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SYNTHESIS OF $NdMnO_3$, $Nd_{0.6}Pb_{0.4}MnO_3$ AND $(La_{0,7}Nd_{0,3})_{0.6}Pb_{0.4}MnO_3$ NANOPOWDERS BY MECHANO-CHEMICAL ACTIVATION

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ABSTRACT

Nanosized powders of rare-earth manganites $NdMnO_3$, $Nd_{0.6}Pb_{0.4}MnO_3$ and $(La_{0,7}Nd_{0,3})_{0.6}Pb_{0.4}MnO_3$ obtained by mechano-chemical synthesis under different conditions (speed, milling time, temperature) in planetary ball mill were investigated. The starting oxides for the mechanochemical reaction La_2O_3, Nd_2O_3, MnO_2, Pb_3O_4, were mixed in an appropriate ratio corresponding to the stoichiometric compounds. The phase formation was studied by X-ray diffraction, SEM, TEM, DTA and IR-spectroscopy. Phase $(La_{0,7}Nd_{0,3})_{0.6}Pb_{0.4}MnO_3$ was successfully synthesized at 1000 rpm for 3 hours without the application of additional thermal treatment. The phases $NdMnO_3$ and $Nd_{0.6}Pb_{0.4}MnO_3$ were obtained after 5 hours mechano-chemical treatment at 1000 rpm. The particle size of the powders are in the range of 18 - 20 nm. Magnetic properties of the powders were studied. The phase $(La_{0,7}Nd_{0,3})_{0.6}Pb_{0.4}MnO_3$ is ferromagnetic at room temperature and it is appropriate for the preparation of the bulk sintering polyfunctional ceramics composites.

Keywords: rare earth manganite, mechano-chemical reactions, nanopowders.

INTRODUCTION

Rare earth manganites are known for their ferromagnetic and electrical properties, giant magneto resistance (GMR), catalytic properties, which activates their intensive study [1 - 4]. Although the effect of colossal magnetoresistance has not yet been widely used due to the need to use strong magnetic fields to observe large magnitude of this effect, the research it stimulated significantly deepened understanding of the nature and laws of electrical and magnetic properties of perovskites and complex oxides in general. The lantanium manganites have a large potential for technological applications, such as in transducers, nonvolatile memory devices and cathode materials in solid oxide fuel cells. The presence of the Mn^{3+} and Mn^{4+} mixed valence ions is responsible for ferromagnetic coupling and charge transport. The appropriate ratio of this ions is achieved by introduction of the two valent ions (Sr^{2+}, Ca^{2+}, Pb^{2+}), which substitute La^{3+} ion. Particular attention is paid to obtain nanosized powders which have a number of specific properties. For their preparation low temperature techniques such as Pecini method [5], the sol-gel method [6, 7], co-precipitation in aqueous solution [8 - 12] are suitable. Good alternative for easily and cheaply obtaining of nanosized powders is mechano-chemical synthesis. It is an interesting and promising method enabling synthesis of superfine powders and phases with improved physical and chemical properties. The powders produced by mechano-chemical synthesis have a large specific surface area of the particles. Mechano-chemical synthesis has become popular as an option for the synthesis of stable and metastable phases for many years of research by several leading laboratories [13, 14] - monographs. Only a few papers were published for the preparation of rare-earth manganites by mechano-chemical method [15 - 17]. This motivated us to perform experiments in these directions because we have some experience in the application of other low temperature methods for similar rare earth manganites. Phases $NdMnO_3$, $Nd_{0.6}Pb_{0.4}MnO_3$ and $(La_{0,7}Nd_{0,3})_{0.6}Pb_{0.4}MnO_3$ are objects of this study.

According to the published data the phase $NdMnO_3$ is synthesized by solid state reaction at 1400°C. Doping of two valent cation leads to the transition of structure from orthorhombic to cubic. Magnetic and thermodynamic properties of phase $NdMnO_3$ have been studied and it is defined Neel temperature T_N = 100K. With the reduction of the oxygen content of x = 2.85 the phase is converted to antiferromagnetic state with a temperature of Neel T_N = 85 K [18 - 21]. Mono crystals of $Nd_{1-x}Pb_xMnO_3$ with x = 0.2 have transition in ferromagnetic state at Tc ~ 125K and in the temperature range of T = 50 - 300 K. This phase is an insulator [22].

