



# Solvothermal synthesis and characterization of mixed oxides with perovskite-like structure



N. Miniajluk<sup>a,\*</sup>, J. Trawczyński<sup>a</sup>, M. Zawadzki<sup>b</sup>, P.E. Tomaszewski<sup>b</sup>, W. Mišta<sup>b</sup>

<sup>a</sup> Division of Chemistry and Technology of Fuels, Wrocław University of Technology, 50-344 Wrocław, ul. Gdańska 7/9, Poland

<sup>b</sup> Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-422 Wrocław, ul. Okólna 2, Poland

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## ABSTRACT

Solvothermal synthesis was successfully used to prepare  $\text{LaMeO}_3$  ( $\text{Me} = \text{Mn, Co, Fe}$ ) and  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  ( $x = 0.1, 0.3, 0.5$ ), mixed oxides with perovskite-like structure. The prepared materials were examined by X-ray diffraction (XRD), nitrogen adsorption at low temperature (BET), transmission electron microscopy (TEM), decomposition of cyclohexanol (CHOL), temperature programmed reduction with hydrogen (TPRH<sub>2</sub>), temperature programmed desorption of oxygen (TPDO<sub>2</sub>) and X-ray photoelectron spectroscopy (XPS). Furthermore, catalytic activity for combustion of 0.6% vol. methane in air ( $\text{GHSV} = 40\,000\text{ h}^{-1}$ ) was determined.

All prepared materials are nanocrystalline and well-crystallized, and they exhibit relatively well-developed specific surface area (9.2–39.2 m<sup>2</sup>/g). The trigonal structure of the Mn-containing samples corresponds to the structure of the high-temperature bulk phase, which cannot be recovered at ambient conditions. Generally, the Mn-containing materials exhibit higher SSA, more basic character of the surface, lower temperature of maximum H<sub>2</sub> consumption and higher catalytic activity in lean methane combustion than the corresponding Co- and Fe-based nanocrystals. The highest catalytic activity for lean methane combustion (100% of CH<sub>4</sub> conversion at 451 °C) is observed for LaMnO<sub>3</sub>. A partial substitution of La by Sr lowers content of Mn<sup>4+</sup> on the surface of the corresponding materials, resulting in lower catalytic activity in lean methane combustion.

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## 1. Introduction

An increase of methane concentration in the atmosphere presents the serious threat to the environment. The main sources of methane emissions to the atmosphere include: coal mining, extraction and use of natural gas, agriculture, animal husbandry and landfills. In Poland, the amount of methane emitted into the atmosphere has increased in recent years, despite of coal production decrease [1]. In a typical coal mine, methane is emitted to the atmosphere by three ways. The first of them, the most diluted (0.1–1% vol. CH<sub>4</sub>), is the CH<sub>4</sub> released along with the ventilation air. Methane is also gradually released from the wellbore (60–95% vol. CH<sub>4</sub>) as well as from the excavation (30–95% vol. CH<sub>4</sub>) [2]. Methane

included in the ventilation air is difficult for disposal because its concentration is low (for safety reasons, less than 0.75% vol.) and furthermore the ventilation air streams are characterized by a large and time varying flow rate [2,3]. The value of the global warming potential (GWP) of methane is 21 times greater than carbon dioxide. Therefore, this gas creates the great danger to the environment and it became significant to work out a method of lowering its emission into the atmosphere. Among methods preventing methane emission, one can distinguish primary methods using methane of high concentration, such as drainage systems on mining excavations or biofermentation of biological waste. Secondary methods deal with lean methane, which has been already emitted into the atmosphere and reduce its harmful effects by burning it thermally or catalytically.

Catalytic combustion of methane is an interesting and promising issue because of its practical use in the production of energy and reduction of pollutants emission. The use of a heterogeneous catalyst significantly lowers the combustion temperature compared to the thermal process, what causes the decrease of NO<sub>x</sub> emissions [4]. Hence, development of active, low-cost and efficient catalysts

\* Corresponding author. Tel.: +48 0713206542.

E-mail addresses: [natalia.miniajluk@pwr.wroc.pl](mailto:natalia.miniajluk@pwr.wroc.pl), [karaiby5@gazeta.pl](mailto:karaiby5@gazeta.pl) (N. Miniajluk), [janusz.trawczynski@pwr.wroc.pl](mailto:janusz.trawczynski@pwr.wroc.pl) (J. Trawczyński), [M.Zawadzki@int.pan.wroc.pl](mailto:M.Zawadzki@int.pan.wroc.pl) (M. Zawadzki), [petomasz1@wp.pl](mailto:petomasz1@wp.pl) (P.E. Tomaszewski), [W.Mista@int.pan.wroc.pl](mailto:W.Mista@int.pan.wroc.pl) (W. Mišta).

for the combustion of diluted methane has become a challenge to be overcome. Among materials proposed as catalysts for such process, noble metals and metal oxides (simple and mixed) can be distinguished. Noble metals based catalysts are very active in methane combustion, however they are expensive, sensitive to poisons and sometimes demonstrate a poor thermal stability [5,6]. Metal oxides based catalysts are characterized by stable structure, resistance to sintering and low price, but also the lower activity in reactions with the participation of oxygen. Among mixed metal oxides, perovskites seem to be the very interesting and attractive catalytic materials. Their catalytic properties are closely related to the nature of the A and/or B cations, which can be modified by the partial substitution, leading to the formation of mixed oxides with the general formula  $A_{1-x}A'_x B_{1-y}B'_y O_3$ . Partial substitution of the cation in position A by another cation may be accompanied by formation of structural defects, which leads to non-stoichiometric compounds, creating oxygen vacancies, increasing the mobility of oxygen ions, thereby improving the catalytic activity of material [7]. However, activity in the combustion depends also on the properties of the B cation [4]. Selection of suitable conditions and methods of synthesis enables one controlling properties of these materials, particularly their catalytic activity. In general, there are a lot of preparation methods of materials with perovskite like structure, for example sol-gel, chemical combustion, spray pyrolysis, co-precipitation.

