We established that a thermal treat-

ment at temperature not lower than 1100°C is necessary for synthesis of LaSr₃Fe₃O₁₀ phase. The lattice parameters are given in table 1 for the synthesized layered perovskites. The presented parameters are comparable with lattice parameters reported by Nishi et al. [14].

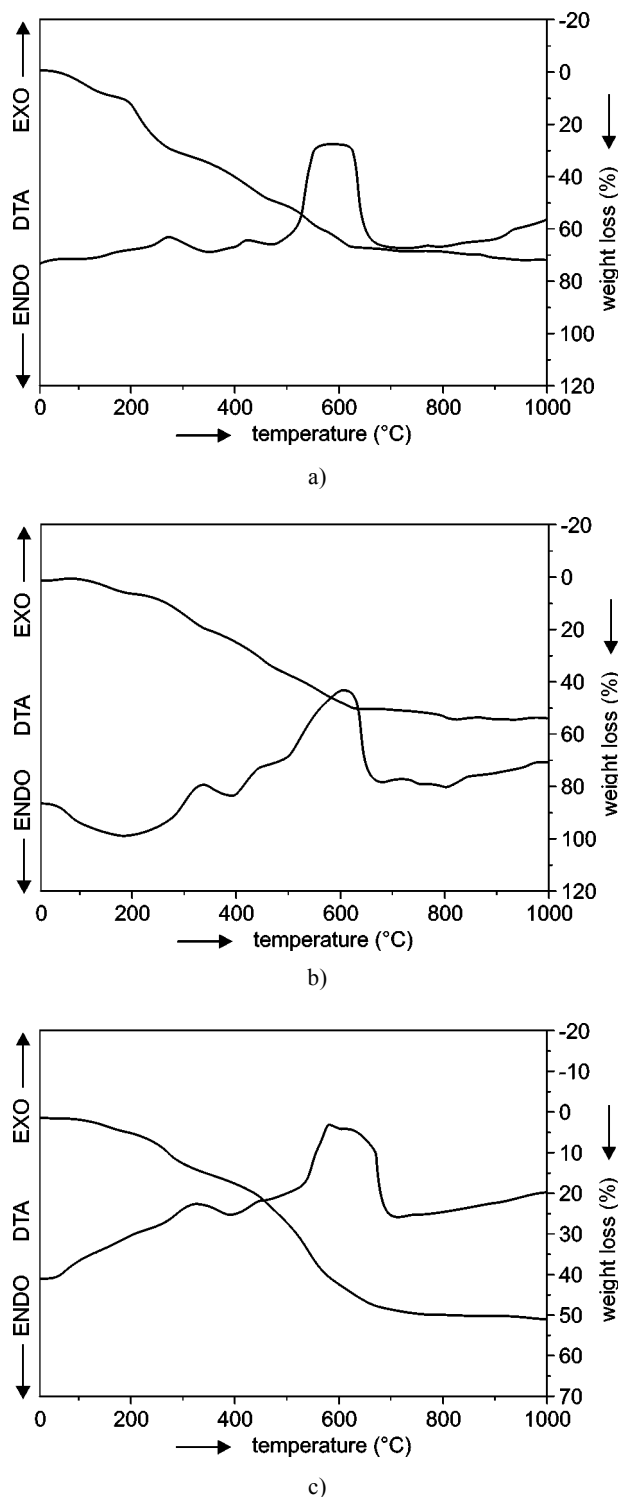


Figure 1. TG/DTA of the gels with nominal compositions; a) LaSrFeO₄, b) La₂SrFe₂O₇, c) LaSr₃Fe₃O₁₀ after drying at 200°C/2 h.

