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Mechanism of a Solid-State Formation of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$ ($0 < x < 0.5$) and Magnetic Characterization Thereof

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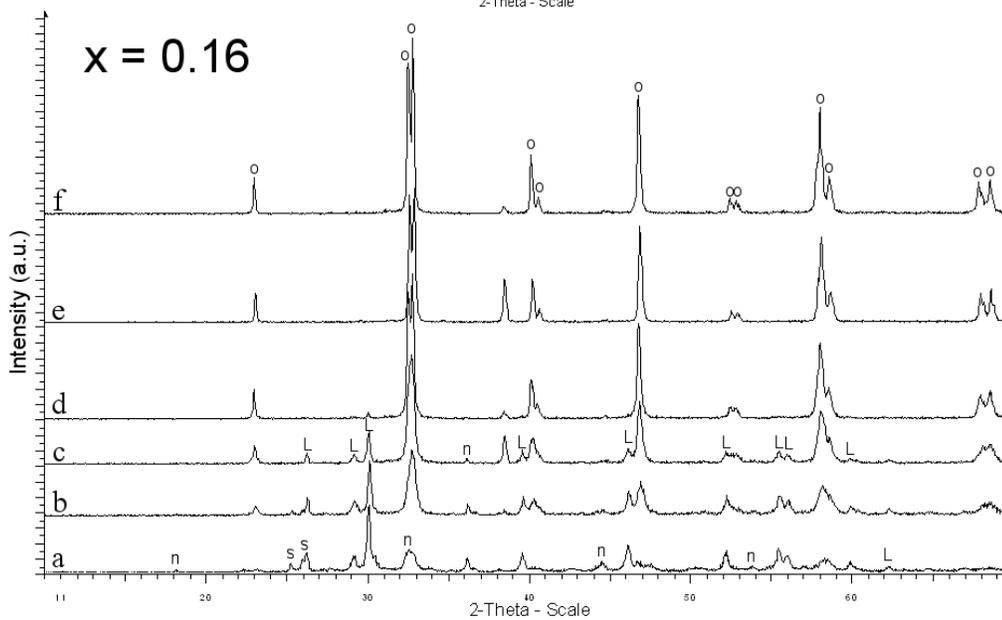
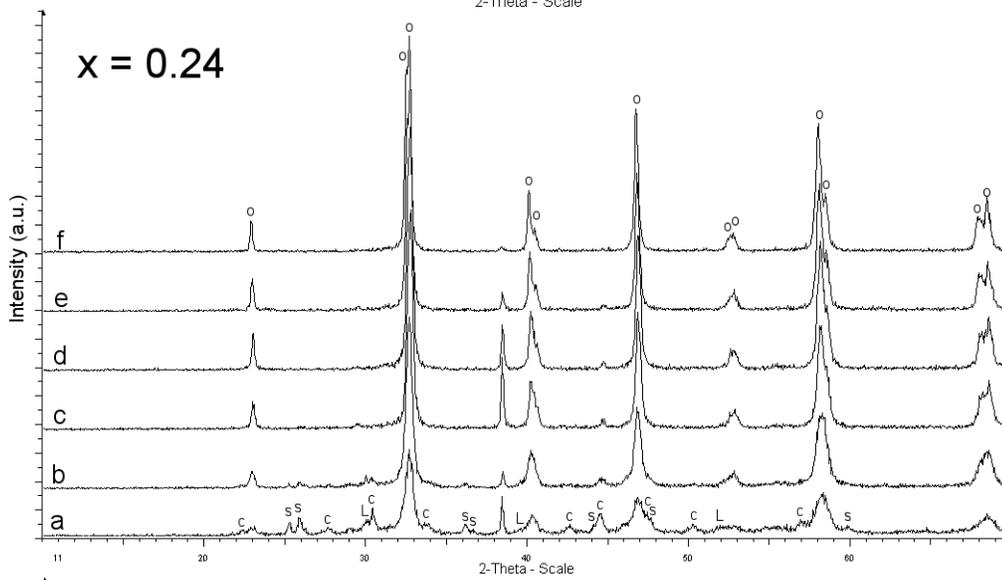
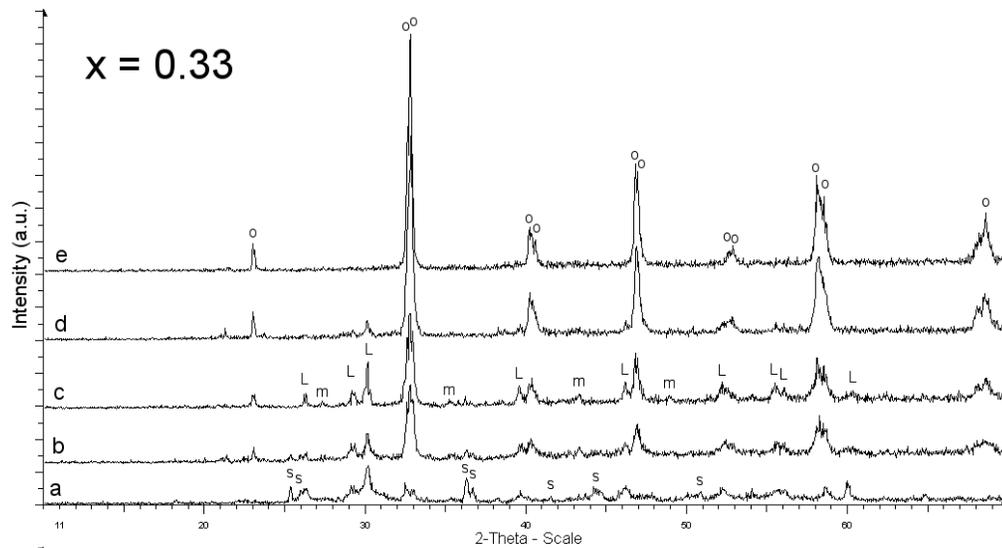
Abstract Rich diversity of potential, substantially different micro-structural arrangements - reflecting on the wide potential set of interesting properties, ranging from high electrical conductivity to giant, colossal and/or low-field magnetoresistance to low Curie point - of LaSr-manganite materials opens possibilities for numerous scientific investigations oriented towards revealing correlations on the influence line: procedure of synthesis → inherent properties → measured properties → application of the material. The investigations of the influence of synthesis procedures and LaSr-manganite stoichiometries on the Curie point (and other magnetic characteristics) of the material, being the topic of this work, are attractive since they present a necessary primal step in the development of nano-magnetic drug carriers based on these materials. In the course of such an investigation, the mechanism of the formation of the desired manganite compounds by following a classical solid-state preparation method, was also studied.