The addition of Pb^{2+} at the expense of part of lanthanum in the lanthanum manganite affects the ratio between the ions Mn^{4+}/Mn^{3+} and also influences the electrical and magnetic properties, lowers the temperature of synthesis, increases the density and conductivity of the material [23 - 26]. The phase $La_{1-x}Pb_xMnO_3$ possesses colossal magneto resistance and ferromagnetic properties at room temperature [27, 28]. Samples of composition $La_{0,7-x}Nd_xPb_{0.3}MnO_3$ (x = 0, 0.05, 0.01) were prepared by the sol-gel technique. Electric resistance and CMR as a function of temperature were studied. It was established the double metal-isolator transition and ferromagnetic ordering transition above the room temperature [29]. The review shows that these phases have interesting properties and further expansion of the combinations of the composition and production of new solid solutions involving Nd and Pb represent a technological interest.

Strontium-substituted lanthanum manganite nanoparticles ($La_{0.7}Sr_{0.3}MnO_3$) were synthesized via the low-temperature calcination of the precursor at 600°C, which was prepared using a mechano-chemical route. The obtained LSMO nanoparticles and LSMO/hydroxyapatite composites are promising candidates for magnetic hyperthermia treatments [30]. It is proved the positive effect of high energy ball milling on the magnetocaloric properties of materials based on strontium-calcium doped lanthanum manganite [31]. All the synthesized manganites show higher magnetocaloric effect as compared to that of the parent compounds synthesized by other methods.

The purpose of this study is to identify the conditions for a mechano-chemical solid phase synthesis of $NdMnO_3$, $Nd_{0.6}Pb_{0.4}MnO_3$ and $(La_{0,7}Nd_{0,3})_{0.6}Pb_{0.4}MnO_3$ as nano powders and verify the possibility for the preparation of polyfunctional ceramics and composites based on them.

EXPERIMENTAL

Materials and methods

Mechanochemical method which we applied is based on the interaction between metal oxides by mechano-chemical activation using planetary mill reactors. The initial raw materials La_2O_3, Nd_2O_3 MnO_2 and Pb_3O_4 were used for the synthesis of $(La_{0.7}Nd_{0.3})_{0,6}Pb_{0,4}MnO_3$, $NdMnO_3$ and $Nd_{0,6}Pb_{0,4}MnO_3$ phases. The oxides were mixed in stoichiometric amounts and homogenized in an agate mortar. The resulting batch was subjected to a subsequent milling for 1 to 5 hours in a planetary mill model FRITSCH premium line at 500 and 1000 rpm at atmospheric conditions. Approximately 2 g of the batch was placed in a steel mortar of the mill with 20 g steel milling balls (5 mm diameter, 40 in number), then the samples were subjected to mechanical processing for varying periods of milling time (1, 2, 3, 4 and 5 hours). The resultant powders with nominal compositions $(La_{0.7}Nd_{0.3})_{0,6}Pb_{0,4}MnO_3$, $NdMnO_3$ and $Nd_{0,6}Pb_{0,4}MnO_3$ were investigated using X-ray, DTA, IR. It was defined the phase formation, the basic structural units and temperatures of phase transformations.

RESULTS AND DISCUSSION

Mechanochemical synthesis of $(La_{0.7}Nd_{0.3})_{0,6}Pb_{0,4}MnO_3$

The XRD patterns of the samples after mechano-chemical treatments at 1, 2, 3, 4, and 5 h at 1 000 rpm are shown in Fig. 1. After milling for 1 to 2 hours mainly an amorphous phase is obtained (Fig. 1). This shows that the mechanical treatment leads to the complete destruction of the crystal structure of the starting oxides. Upon increasing the milling time up to 3 hours crystallization was observed of the phase, $(La_{0.7}Nd_{0.3})_{0,6}Pb_{0,4}MnO_3$ in the presence of minor amounts of Pb_3O_4. The size of the particles was 21 nm. The X-ray pattern was not changed up to 4 hours of milling. After 5 hours we obtain a mono-phase product with a particle size of 18 nm. It is ferromagnetic at room temperature. This experiment demonstrates the successful synthesis of ferromagnetic phase $(La_{0.7}Nd_{0.3})_{0,6}Pb_{0,4}MnO_3$.