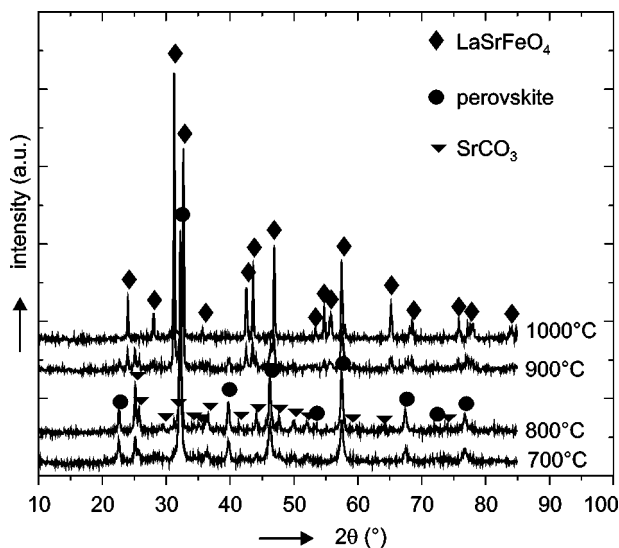


Figure 2. X-ray diffraction patterns of LaSrFeO_4 precursor powders, calcined at different temperatures.

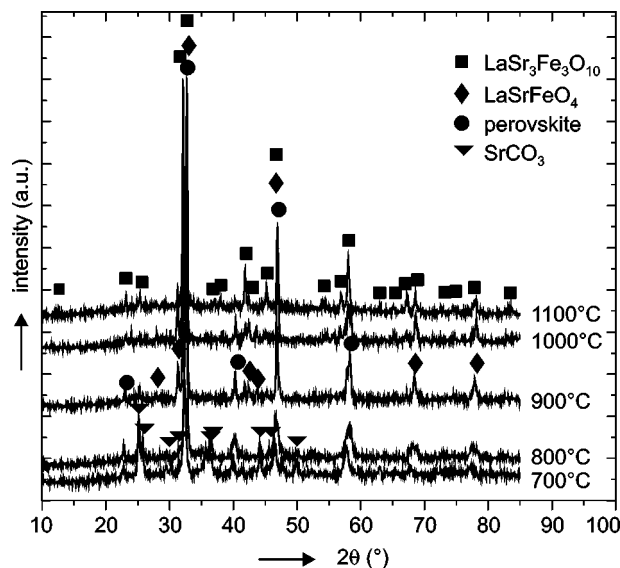


Figure 4. X-ray diffraction patterns of the $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$ precursor powders, calcined at different temperatures.

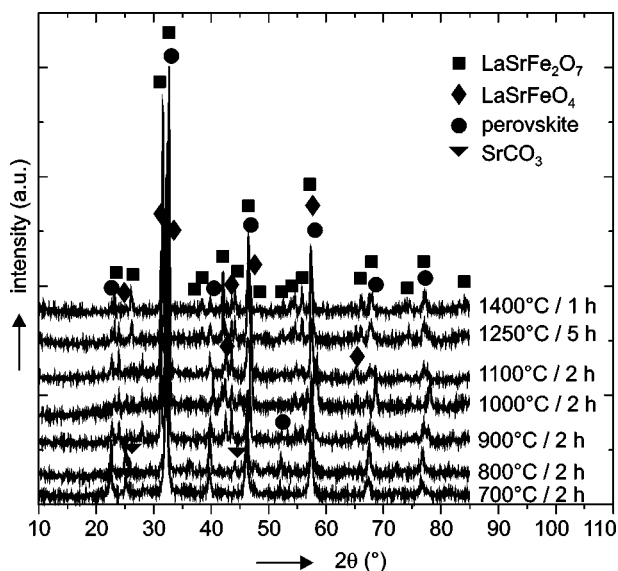


Figure 3. X-ray diffraction patterns of $\text{La}_2\text{SrFe}_2\text{O}_7$ precursor powders, calcined at different temperatures.

Table 1. Structural parameters for La-Sr-Fe-O layered perovskites.

