SYNTHESIS OF POWDERS OF SOLID SOLUTIONS (1-X) $LA_{1-Y}ME'_YMNO_3$ – $XLA_{1-Z}ME''_ZMNO_3$ (ME′AND ME″:CA, SR, PB) BY USING SOL-GEL METHOD

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Introduction

The observation of "colossal" magnetoresistance (CMR) in manganese oxides crystallizing in the perovskite structure has generated considerable interest in the physical properties of this class of compounds, particularly the interplay of structure, magnetism and electronic transport. CMR has been reported for (among others) $La_{1-x}M_xMnO_{3+\delta}$ (M=Sr, Ca, Ba, Pb) and a vigorous search for new materials exhibiting this important property is currently underway. This effect occurs in the temperature range 77-300 K when the material is nearly metallic and ferromagnetic. $La_{1-x}M_xMnO_3$ perovskites become ferromagnetic at relatively low temperatures because of Mn^{3+}–O–Mn^{4+} interactions. Fast hopping of the d-electrons between the two oxidation states of Mn produces metallic behavior as the materials become ferromagnetic, giving rise to an insulator-metal (I-M) transition at temperatures slightly below the ferromagnetic Curie temperature.

Nowadays there is a great interest in so-called «double» systems of manganites (1-x)$La_{1-Y}Me'_YMnO_3$ – x$La_{1-Z}Me''_ZMnO_3$ (where Me' and Me": Ca, Ba, Sr, Pb) because new unique properties are expected to appear in them. Recent studies have pointed out that, in addition to the chemical, thermodynamic, and structural parameters, the extrinsic characteristic (such as the microstructure and the grain sizes) plays a significant role in the electrical, magnetic, transport and CMR performances of the granular systems. These characteristics depend on the method and the preparation conditions, but are hardly controllable in the conventional ceramic syntheses based on the diffusion of the components in the solid state at high temperature. This is the reason for search and devise of a new methodic of syntheses of solid solutions. The using of liquid precursors such as multicomponent liquid solutions is the main feature of these methods. The sol-gel method is among the "solution" methods.

Experimental procedure

We have already obtained the solid solutions of manganites $La_{1-X}Me_XMnO_3$ (where Me: Ca, Sr, Pb) by using sol-gel procedure [1,2]. This method was also developed by us for the synthesis of solid solutions of double manganites, such as (1-x)$La_{0,7}Ca_{0,3}MnO_3$ – x$La_{0,75}Sr_{0,25}MnO_3$ and (1-x)$La_{0,75}Sr_{0,25}MnO$ – x$La_{0,6}Pb_{0,4}MnO_3$. The distinguish of sol-gel method from the ceramics is that the solid solutions are formed after annealing the powders, which were obtained with the sol-gel procedure. This method includes:

– preparation of solution by mixing stoichiometric amounts of La, Ca, Sr, Pb, Mn nitrate solutions;
– addition to it of citric acid (which molar excesses with respect to the cations is 2:1) and ethylene glycol (which, as has been reported early, increases the solution viscosity and stabilizes the metal citrate solutions);
– increasing solution pH to 6÷7 by adding NH_4OH (25%);
– dehydrating of the solution by heating at 60–70°C for turning sol into gel;
– heating gel at 200–230°C in air to obtain from it solid foam (xerogel) and grinding xerogel into powder.

We would like to suggest that the solutions without NH_4OH have low pH (<1) and are stable. The white precipitates were formed (at pH~3) by adding the NH_4OH (increasing pH), but after further increasing NH_4OH the precipitates dissolved (pH>4). During the dehydrating process the solution remained stable and turned into coloured transparent gel (the colour depended on Me' and Me" nature). The gel was slowly heated in air (up to ~230°C in an oven with suction) and it yielded brown and solid foam (xerogel) after developing abundant smelling vapors. The foam was easy ground into fine powder.