Fig. 2 shows results of IR- spectroscopy. The bands around 600 cm^{-1} - 610 cm^{-1} and 400 cm^{-1} are associated

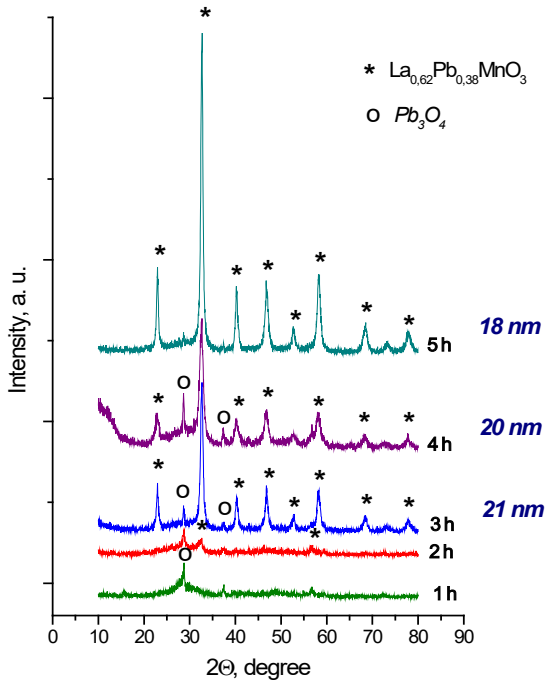

Fig. 1. XRD patterns of samples $(La_{0.7}Nd_{0.3})_{0,6}Pb_{0,4}MnO_3$ milled for various times at 1 000 rpm.

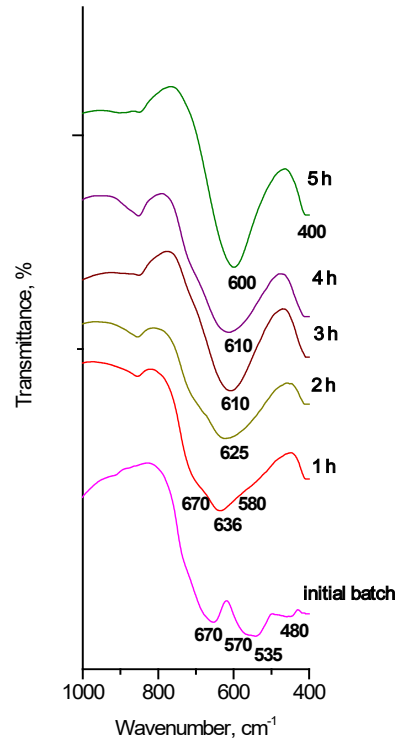

Fig. 2. IR specroscopy of $(La_{0.7}Nd_{0.3})_{0,6}Pb_{0,4}MnO_3$ batch and powders milled for various times.

with valence vibrations of MnO_6-octahedra [32]. Upon application of mechano-chemical processing for 1 to 2 hours the spectrum is dominated by broad bands about 636 cm^{-1} and 625 cm^{-1}, with shoulders around 670 cm^{-1} and 580 cm^{-1}. The change in intensity of some of the bands is associated with the transition of the material from the crystalline to the amorphous state. Upon application of mechano-chemical treatment for 3 h there is a transition from amorphous to the crystalline state according to X-ray patterns (Fig. 1). In the spectrum it is observed narrowing of the band associated with the asymmetric vibrations of Mn-O bonds in MnO_6 poliedra and a shift to smaller wave number - 610 cm^{-1}. This trend is increased and the band becomes more symmetric and is shifted to 600 cm^{-1} at 4 and 5 h of mechanical treatment. According to [33] in mechanochemical processing, pyrolusite (MnO_2) was transformed in Mn_2O_3. This phase was converted to Mn_3O_4 - hausmannite at 1100°C. The result is a partial reduction of Mn^{4+} to Mn^{3+} to Mn^{2+}. This transformation is reflected by the disappearance of the bands at 400 cm^{-1} in the spectrum, retaining band around 600 cm^{-1} and a reduction of its intensity. This may be associated with the vibrations of MnO_6 groups in one non-stoichiometric phase, which includes Mn ions with varying degrees of oxidation [33, 34]. According to C. Roy the transition from orthorhombic to rhombohedral structure, which proceeds at introduction of divalent ions in manganite phase leads to a strong decrease of the intensity of the band at 400 cm^{-1}. This is an indirect indication, that the obtained structure involved both Mn^{3+} and Mn^{4+} ions.

