PHASE FORMATION AND MICROSTRUCTURE OF THE $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ OBTAINED BY LOW TEMPERATURE METHODS

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ABSTRACT

This work is a continuation of previous studies, presented at the 5th National Conference of Chemistry, Sofia, 2004 and Jubilee Conference with international participation “60 Years Department of General and Inorganic Chemistry”, 2005, UCTM, Sofia. The purpose is to be obtained nanosized powders of the phase $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$ using low temperature coprecipitation methods. By SEM, IR-spectroscopy, X-ray diffraction the structural and phase transformations during the heat treatment at a wide temperature range have been determined. The formation of the manganite phase was detected at 600°C. A mono phase crystalline material was obtained at 800 °C after 24 h heat treatment. According EDS analysis the ratio between the elements in the synthesized product corresponds to $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$. The applied nontraditional low temperature methods are suitable for the preparation of mono phase powders with a particle size distribution below 0.2 μm.

Keywords: low temperature methods, phase formation, microstructure, manganites, powders.

INTRODUCTION

Rare earth perovskite-type compounds have been investigated for their functional properties and used as catalysts, fuel cells, gas sensors. They are promising materials also due to their high electrical conductivity and large negative magnetoresistance. For most of them the wet chemical methods for the preparation have been successfully applied: Pechini process [1]; aqueous solution-coprecipitation [2-7]; sol-gel method [8, 9]. The main advantages of the liquid precursor with respect to the solid ones are the degree of chemical homogeneity and the atomic-level dispersion of the reagents, obtainable even in very complex composition [10].

In our previous studies [11, 12] a comparison was made of different methods for the preparation of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ phase. The obtained nanosized powders were applied for the preparation of magnetic glass-ceramic composites by sintering [13].

Another interesting phase from the series with general formulae $\text{La}_{1-x}\text{M}^{2+}\text{Mn}^{3+}\text{Mn}^{4+}\text{O}_3$ M=Ca, Sr, Ba, Cd, Pb [14, 15] is $\text{La}_{1-x}\text{Pb}\text{MnO}_3$. Single crystal of $\text{La}_{1-x}\text{Pb}\text{MnO}_3$, 0.25<x<0.45 has been grown by the flux technique [16]. It was established that the cubic perovskite structure was slightly distorted to rhombohedral. The same team has studied the ferromagnetic properties and it was found that the Curie temperature is almost a linear function of composition $x$ ($T_c=315$-
350K) [17-21]. The introduction of Pb\(^{2+}\) in the crystal lattice of the manganite stimulates a high ratio Mn\(^{4+}/Mn^{3+}\) [22], decreases the temperature of the synthesis and improves the conductivity. Polycrystalline solid solutions containing Pb\(^{2+}\) in larger concentrate range (0.1<x<0.6) are synthesized by ceramic method [23]. It was confirmed the formation of rhombohedral distorted structure at x<0.5 and an increasing of the conductivity with increasing of the lead to x=0.4. The discovered of the Giant Magnetoresistans (GMR) renewed the interest in perovskite manganites [24]. This propertie was called by Jin [25] Colossal Magneto Resistans (CMR). Magnetotransport properties for La\(_{1-x}\)Pb\(_x\)MnO\(_3\) were investigated for single crystals [26-28] and for films [29, 30]. It was found a close relationship between giant magnetoresistance and the ferromagnetic ordering transition. A sigh change in the curvature of temperature dependence of the resistance in magnetic field below and above Curie point has been observed. These results motivated our interests to study the synthesis of La\(_{0.6}\)Pb\(_{0.4}\)MnO\(_3\) phase. We orientated our experiments for the preparation of stoichiometric powders with submicron particle size distribution taking in to account our experience in the field of wet chemical methods.

The purpose of this study is to determine the transition of the initial fine powders, obtained by a low temperature carbonate method into a mono phase product La\(_{0.6}\)Pb\(_{0.4}\)MnO\(_3\), using different heat treatment regimes.