The scanning electron microscope investigations were taken for powders before and after heat treatment. For heat treatment the powders were pressed into tablets and than were annealed in air for 1 h at different temperatures (°C) 500, 700, 900, 1100. X-ray powder diffractograms (XRDs) were received after each annealing of tablets.

By scanning electron microscope investigations it was obtained that powders of xerogels had a nanoparticles. After annealing (in air for 1 h) the structure of powders became more homogeneous and there were grains in which size of particles were preserved.

By X-ray powder diffraction analyses it was established that powders of xerogels (as it was expected) remained amorphous. The process of crystallization was observed after heating at 500°C (for 1 h) and at the 700°C XRDs correspond to a well-crystallized perovskite pattern for all samples (Fig 1). With increasing the annealing temperature (from 700 to 1100°C) the intensity of XRD_S reflections of patterns was increased and splitting of some of reflections was observed. It should be noted that formation of the phase of solid solution of manganites (1-x)$La_{0,7}Ca_{0,3}MnO_3$ – x$La_{0,75}Sr_{0,25}MnO_3$ and (1-x)$La_{0,75}Sr_{0,25}MnO$ – x$La_{0,6}Pb_{0,4}MnO_3$ by using ceramic synthesis occurs at higher temperatures (~1200–1300°C) and requires more time (not less than 5-6 h) [3].