1. Introduction

The compound $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$ was first studied at the midst of the 20th century [1], but a renewed interest was devoted to the researches of the complex dependencies that correlate various compositional, stoichiometric, micro- and nano- structural properties of the material with its physical properties, after the discovery of the exhibition of colossal magnetoresistance effect [2] by many of the materials typical of such basic chemical formula. Knowing structural properties of perovskite manganite compounds is a necessary precondition for understanding the complex interplay between structural, magnetic and electronic transport properties [3], important for the advanced design of novel functional materials. The main motivating idea behind the present work is the investigation of the dependence of Curie point on the inherent material properties and parameters of the given procedure of synthesis. By the way, the pathways of the formation of the prepared stoichiometries of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$ compound were discussed, promoting an insight into complex structure of these compounds.

2. Experimental

A planetary ball mill was used for the grinding homogenization of various starting stoichiometric mixtures of Mn_3O_4 , La_2O_3 and SrCO_3 . Suspended in ethanol, 20g of the initial mixture was poured into a 125 cm³ YZrO_2 pot with the addition of ~ 100 YZrO_2 balls of 2 mm in diameter and the overall weight of 70 g, and ground under atmospheric conditions at 300 rpm for 2h. After drying, the mixture was pressed at 0.175 GPa into pellets of 10 mm in both diameter and thickness, and in order to determine the optimal annealing conditions, calcined at different temperatures in air for 2h.



