

Structure and morphological properties of Ca-containing La-Pb-Mn-O perovskites for catalytic applications

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This paper is focused on less-studied system La-Pb-Ca-Mn-O perovskite like manganites. Calcium was introduced as partial substitution for Pb or as addition to the basic composition $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ (LPMO). $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$, $\text{La}_{0.6}\text{Pb}_{0.2}\text{Ca}_{0.2}\text{MnO}_3$ and $\text{La}_{0.6}\text{Pb}_{0.4}\text{Ca}_{0.2}\text{MnO}_3$ perovskite manganite powders have been prepared by self-combustion method and heat treatment at 1000°C. The composites were characterized by X-ray diffraction, scanning electron microscopy and nitrogen adsorption/desorption isotherms. Scanning electron microscopy (SEM) pictures showed significant difference in the microstructure of LPMO after CaO incorporation. CaO added LPMO was found to have an average grain size (below 100 nm) much smaller than that of pure LPMO (~ 400 nm) due to Ca segregation on the grain surface. The catalytic tests showed that the combustion of acetone/air, ethanol/air and methanol/air over perovskite manganite catalysts can start at lower temperature (of about 300°C) than in the normal combustion due to nanometric crystallite size, large surface area and high concentration of Mn^{4+} cations.

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1. Introduction

As a novel catalytic material, perovskite-type oxides (general formula ABO_3) are extensively investigated, being recently the subject of great interest for researcher, especially for the development of combustion catalysts and environmental purification catalysts [1-3]. From among perovskite oxides, the lanthanum manganite, LaMnO_3 , has attracted wide interest because of its catalytic properties which are related to the high availability of lattice oxygen due to the presence of manganese with different oxidation states (Mn^{2+} , Mn^{3+} and Mn^{4+}) [4]. It is known that La^{3+} cations in A site are generally catalytically inactive. Moreover, the stable structure of the perovskites allows for the partial substitution of A and/or B by other metals (transition of rare metal ions), which can improve the perovskite structure or its properties. Thus, a partial substitution of the La^{3+} cations with lower valence cations forces a large part of the Mn^{3+} to oxidize to Mn^{4+} and allows the formation of oxygen vacancies which enhance the catalytic activity [5-7]. Many studies regarding the effect of composition and preparation methods on the physico-chemical and catalytic properties of the substituted manganites have been done in the last time [8,9,10]. But the substituted perovskite type manganites, $\text{La}_{1-x}\text{Pb}_x\text{MnO}_3$, have been less studied [11,12] due to the toxicity of Pb. The partial substitution of Pb^{2+} for La^{3+} in the crystal lattice of the lanthanum manganite induces the presence of Mn^{3+} and Mn^{4+} cations [12] and creates surface defects, such as oxygen vacancies, which are active sites for oxygen adsorption [13-15].

The present paper is focused on $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ perovskite manganite. The purpose was to investigate the effect of Ca^{2+} ions on the structure and catalyst properties of $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ oxide compound in order to find new perovskite compositions with suitable properties for catalyst applications. Ca ion was introduced as partial substitution for Pb^{2+} ion ($\text{La}_{0.6}\text{Pb}_{0.2}\text{Ca}_{0.2}\text{MnO}_3$) and as addition over stoichiometric composition ($\text{Ca}_{0.2}\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$).

Self-combustion nonconventional method was used to synthesize fine perovskite powders with molecular scale homogeneity [16-18]. The self-combustion method has advantage to be an exothermic fast and self-sustaining chemical reaction. This method is a simple method for oxide synthesis and has been used to produce homogeneous crystalline nanopowders.

2. Experimental

Three perovskite powders of nominal compositions $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$, $\text{La}_{0.6}\text{Pb}_{0.2}\text{Ca}_{0.2}\text{MnO}_3$ and $\text{Ca}_{0.2}\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ were prepared by self-combustion procedure followed by heat treatment at 1000°C in air for 320 min. This simple and fast route implies low energy consumption. As starting materials were used metal nitrates of high purity. The preparation procedure by self-combustion is schematic presented in Fig. 1 and more details on the procedure have been reported elsewhere [16-18].

