La-Pb-Mg-Mn-O PEROVSKITES: PREPARATION AND STRUCTURAL/MICROSTRUCTURAL CHARACTERIZATIONS FOR CATALYST APPLICATIONS[*]

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Abstract. In this paper we focus on less studied system, La-Pb-Mg-Mn-O manganite perovskite due, to its application as promising catalysts in the combustion of volatile organics (VOC). Highly pure fine perovskite powders were prepared by self-combustion method, followed by heat treatment at $1000^{o}C$. The MgO incorporation in $La_{0.6}Pb_{0.4}MnO_3$ manganites acts both as an inhibitor of grain growth as a sulphur poisoning limiting agent. The morphological and structural characterization of the perovskite powders was performed using XRD, SEM and BET techniques. All samples have a cubic perovskite structure (Pm3m) and the lattice parameter decreases by partial substituting of Pb^{2+} with Mg^{2+} ions. Small crystals with size of about 100 nm were detected by SEM in Mg doped perovskite. The specific surface area, S_{BET}, of about 8.5 m^2/g was evaluated from nitrogen adsorption/desorption isotherms at ~77 K, being a very important parameter for catalyst application. The catalyst tests evidenced a lower combustion temperature of diluted gases (ethanol, methanol and acetone in air) over Mg containing perovskites.

Key words: perovskite; structure; catalytic activity.

1. INTRODUCTION

The high cost and susceptibility to sulphur dioxide poisoning of the noble metal (Pt, Pd) based catalysts have determined extensive studies in order to discover new catalysts which replace the expensive catalysts [1, 2]. In the last years new catalytic systems especially oxides with perovskite, granat or spinel structure were investigated [3–5]. It is known that the catalytic combustion make possible to drastically reduce the temperature required for complete combustion of the volatile organic compounds (VOCs).

Perovskite-type oxides appear to be a promising alternative to noble metal catalysts due to their low cost, thermochemical stability at relatively high temperature and catalytic activity [6].

Perovskite-like lanthanum manganites, $La_{1-x}A_xMnO_3$ (A= Ca, Sr, Ba, Pb) are known especially as magnetoresistive materials: a decrease of the electrical resistivity occurs when a magnetic field is applied [7–10]. Partial substitution of trivalent La^{3+} ions by divalent A^{2+} ions is known to produce a partial oxidation of Mn^{3+} ions to Mn^{4+} ions. This property is very important for application of these materials as catalyst in chemical depollution reactions.

In this paper we investigated a less studied perovskite system, La-Pb-Mn-O manganite, and the effect of Mg^{2+} substitutions for Pb^{2+} in the stoichiometric composition $La_{0.6}Pb_{0.4}MnO_3$ for its application as catalyst. Most researches on manganites are concerned with alkaline-earth elements like Sr, Ba or Ca [11]. Huang *et al.* [12] have studied $La_{1-x}Pb_xMnO_3$ perovskites. The partial replacement of La^{3+} ions by a lower-valence ion Pb^{2+} induces a mixed valence state of Mn^{3+}/Mn^{4+} and improves the conductivity.

The role of the Mg ion in a ceramic is to prevent the growth of the grains by reducing the grain boundary mobility [13, 14]. Previous studies on $LaMn_{1-x}Mg_xO_3$ [15] have shown a promoting effect of the Mg substitution on the catalytic activity of the resulting perovskite. Other studies [16, 17] reported that Mg containing manganites exhibit a good resistance to high temperatures (900–1000 ^oC).

This communication presents the results regarding the preparation method of highly pure fine perovskite powders, La-Pb-Mg-Mn-O, and their structural/ microstructural characteristics. The results are preliminary, but the perovskite-type oxide catalyst La-Pb-Mg-Mn-O seems to be a promising catalyst due to its low active temperature.