The solvothermal method has been proposed to be an effective method for synthesizing well-crystallized powder with uniform shape and narrow particle size distribution and large surface area [8–11]. Some authors reported that microwave heating during the hydrothermal ageing step has a pronounced effect on the physico-chemical and catalytic properties of the perovskite-type catalysts. Ifrah et al. [12] demonstrated that microwave-assisted hydrothermal synthesis (MHT) of  $La_{1-x}Ag_x MnO_{3+\delta}$  ( $x=0, 0.2$ ) perovskites leads to the improved activity and stability in methane combustion as compared to the conventional hydrothermal process (CHT). The better catalytic performances of microwave-prepared perovskites seem to arise from their atomic surface composition, lower amount of  $\alpha$ -oxygen species and their moderate mobility. Kaddouri et al. [13] found superior methane combustion activity of La-Ce-Mn-O perovskite prepared using MHT method which was attributed to a well dispersed cerium oxide species strongly interacting with the  $LaMnO_3$  host structure. Shi et al. [14] reported that

$NaTaO_3$  perovskite prepared by the MHT method showed photocatalytic activity for overall water splitting more than two times greater than those prepared under CHT conditions. Thus, the potential of improving the activity of perovskite-type catalysts using the microwaves under the solvothermal conditions seems to be very promising.

The aim of this work was to determine catalytic properties of mixed metals oxides with perovskite-like structure in combustion of lean methane, which could be prepared by solvothermal method using ethylene glycol as a solvent.

All studied crystals belong to the well-known family of perovskites. The structure of perovskites and their phase diagrams were widely studied in the past. In general, their structure is orthorhombic at room temperature (space group  $Pbnm$ , No. 62) and under heating this phase undergoes the phase transitions to another orthorhombic phase (metrically cubic, space group  $Pbnm$ , No. 62), and finally to trigonal phase described by  $R-3c$  space group (No. 167) [15]. The transition temperature depends on stoichiometry of the sample (mainly on oxygen and  $Mn^{4+}$  content).

## 2. Experimental

### 2.1. Samples preparation

Mixed oxides of general formula  $LaMeO_3$  ( $Me=Mn, Co, Fe$ ) and  $La_{1-x}Sr_x MnO_3$  ( $x=0.1, 0.2, 0.3, 0.5$ ) were prepared using microwave-assisted solvothermal method. Nitrates of corresponding metal were dissolved in ethylene glycol and reacted in a teflon melting pot in an autoclave (90 min,  $200^\circ C$ , 40 bar) under microwave heating. The resulting suspensions were centrifuged, washed with acetone, dried (24 h/ $110^\circ C$ ) and then calcined (4 h/ $750^\circ C$ ).

The temperature of calcination ( $750^\circ C$ ) was chosen due to the best quality of obtained samples. The calcination at lower temperatures ( $300$ – $550^\circ C$ ) give an amorphous material; the diffraction patterns have no peaks. The crystallization starts at the temperatures between  $550$  and  $600^\circ C$  (see Fig. 1).

Using above described protocol we have obtained following materials:  $LaMnO_3$  (LM),  $LaCoO_3$  (LC),  $LaFeO_3$  (LF),  $La_{0.9}Sr_{0.1}MnO_3$  ( $L_{0.9}S_{0.1}M$ ),  $La_{0.7}Sr_{0.3}MnO_3$  ( $L_{0.7}S_{0.3}M$ ) and  $La_{0.5}Sr_{0.5}MnO_3$  ( $L_{0.5}S_{0.5}M$ ).

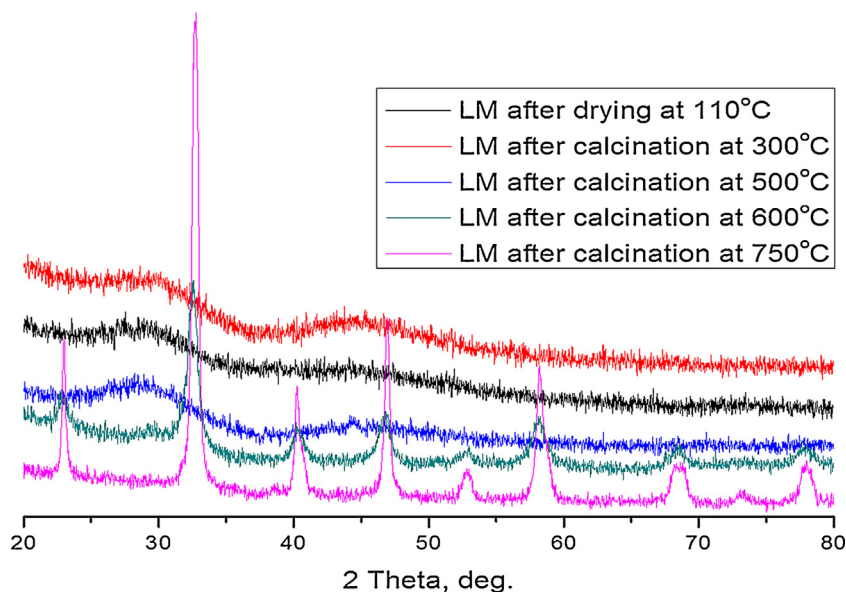


Fig. 1. X-ray diffraction patterns of  $LaMnO_3$  samples calcined at different temperatures.

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