The phase composition, lattice parameters and the crystallite size of the heat treated powders were determined from X-ray diffraction (XRD) patterns

obtained with DRON-2 diffractometer and Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). The average crystallite size was calculated by using Scherer equation [19].

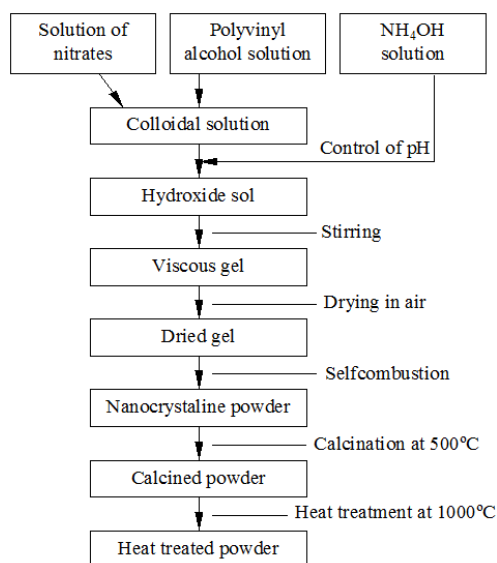


Fig. 1. Processing of perovskite powders by self-combustion route.

The morphology of the powders was analyzed by a scanning electron microscope (SEM). The average grain size was determined from SEM images by the linear intercept method.

The specific surface area (S_{BET}) was calculated from the nitrogen sorption data using the Brunauer-Emmett-Teller (BET) equation [20]. Adsorption/desorption isotherms of nitrogen were measured at $\sim 77\text{K}$ with NOVA 2200 apparatus. The pore size distribution (PSD) curves were obtained from the sorption isotherms using BJH (Barret, Joyner and Halenda) method [20].

The perovskite manganite powders have been tested in combustion reaction of three diluted gases: acetone/air, ethanol/air and methanol/air. Was determined the lowest combustion temperature of the gases over the manganite powders.

3. Results and discussion

The X-ray diffraction patterns at room temperature (Fig. 2) of the three manganite powders after heat treatment at 1000°C indicate a cubic perovskite structure (space group Fm3m) for all samples and the presence of some peaks belonging to nonidentified secondary phases.

The lattice parameters and average crystallite size derived from XRD data are given in Table 1. The lattice parameters are in good agreement with those found in analogous compounds [21]. The decrease of the lattice parameters by substituting Ca^{2+} ions for half of Pb^{2+} ions (sample 2) is induced by the smaller ionic radius of Ca^{2+} ion (0.114 nm) in comparison with that of Pb^{2+} (0.133 nm) [13] and indicates the solubility of Ca ions in the

perovskite structure of La-Pb-Mn-O (LPMO). For the composition with calcium addition (sample 3) the lattice parameter does not differ too much from that of basic composition LPMO. In this case, it is possible that a part of Ca^{2+} ions added over stoichiometric composition LPMO to be segregated on the grain boundaries.

The crystallite size was found to be of about 24 – 26 nm and attests that perovskite powders with nanosized crystallites have been synthesized.

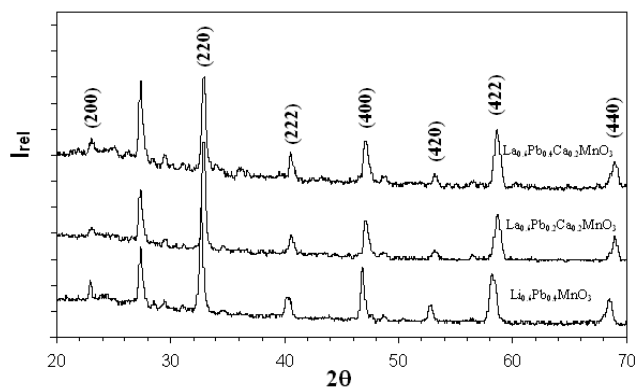


Fig. 2 XRD patterns for studied manganites (heat treated at 1000°C for 320 min).