2. EXPERIMENTAL

Perovskite powders of nominal composition $La_{0.6}Pb_{0.4-x}Mg_{x+y}MnO_3$, ($x = 0$, 0.1, 0.2, $y = 0$ and $x = 0$, $y = 0.2$), were prepared by self-combustion route [18, 19, 20]. This simple and fast route implies low energy consumption and allows a controlled growth of the crystallites by subsequent heat treatment. As starting materials were used metal nitrates and ammonium hydroxide of high purity. An aqueous solution of polyvinyl alcohol was used to make a colloidal solution. By coprecipitation into a colloidal medium a viscous gel was obtained. After drying, the gel was ignited in a corner. An exothermic combustion reaction began and the combustion front spontaneously propagated through all the gel and converts the dried gel in a loose powder. The combusted powder was calcined at 500^oC in air for one hour to eliminate the residual organic compounds. Then, the calcined powders were heat treated at 1000^oC in air, for two different times, of 40 and 320 minutes with heating and cooling rate of 5 deg/minute. The phase composition of the heat treated samples was identified by powder X-ray diffraction (XRD) using CuKα radiation

(λ = 1.54 Å). Microstructural studies have been performed with scanning electron microscope (SEM) QUANTA 200 3D Dual Beam model. The average grain size D_m was determined from SEM images, by the linear intercept method [21].

The specific surface area (S_{BET}) was calculated from the nitrogen sorption isotherms at ~77 K. using the Brunauer-Emmet-Teller (BET) equation [22]. Adsorption/desorption of nitrogen isotherms were determined at ~77 K with NOVA 2200 apparatus. The pore size distribution (PSD) curves were obtained from the adsorption/desorption isotherms using BJH (Barret, Joyner and Halenda) method [22].

The catalyst properties were investigated with a set-up which can determine the minimum temperature of gas combustion in the presence or absence of the catalyst.

3. RESULTS AND DISCUSSION

The X-ray diffractograms (Fig. 1) indicate cubic perovskite structure (Pm3m) of prepared powders and heat treated at 1000°C for 40 min. The lattice parameters for samples heat treated at 1000°C for 40 and 320 minutes, respectively, are given in Table 1. These values are in good agreement with those found in analogous compounds [21]. Prolonged heat treatment did not result in the lattice parameter change. A decrease lattice parameter change in the lattice parameter by partial substitution of Pb^{2+} ions with Mg^{2+} ions (samples 2 and 3) was obtained, which is in concordance with smaller ionic radius of Mg (0.086 nm) than that of Pb (1.33 nm) [22]. It is noted that the lattice parameter of the last sample, $La_{0.6}Pb_{04}Mg_{0.2}MnO_3$ ($x = 0$, $y = 0.2$) does not differ too much from that of the parent composition, $La_{0.6}Pb_{0.4}MnO_3$. This suggests that the Mg ion addition over stoichiometric composition $La_{0.6}Pb_0.4MnO3$ does not enter in perovskite structure; this addition can form secondary phases (in small amount) on the grain boundaries preventing the grain growth.
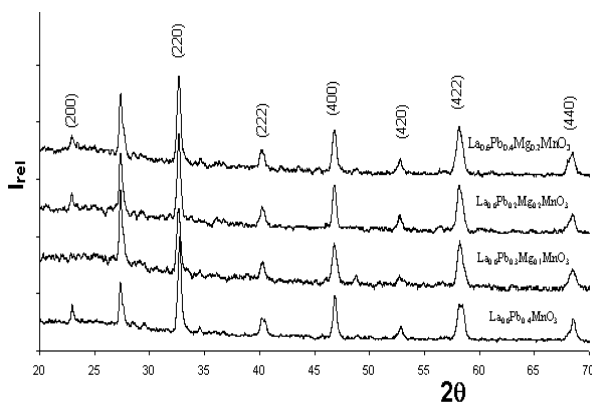

Fig. 1 – XRD paterns for studied perovskites (heat treated at 1000°C for 40 min).

Table 1

Lattice parameters for studied samples

Sample number	Sample composition	a (nm)	
		40 minutes	320 minutes
1	$La_{0.6}Pb_{0.4}MnO_3$	0.7755	0.7752
2	$La_{0.6}Pb_{0.3}Mg_{0.1}MnO_3$	0.7742	0.7744
3	$La_{0.6}Pb_{0.2}Mg_{0.2}MnO_3$	0.7733	0.7740
4	$La_{0.6}Pb_{0.4}Mg_{0.2}MnO_3$	0.7751	0.7749