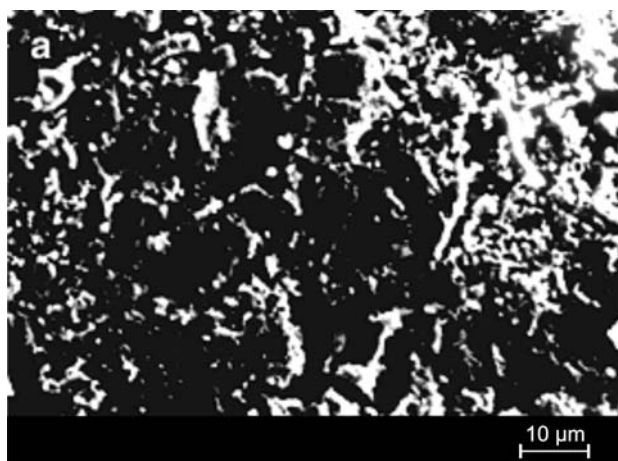
Parameters	LaSrFeO_4 1000°C/2 h	$\text{La}_2\text{SrFe}_2\text{O}_7$ 1400°C/1 h	$\text{LaSr}_3\text{Fe}_3\text{O}_{10}$ 1100°C/2 h
Space group	<i>I4/mmm</i>	<i>I4/mmm</i>	<i>I4/mmm</i>
<i>a</i> (Å)	3.869	3.899	3.870
<i>c</i> (Å)	12.722	20.475	28.059
<i>V</i> (Å ³)	190.4	311.3	420.2
<i>Rwp</i>	10.56	7.50	7.74
Impurity phase detected	–	LaSrFeO_4 (11.2%) Perovskite (7.9%)	–

The microstructure of synthesized materials was investigated by scanning electron microscopy (SEM). Figure 5 (a, b and c) shows a polished surface of LaSrFeO_4 , $\text{La}_2\text{SrFe}_2\text{O}_7$ and $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$ samples sintered at 1250°C/5 h, 1400°C/1 h and 1250°C/5 h, respectively. We observed a uniform distribution and size of the grains and pores in the samples LaSrFeO_4 (figure 5a) and $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$ (figure 5c). In the sample $\text{La}_2\text{SrFe}_2\text{O}_7$ (figure 5b) a presence of crystals with different morphology is observed and confirmed by X-ray diffraction data.

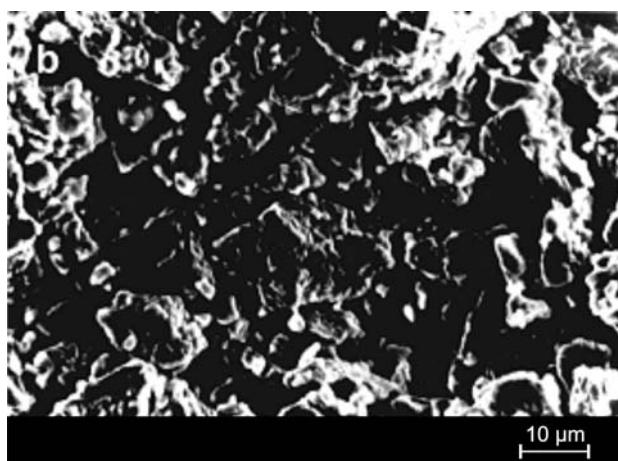
Electrical conductivity measurements were performed by DC 4-terminal method. Figure 6 presents the temperature dependence of the total conductivity in the temperature range from 30°C to 800°C of LaSrFeO_4 , $\text{La}_2\text{SrFe}_2\text{O}_7$ and $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$ samples, sintered at 1400°C for 1 h. It is interesting to remark that at low temperature (from 30 to 130°C) the conductivity of $\text{La}_2\text{SrFe}_2\text{O}_7$ sample is higher than single and triple layer perovskite. From 140°C to 800°C the conductivity of LaSrFeO_4 and $\text{La}_2\text{SrFe}_2\text{O}_7$ samples increase with similar values. The curve of conductivity of triple layer $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$ perovskite in the same temperature range is distinguished by quickly increasing values of conductivity and maximum of 58 S/cm at 580°C.