By chemical analysis it was determined a considerable amount of Mn^{4+} (about 36% – 38% concentration) (Table 1). One can observe that the partial substitution of Ca^{2+} for Pb^{2+} (sample 2) does not change the Mn^{4+} concentration. The $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio is controlled by the concentration of divalent cations (Pb, Ca) which partial replace La^{3+} on A sites. The plausible explanation for smaller Mn^{4+} concentration in the last sample can be a Ca segregation at the grain surface which impedes the conversion of Mn^{3+} to Mn^{4+} during the heat treatment at 1000°C . This implies less oxygen vacancies and a smaller number of adsorbed oxygen ion-species (O_2^- , O^{2-} , O^\cdot).

Table 1. Structure characteristics and Mn^{4+} concentration for perovskite powders annealed at 1000°C for 320 minutes.

Sample nr.	Nominal composition	Lattice parameter (nm)	Crystallite size (nm)	$C_{\text{Mn}^{4+}}$ (%)
1	$\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$	0.7752	24.05	37.8
2	$\text{La}_{0.6}\text{Pb}_{0.2}\text{Ca}_{0.2}\text{MnO}_3$	0.7708	25.84	37.2
3	$\text{La}_{0.6}\text{Pb}_{0.4}\text{Ca}_{0.2}\text{MnO}_3$	0.7742	25.05	35.9

Figs. 3a, 3b and 3c show micrographs of LPMO and Ca containing LPMO perovskites. One can see the presence of the grain agglomerates. Also one can remark significant differences between the microstructures of the three samples. A marked decrease in the grain size of the Ca containing LPMO compared to pure LPMO can be seen. The sample with Ca addition (Fig. 3c) has the smallest grains (below 100 nm) and form large aggregates. This is due to Ca segregation on the grain

boundaries, which hinders the development of the grain of perovskite phase during the heat treatment. But the perovskite powder without Ca (Fig. 2a) has the biggest grains, of about 300 – 400 nm and form small grain agglomerations.

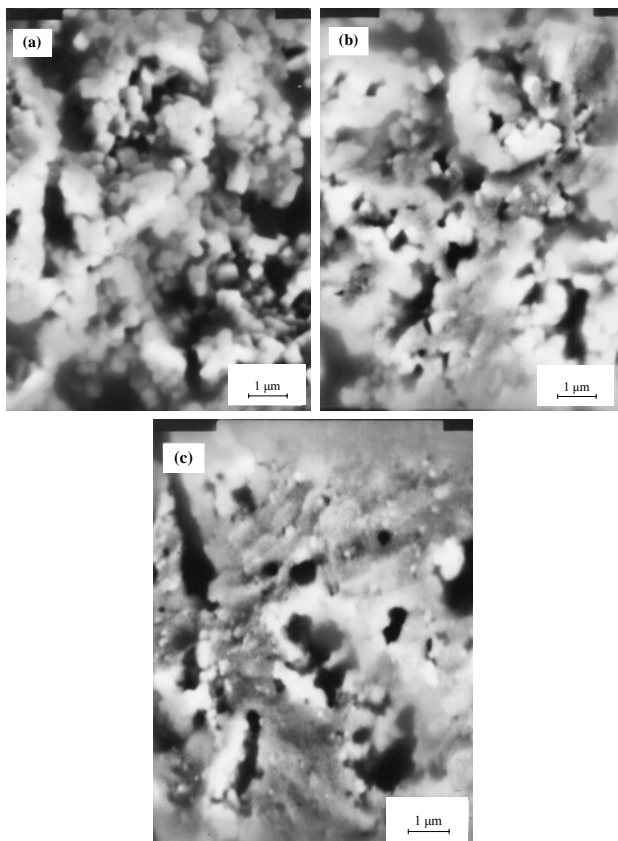


Fig. 3. SEM micrographs: (a) $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ (b) $\text{La}_{0.6}\text{Pb}_{0.2}\text{Ca}_{0.2}\text{MnO}_3$; (c) $\text{La}_{0.6}\text{Pb}_{0.4}\text{Ca}_{0.2}\text{MnO}_3$ (heat treated at 1000°C for 320 min).