The surface morphology of samples examined by SEM is illustrated in Fig. 2. It is clear from the micrographs that the microstructure changes with changing the perovskite composition. One can observe a decrease of the grain size from 300 – 400 nm to about 100 nm by magnesium addition and the finer granulation led to formation of large agglomerates (of about 4 μm).
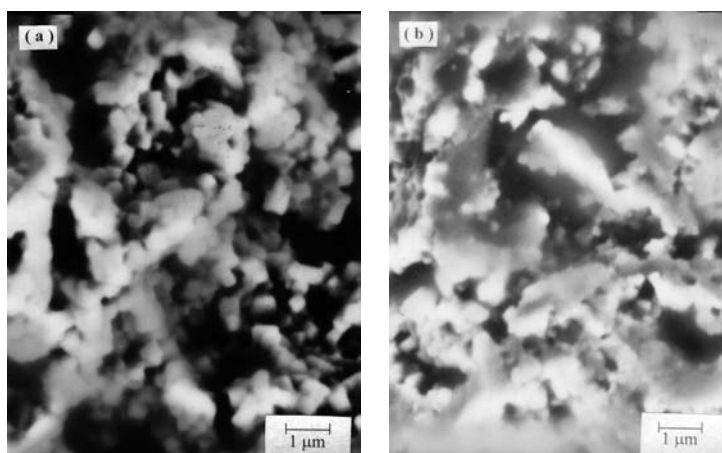

Fig. 2 – SEM micrographs: (a) $La_{0.6}Pb_{0.4}MnO_3$ and (b) $La_{0.6}Pb_{0.4}Mg_{0.2}MnO_3$ samples heat treated at 1000^oC for 320 min.

Nitrogen adsorption/desorption at 77 K was used to obtain informations about the specific surface area and the pore volume of the perovskite particles. The characteristic isotherms are presented in Fig. 3 for two perovskite powders. These isotherms can be classified as type II in IUPAC classification with a type H_3 hysterezis [22]. The pore size distribution graphs are shown inset of Fig. 3. The obtained results are summarized in Table 2. One can see that the specific surface area, S_{BET}, has reasonable values (about 8.6 m^2/g) and the total pore volume is very small. Having a large surface area is one of the most essential requirements for active catalyst. The pore sizes are in the mesoporous range (5–15 nm) and the pore size distribution changes with the increase of Pb content. The total pore volume was correlated with adsorbed nitrogen volume.

Composition, surface area and total pore volume for two samples

Sample	Surface area (m^2/g)	Total pore volume (cc/g)
$La_{0.6}Pb_{0.2}Mg_{0.2}MnO_3$	8.453	0.0212
$La_{0.6}Pb_{0.4}Mg_{0.2}MnO_3$	8.584	0.0187
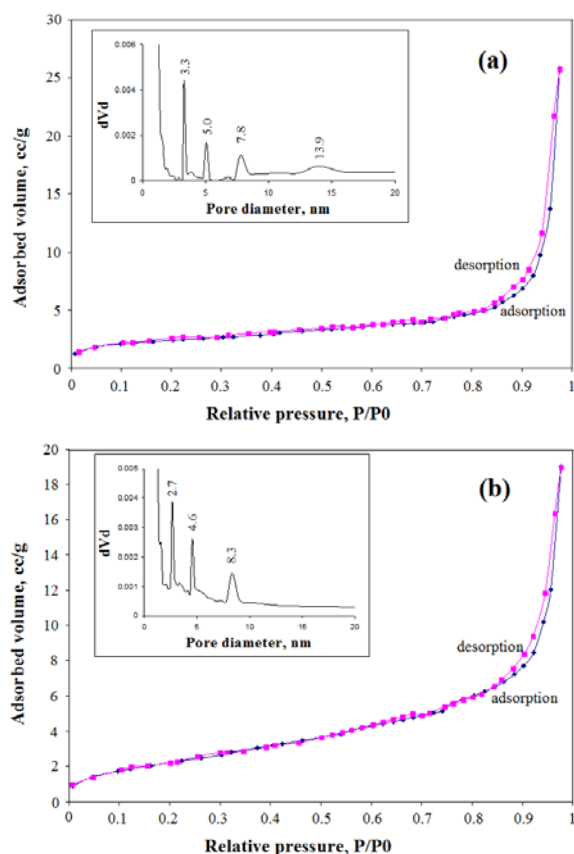
Fig. 3 – Nitrogen adsorption/desorption izoterms at 77K for two perovskite powders:
a) $La_{0.6}Pb_{0.2}Mg_{0.2}MnO_3$; (b) $La_{0.6}Pb_{0.4}Mg_{0.2}MnO_3$. Inset: the pore size distribution graphs.