**EXPERIMENTAL.**

A coprecipitation route with three versions (Fig. 1) were used in this experiment for the preparation of the fine powders of La\(_{0.6}\)Pb\(_{0.4}\)MnO\(_3\) (a - solution-coprecipitation route; b - reverse solution-coprecipitation route; c - pH controlled reverse solution-coprecipitation route). Heat treatment proceeded over the temperature range 120-1000°C. The steps of the phase formation in the different technological schemes were controlled by X-ray diffraction using diffractometer Phillips with CuK\(_\alpha\) - radiation, quartz monochromator and scanning area from 10 to 35 \(\theta\). Infrared spectra (IR) were recorded in the range from 400 to 4500 cm\(^{-1}\) with an FT-IR BRUCKER IFS F-113 spectrometer. The samples were prepared by mixing the finely ground powders with dry KBr and were pelletized in the form of thick discs. The microstructure was observed by transmission electron microscope (TEM-Phillips EM-400) using replica method and scanning electron microscopy (SEM Hitachi S-4100).

**RESULTS AND DISCUSSION**

The analysis of the obtained results by the applied different coprecipitate versions shows that more reproducible results have been obtained by pH controlled reverse solution-coprecipitation route (Fig. 1c). These data will be discussed in details. After drying at 120°C and heating up to 600°C the samples are almost amorphous with small amount of intermediate by-products such as La\(_2\)CO\(_3\) and MnCO\(_3\) (Fig. 2). The formation of the manganite phase was detected at 600°C. A mono phase
Fig. 2. X-ray patterns of powders, obtained by carbonate reverse method; heat treatment at: a – 400°C – 18 h; b – 600°C – 6 h; c – 700°C – 12 h; d – 800°C – 24 h; e – 1000°C – 2 h; f – 1000°C – 12 h; • - La$_{0.6}$Pb$_{0.4}$MnO$_3$; ○ - La$_2$CO$_3$.

Fig. 3. Microanalysis by EDS of the phase La$_{0.6}$Pb$_{0.4}$MnO$_3$, obtained by Coprecipitation method, heat treatment at 1000°C for 1 h.

Fig. 4. IR-spectra of the sample, obtained by Coprecipitation method, heat treatment at: a - 400°C – 18 h; b – 600°C – 6 h; c – 700°C – 6 h; d – 800°C – 6 h; e – 1000°C – 1 h.
Fig. 5. SEM micrograph of the phase $\text{La}_{0.6}\text{Pb}_{0.4}\text{MnO}_3$, obtained by Coprecipitation method, heat treatment at: a - 400°C – 18h; b – 600°C – 6 h; c – 700°C – 6 h; d – 800°C – 6 h.
crystalline material was obtained at 800°C after 24 h heat treatment and after 1000°C – 1 h.

With EDS analyses it was determined the ratio of the elements in the different points of the sintering mono phase material. It is proved that the content of the La: Pb: Mn (33:9:14:11:51:89) is similar to that of the pure La$_{0.5}$Pb$_{0.5}$MnO$_3$ (Fig. 3).

The IR-spectra give additional information about the phase formation. The spectra of the samples calcined at 400 and 600°C (Fig. 4) show the presence of CO$_3$ - groups (1460 cm$^{-1}$, 860 cm$^{-1}$), and Mn$^{4+}$O$_6$ - groups (540-560 cm$^{-1}$). Transformation of the IR-spectra occurs after heat treatment at 700°C (Fig. 4). The carbonate groups disappear and MnO$_6$ - units only remain. Part of them are Mn$^{4+}$O$_6$, which is determined by the displacement of the characteristic band to 600-620 cm$^{-1}$ and the formation of a shoulder around 520 - 540 cm$^{-1}$ [13]. Small crystals with size below 0.2 μm were detected by scanning electron microscopy (Fig. 5).

CONCLUSIONS

A mono phase crystalline powder of the La$_{0.5}$Pb$_{0.5}$MnO$_3$ was obtained by pH controlled reverse solution-coprecipitation route after heat treatment at 800-1000°C.

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REFERENCES