Mechanochemical synthesis of the phases: $NdMnO_3$ and $Nd_{0,6}Pb_{0,4}MnO_3$

The received samples obtained by different duration of milling and at two different rotational speeds - 500 and 1000 rpm were characterized by XRD (Fig. 3 and Fig. 4). All samples were milled at 500 rpm contain initial oxides MnO_2 and Nd_2O_3. With increasing the duration of the milling, it is observed broadening of the diffraction maximums and a reduction of their intensity, which is associated with a decreasing of particle size and partially

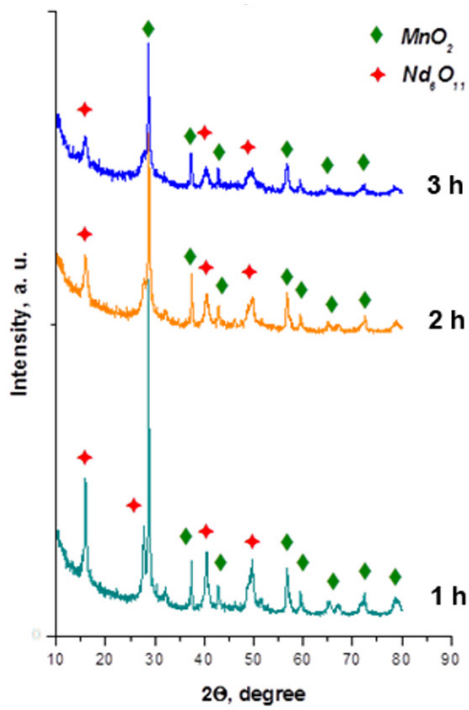

Fig. 3. XRD patterns of the $NdMnO_3$ milled for different times at 500 rpm.

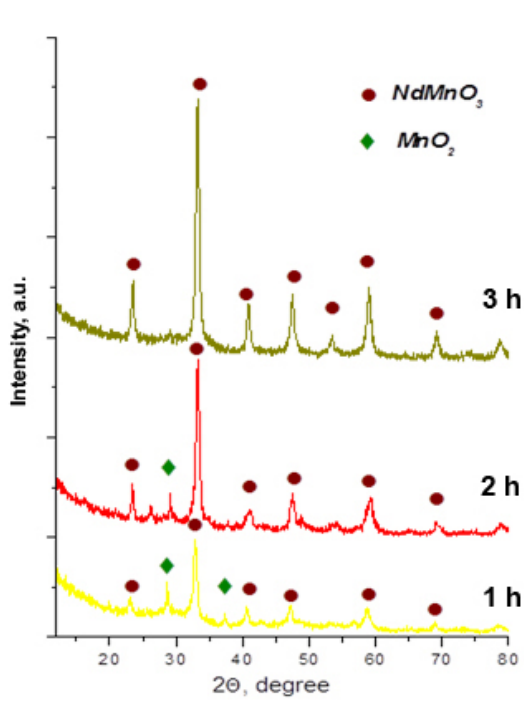

Fig. 4. XRD patterns of the $NdMnO_3$ milled for different times at 1000 rpm.

amorphization of the sample (Fig. 3). At 1 000 rpm even after 1 hour a new phase is synthesized together with MnO_2. After 5 hours of milling it was obtained a mono-phase product (Fig. 4).