The catalytic activity of the perovskite powders was appreciated by determining the minimum temperature at which the combustion reaction of acetone/air, ethanol/air and methanol/air mixtures over perovkites appears at atmospheric pressure. The experiments were carried out with a set-up which can realize an isotherm combustion reaction. In a branch of the Wheatstone bridge is connected a tungsten filament, electrically isolated and covered with a perovskite powder layer. Tungsten has not catalytic properties in the investigate temperature

range, 20–500 ^{o}C. In the presence of gas/air mixture, the filament is heated to a certain temperature and the bridge is equilibrated. When the combustion reaction of the gas over perovskite surface starts, an increase of the filament temperature occurs which is automatically counterbalanced by a decrease in the filament voltage. The temperature at which a decrease in the filament voltage appears is the minimum temperature for the catalytic combustion reaction of the gas over the perovskite powder surface. The obtained results are given in Fig. 4. For comparison, it is given the minimum temperature required to ignite acetone, ethanol or methanol vapor in air without a spark or catalyst being present. From this bar diagram one can remark that the combustion reaction of diluted gases catalyzed by perovskite powders takes place at lower temperatures (below 300°C). One can suppose that in the case of Mg containing perovskites the presence of Mg ions lower the gas activation barrier and thus the much more intensive interactions between perovskite surface and the test gas increase the gas oxidation rate at low temperatures. Thus, the temperature for the beginning the combustion reaction of gases will be lower than in the case of perovskite catalyst La-Pb-Mn-O without Mg.
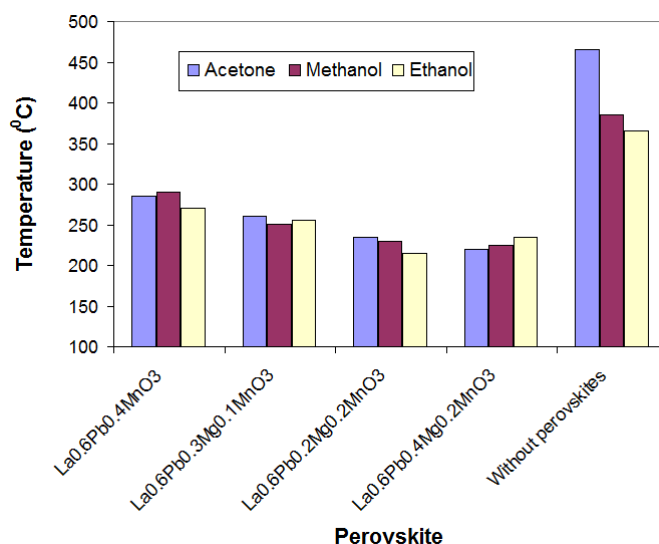

Fig. 4 – Bar diagram for the minimum combustion temperature of acetone, ethanol and methanol vapor in air in the presence of perovskite catalysts and without catalyst.

4. CONCLUSIONS

Highly pure fine perovskite powders were prepared by self-combustion method, followed by heat treatment at 1000°C. Mg^{2+} ions substitute Pb^{2+} ions in La$_{0.6}$Pb$_{0.4}$MnO$_3$ stoichiometric manganite, or was added over stoichiometric composition.

X-ray diffractograms show a monophase cubic perovskite structure (Pm3m). The lattice parameter decreases by partial substituting of Pb^{2+} with Mg^{2+}ions.

If Mg was added over $La_{0.6}Pb_{0.4}MnO_3$ stoichiometric composition, small particles of about 100 nm were detected by SEM and the best surface area, S_{BET}, of about 8.6 m^2/g, was obtained.

The catalyst tests evidenced that the combustion of diluted gases (ethanol, methanol and acetone in air) over Mg containing $La_{0.6}Pb_{0.4}MnO_3$ perovskite catalyst takes place at lower temperatures than in the case of perovskite catalyst without Mg. The results are preliminary, but the perovskite-type oxide catalyst La-Pb-Mg-Mn-O seems to be a promising catalyst due to its low active temperature.

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