Nitrogen adsorption/desorption isotherms at $\sim 77\text{ K}$ was used to obtain the informations about the specific surface area S_{BET} and the pore volume of the manganite particles. Two characteristic isotherms are presented in Fig. 4 for Ca containing perovskite powders after heat treatment at 1000°C . These isotherms can be classified as type II in IUPAC (International Union of Pure and Applied Chemistry) classification [18]. One can see that the desorption branch does not follow the adsorption branch, but forms a distinct hysteresis loop of type H3 [20]. The pore size distribution (PSD) graphs obtained from N_2 sorption isotherms by BJH method [20] are shown inset of Fig. 4. The obtained results for S_{BET} from the nitrogen physisorption data and total pore volume for Ca containing manganite are given in Table 2. One can see that S_{BET} ($12.6\text{ m}^2/\text{g}$) for the manganite with Ca substitution, $\text{La}_{0.6}\text{Pb}_{0.2}\text{Ca}_{0.2}\text{MnO}_3$, is much larger than S_{BET} ($8\text{ m}^2/\text{g}$) of manganite with Ca addition, $\text{La}_{0.6}\text{Pb}_{0.4}\text{Ca}_{0.2}\text{MnO}_3$. The pore sizes are in the mesoporous range (5 – 15 nm).

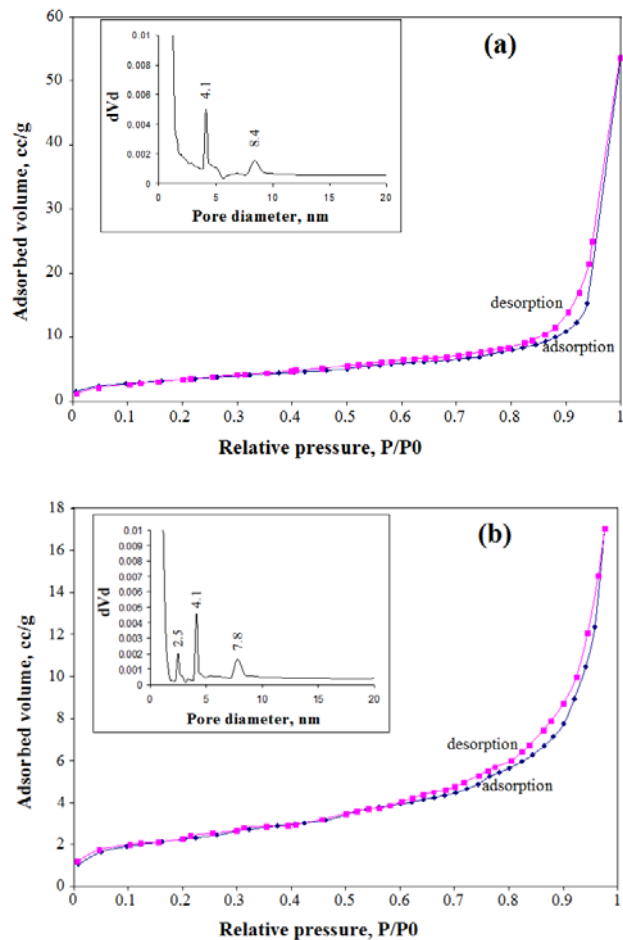


Fig. 4 Nitrogen adsorption/desorption izotherms at 77K for two perovskite powders: a) $\text{La}_{0.6}\text{Pb}_{0.2}\text{Ca}_{0.2}\text{MnO}_3$; b) $\text{La}_{0.6}\text{Pb}_{0.4}\text{Ca}_{0.2}\text{MnO}_3$. Inset: the pore size distribution graphs.