From IR-spectroscopy (Fig. 5) a shift of the band, associated with vibration of $[MnO_6]$-groups from 610 cm^{-1} to 590 cm^{-1} is observed, which can be due to a transformation of $[MnO_6]$ polyhedra from initial oxide to $[MnO_6]$ groups in the new phase.

The obtained powders were subjected to differential thermal analysis (DTA). T_G curves show the change in mass of the sample in dependence on temperature (Fig. 6.). The endothermic effects at 133, 379 and 660°C are assigned to the total mass loss of 12.89 %. Endothermic effect at 133°C is associated with the release of water from the phase. The endothermic effect at 379°C corresponds to dehydration of the pyrolusite, and the effect at 660°C is associated with the dissociation of pyrolusite β-MnO_2. At temperatures above 800°C transformation in Mn_3O_4 takes place. The endothermic effect at 963°C is associated with the appearance of a liquid phase.

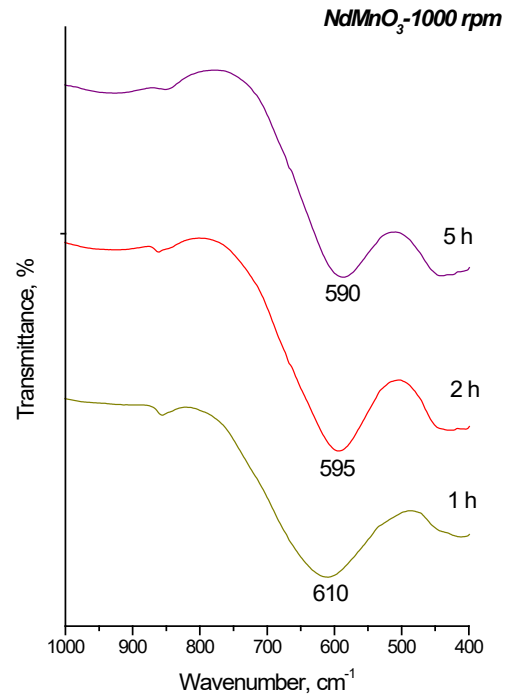

Fig. 5. IR- spectroscopy of $NdMnO_3$ powders milled for different times.

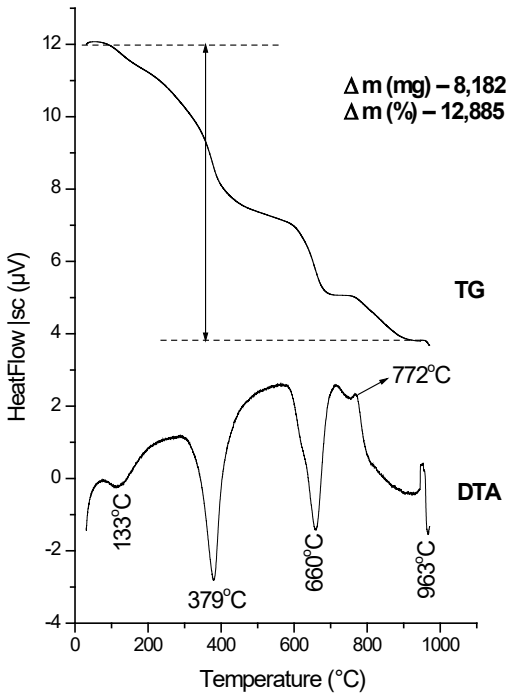

Fig. 6. DTA of sample $NdMnO_3$ subjected to mechano-chemical activation for 3 h at 500 rpm.