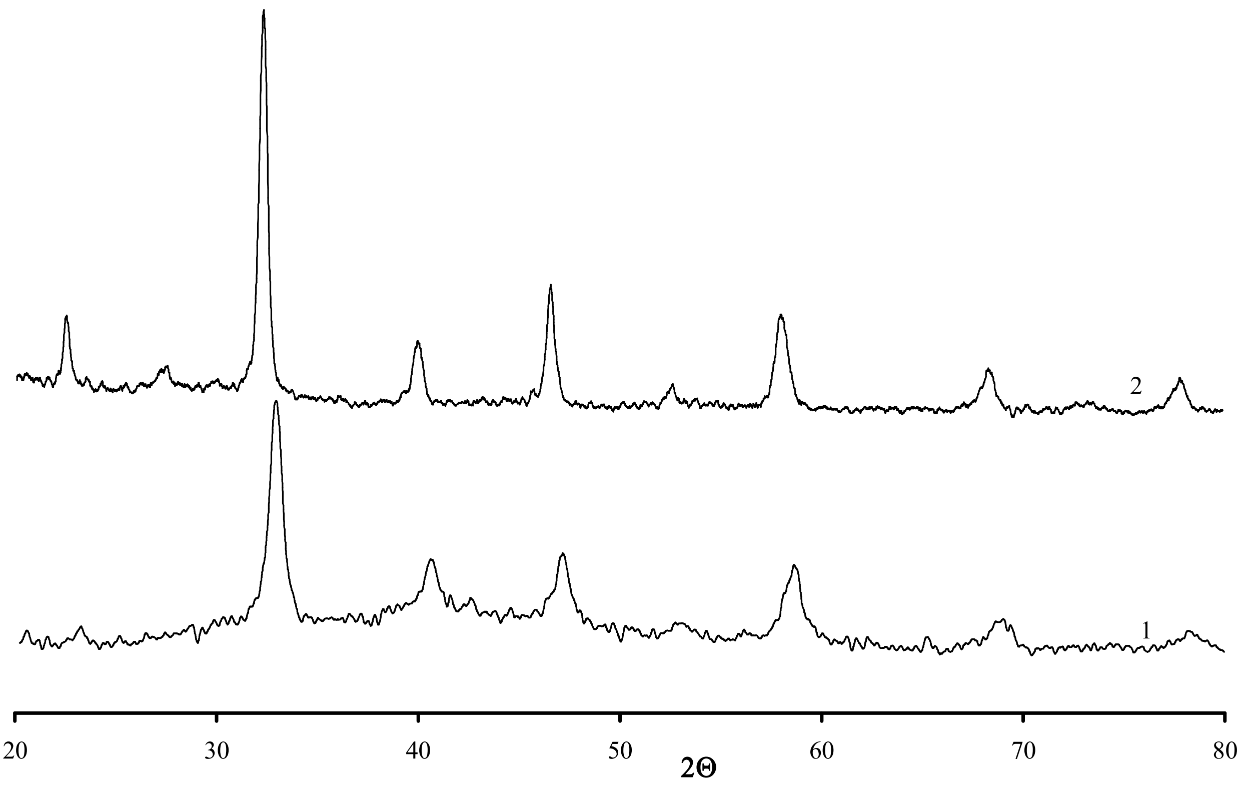

FIG. 1 – The X-ray powder diffractograms (XRDs) of the powders which correspond (by composition) to binary system of manganites 0,5$La_{0,7}Ca_{0,3}MnO_3$ – 0,5$La_{0,75}Sr_{0,25}MnO_3$ (1) and 0,5$La_{0,75}Sr_{0,25}MnO_3$ – 0,5$La_{0,6}Pb_{0,4}MnO_3$ (2). (After annealing in air at 700°C for 1 h).

Specific magnetization of saturation (σ) of synthesized by using sol-gel method solid solutions was measured by Faraday method (in 100–400 K temperature interval). The results show that σ-value and the temperature of ferromagnetic-paramagnetic phase transition (Curie temperature) of the samples depend on metals nature (Me' and Me''), x-value and annealing temperature of the powders (temperature of synthesis of solid solution). The measured at 100 K σ-value, i. e. σ_{100} for solid solutions of all compositions rose by increasing the annealing temperature and was the highest if the solutions were obtained at the temperature 900–1100°C. For example, for powders of solid solutions $0{,}5La_{0,7}Ca_{0,3}MnO_3 - 0{,}5La_{0,75}Sr_{0,25}MnO_3$ and for $0{,}25La_{0,75}Sr_{0,25}MnO - 0{,}75La_{0,6}Pb_{0,4}MnO_3$ which were synthesized at 1100°C the σ_{100}- value is 55-60 and 85-90 ($Gs\cdot cm^3/g$) accordingly. At the same time the Curie temperature of solid solutions synthesized by sol-gel method as a rule is lower.

The results

The sol-gel method was developed for the synthesis of solid solutions of double manganites $(1\text{-}x)La_{1\text{-}Y}Me'_YMnO_3 - xLa_{1\text{-}Z}Me''_ZMnO_3$ (where Me' and Me'': Ca, Sr, Pb). According to last experiments, composition of synthesizing manganites (nature and quality of doping metals) could be easily changed by modifying the composition of solution which is used in sol-gel method. The main advantages of the liquid precursors with respect to the solid ones are the high degree of chemical homogeneity and the atomic level dispersion of the reagents. Due to this sol-gel technology allows to obtain (after dehydrating of gel) nanostructural powders with higher reactivity. Heat treatment of highly dispersed powders (powders of xerogels) leads to formation of manganite solid solution phase at lower temperature (~ 700^0C) than one synthesized by ceramic method (~ 1200^0C) and it takes less time (1 hour against 5-6 hours or more). It should be noted that specific magnetization of saturation σ_{100} for synthesized by sol-gel method at 1100°C solid solutions is comparable (for $(1\text{-}x)La_{0,7}Ca_{0,3}MnO_3 - xLa_{0,75}Sr_{0,25}MnO_3$) or higher (for $(1\text{-}x)La_{0,75}Sr_{0,25}MnO - xLa_{0,6}Pb_{0,4}MnO_3$) than a σ_{100}-value for the samples of the same solid solutions obtained by ceramic method (after 6 h heating at 1200-1300°C) [3,4].

In conclusion, this work demonstrates the perspectives of using the sol-gel method for synthesis of solid solutions of manganites. The further step of our research is to investigate the electrical conductivity of synthesized by sol-gel method solid solutions in magnetic field and to find out how the method of synthesis influences on properties of these solutions.

References

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