Table 2. Surface area and total pore volume for two samples.

Sample	Surface area (m^2/g)	Total pore volume (cc/g)
$\text{La}_{0.6}\text{Pb}_{0.2}\text{Ca}_{0.2}\text{MnO}_3$	12.596	0.0235
$\text{La}_{0.6}\text{Pb}_{0.4}\text{Ca}_{0.2}\text{MnO}_3$	8.019	0.0298

The catalytic test of the three perovskite manganites was consisted in determining the smallest temperature at which takes place the combustion reaction over manganites of three diluted combustible gases (acetone/air, ethanol/air and methanol/air mixtures) at atmospheric pressure.

In Fig. 5 one can see that the catalytic combustion of the gases over perovskite manganite surface can begin at lower temperature (of about 300°C) than in the normal combustion.

For comparison in Fig. 5 is given the minimum temperature required to ignite the mentioned gases without catalyst. As expected, all investigated perovskite manganites are active as catalysts at temperatures higher 300°C . The results presented in Fig. 5 can be attributed to

the small crystallite size, large surface area and high concentration of surface Mn^{4+} cations, which creates more reactive surface adsorbed oxygen species.

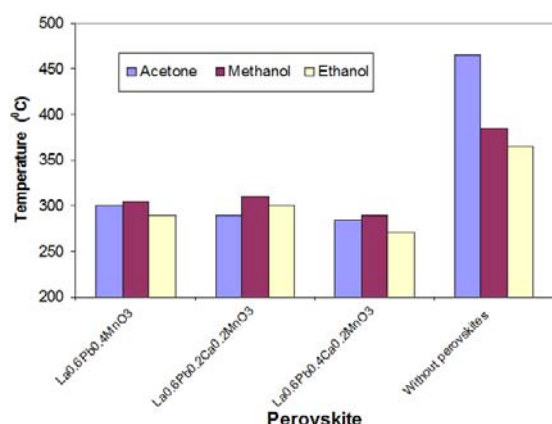


Fig. 5. Bar diagram for the minimum combustion temperature of acetone, ethanol and methanol vapor in air in the presence of perovskite catalysts and without catalyst.

4. Conclusions

In this paper we focused on less-studied system La-Pb-Ca-Mn-O perovskite like manganite. Ca was introduced as partial substitution for Pb or as addition to the basic composition $La_{0.6}Pb_{0.4}MnO_3$ (LPMO). $La_{0.6}Pb_{0.4}MnO_3$, $La_{0.6}Pb_{0.2}Ca_{0.2}MnO_3$ and $La_{0.6}Pb_{0.4}Ca_{0.2}MnO_3$ perovskite type manganite powders have been prepared by self-combustion method and heat treatment at 1000°C . The composites were characterized by X-ray diffraction, scanning electron microscopy and nitrogen adsorption/desorption isotherms. By X-ray diffraction was confirmed the crystallinity and the nanosize of the perovskite crystallites (24 – 26 nm). Scanning electron microscopy (SEM) micrographs showed significant difference in the microstructure of LPMO after CaO incorporation. CaO added LPMO was found to have an average grain size (below 100 nm) much smaller than that of pure LPMO (~ 400 nm) due to Ca segregation on the grain surface. The largest S_{BET} ($12.6 \text{ m}^2/\text{g}$) was obtained for LPMO with Ca substitution, $La_{0.6}Pb_{0.2}Ca_{0.2}MnO_3$.

The catalytic activity of the perovskite manganite nanopowders toward diluted gas combustion (acetone/air, ethanol/air and methanol/air) was evaluated by determining the smallest temperature at which the gas combustion reaction over perovskite catalysts takes place at atmospheric pressure. The experimental results showed that the combustion of gases over perovskite manganite surface can take place at lower temperature (of about 300°C) than in the normal combustion due to small crystallite size, large surface area and high concentration of Mn^{4+} cations.

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