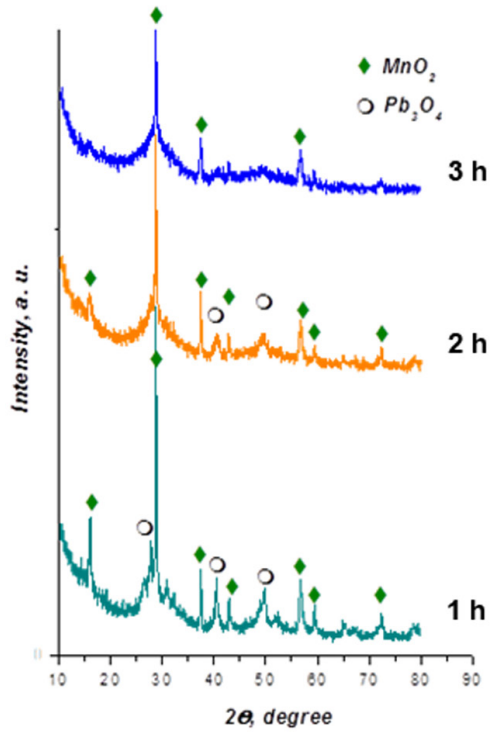

Fig. 7. XRD patterns of the $Nd_{0.6}Pb_{0.4}MnO_3$ milled for different times at 500 rpm.

XRD patterns in Fig. 7 and Fig. 8 show the results from the mechano-chemical reaction leading to the formation of the phase $Nd_{0.6}Pb_{0.4}MnO_3$. It is evident that after 3 hours of milling at 500 rpm, amorphous phase and MnO_2 coexist. After 5 hours of milling at 1000 rpm it is observed complete synthesis of the phase $Nd_{0.6}Pb_{0.4}MnO_3$ (Fig. 8).

The results from IR-spectroscopy are shown in Fig. 9. It is seen that in the spectrums of the samples treated for 1 to 2 hours the band around 630 cm^{-1} is very broad, which is typical for the amorphous sample. Due to the progress of the chemical reaction and the crystallization, the maximum band is sharper and it is shifted to lower wavenumbers after 5 hours of milling. As already mentioned it is due to the vibrations of MnO_6 polyhedra, included in the manganite phase $Nd_{0.6}Pb_{0.4}MnO_3$.

The obtained powders after 3 h milling were subjected to differential thermal analysis (DTA). The mass losses are registered at 332°C and 597°C and the total mass loss is 13.59 %. The endothermic effects at temperatures 332°C, 479°C, 597°C, 645°C and 762°C are associated with the dehydration of MnO_2,

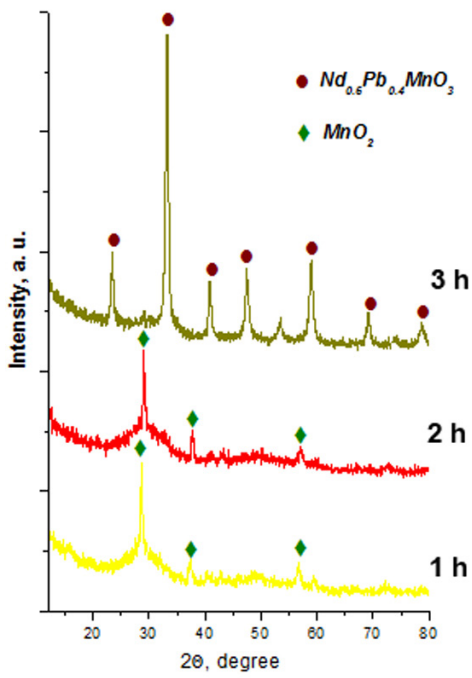

Fig. 8. XRD patterns of the $Nd_{0.6}Pb_{0.4}MnO_3$ milled for different times at 1000 rpm.

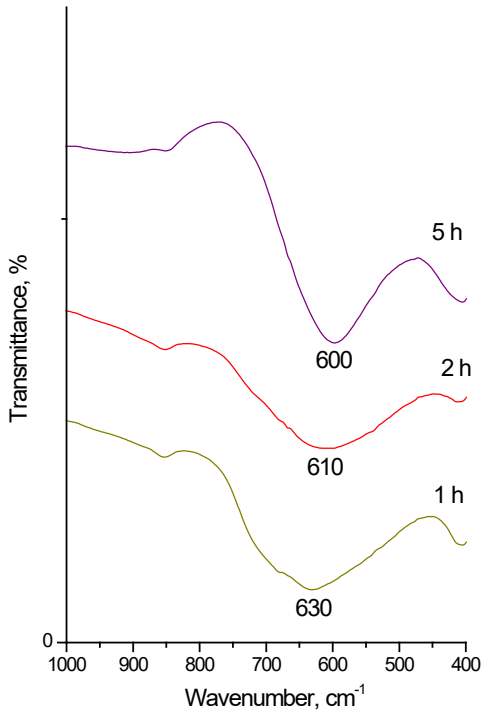

Fig. 9. IR-spectroscopy of $Nd_{0.6}Pb_{0.4}MnO_3$ powders milled for different time at 1000 rpm.