CONCLUSIONS

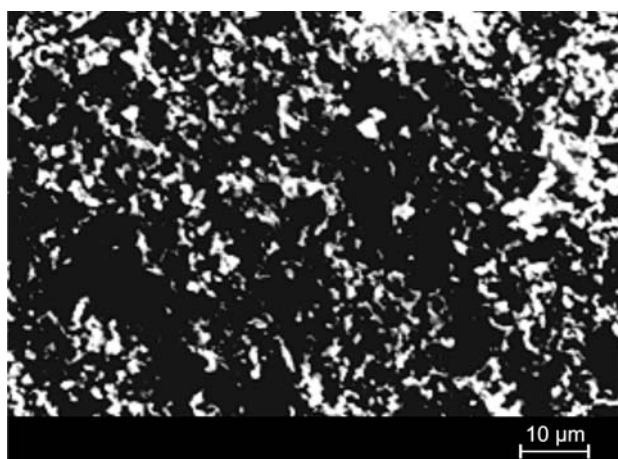
The applied nitrate-citrate method of synthesis is appropriate for obtaining layered perovskites from Ruddlesden-Popper (R-P) phases with compositions LaSrFeO_4 , $\text{La}_2\text{SrFe}_2\text{O}_7$ and $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$. By X-ray diffraction analysis it is established that single layer



a)



b)



c)

Figure 5. SEM microphotographs of a) LaSrFeO_4 , b) $\text{La}_2\text{SrFe}_2\text{O}_7$ and c) $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$.

LaSrFeO_4 perovskite can be synthesized at 1000°C for 2 h, double layer $\text{La}_2\text{SrFe}_2\text{O}_7$ perovskite - 1400°C for more than 1 h and triple layer $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$ - 1100°C for 2 h. SEM analysis proves the presence of microstructure characterized by a uniform distribution and size of the grains and pores in the samples LaSrFeO_4 and $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$. We established that at temperature over 140°C the electrical conductivity of triple layer $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$ perovskite is significantly higher compared with these of single and double layer compounds.

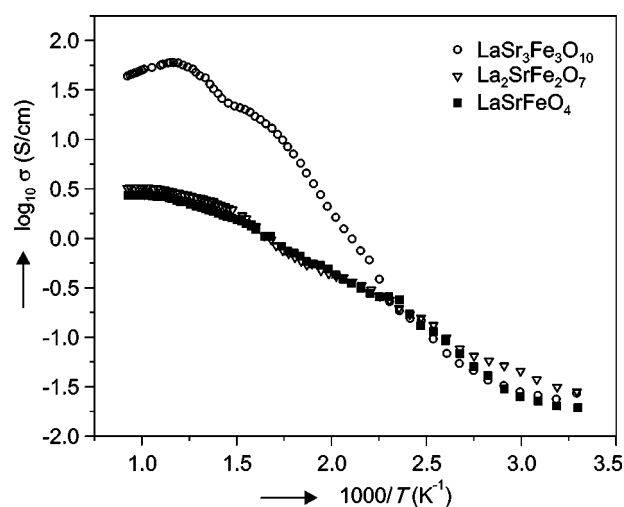


Figure 6. Temperature dependence of the total conductivity of LaSrFeO_4 , $\text{La}_2\text{SrFe}_2\text{O}_7$ and $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$ samples, sintered at 1400°C for 1 h.

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SYNTÉZA, STRUKTURA A VODIVOST
VRSTEVNATÝCH PEROVSKITŮ

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Použitím metody s kyselinou citronovou a dusičnany jsme byli schopni připravit vrstevnaté perovskity typu Ruddlesden-Popperových (R-P) fází $(\text{LaSr})_{n-1}\text{Fe}_n\text{O}_{3n+1}$, kde $n = 1, 2, 3$. V tomto článku ukazujeme výsledky tepelného zabarvení během jejich mokré chemické syntézy a strukturální a mikrostrukturální charakterizaci produktů pomocí termogravimetrie/diferenční termální analýzy, rtg difrakce a řádkovací elektronové mikroskopie. Pokusili jsme se nalézt vztah mezi strukturou a celkovou vodivostí měřenou čtyřbodovou metodou se stejnosměrným proudem. Zjistili jsme, že při teplotě nad 140°C je elektrická vodivost trojvrstvého perovskitu $\text{LaSr}_3\text{Fe}_3\text{O}_{10}$ významně vyšší než u jedno- a dvojvrstvých fází. Materiál je případně použitelný jako smíšený elektronově-iontový vodič a rovněž jako katalyzátor.