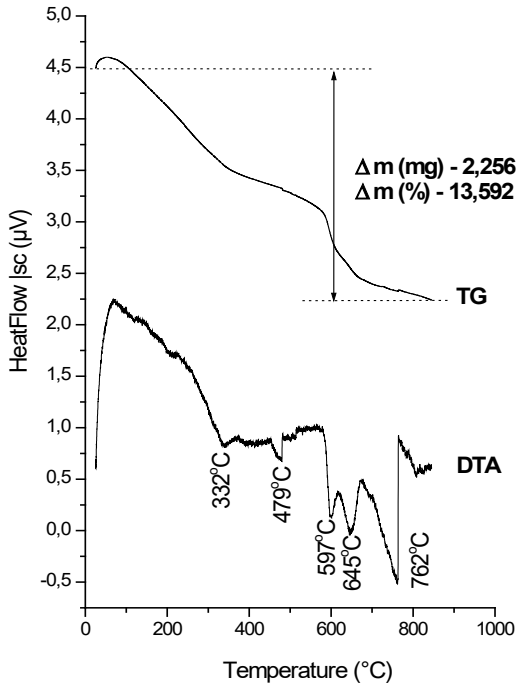

Fig. 10. DTA of sample $Nd_{0.6}Pb_{0.4}MnO_3$ subjected to mechanochemical activation for 3 h at 500 rpm.

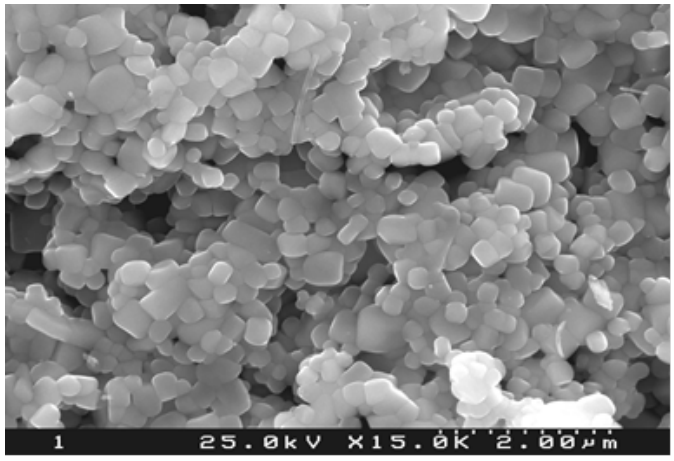

Fig. 11. SEM analysis of the obtained powders $(La_{0,7}Nd_{0,3})_{0.6}Pb_{0.4}MnO_3$ after 3 h milling.

transformation of Pb_3O_4 in PbO and the dissociation of MnO_2 (pyrolusite) to α-Mn_2O_3.

The morphology of the nanoparticles in the powders of $(La_{0,7}Nd_{0,3})_{0.6}Pb_{0.4}MnO_3$ are observed by SEM (Fig. 11). The SEM micrograph confirms the crystalline character of the powder with the tendency for agglomeration.

CONCLUSIONS

The phases $(La_{0,7}Nd_{0,3})_{0.6}Pb_{0.4}MnO_3$, $NdMnO_3$ and $Nd_{0.6}Pb_{0.4}MnO_3$ were successfully synthesized by mechano-chemical activation at 1000 rpm for 3 - 5 hours without the application of additional thermal treatment. While in standard ceramic technology, these phases are

obtained at 1600°C. The particle size of the powders is in the range 18 - 20 nm. It was observed that the samples treated up to 2 hours became mainly amorphous. The obtained nanopowders are suitable as precursors for the preparation of sintering ceramic materials.

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