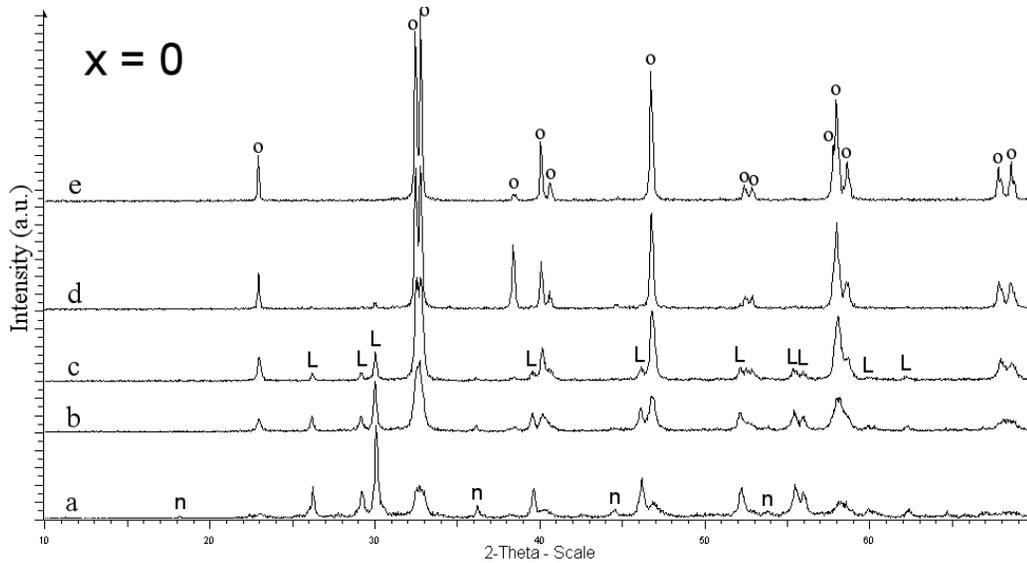


Fig. 1. XRD patterns of the synthesized $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$ samples with $x = 0.5$, $x = 0.33$, $x = 0.24$, $x = 0.16$ and $x = 0$ stoichiometries, calcined at 600, 700, 800, 900, 1000, 1100, and 1200 °C, denoted with a, b, c, d, e, f, and g, respectively. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$ peaks are denoted with an o, La_2O_3 peaks with an L, Mn_3O_4 peaks with an n, SrCO_3 peaks with an s, $\text{La}_2\text{O}_2\text{CO}_3$ peaks with a c, SrMnO_3 peaks with an m. The unassigned peak at $2\theta = 38.6^\circ$ derives from Al reflections from the sample holder.

In case of $x = 0.33$ stoichiometry, La_2O_3 presents the main phase of the sample calcined at 600 °C, whereby perovskite manganite and SrCO_3 are detected as the secondary phases. On increasing the calcination temperature to 700 °C, SrMnO_3 phase appears, and SrCO_3 peaks drastically decrease in intensity, whereas La_2O_3 peaks show rather small decrease in intensity. However, La_2O_3 peaks increase in intensity after heating at 800 °C, which suggests recrystallization of part of the perovskite manganite phase into La_2O_3 and SrMnO_3 in the calcination temperature range between 700 and 800 °C. Structural transitions between hexagonal (orthorhombic space group) and tetrahedral symmetries, that occur in this stoichiometric range [4-6], might be the reason for the observed recrystallization process. Additional increase in the heat content leads first to the disappearance of SrMnO_3 peaks (due to the reaction between SrMnO_3 and La_2O_3 yielding as a result increasing amounts of perovskite manganite phase) in the sample after annealing at 900 °C, and to the formation of monophase LaSr-manganite product after heat treatment at 1000 °C.

In case of $x = 0.24$ stoichiometry, annealing at 600 °C yields perovskite manganite as the major phase, together with SrCO_3 , La_2O_3 and $\text{La}_2\text{O}_2\text{CO}_3$, observed only within this stoichiometry. By comparing the peak intensities of the transient phases between the samples calcined at different temperatures, it becomes evident that the gradual increase in the heat content of the system leads, after the first measured case (calcination at 600 °C), to the incorporation of La and Sr ions into the manganite structure, ending eventually in the formation of pure monophase LaSr-manganite after calcination at 1100 °C.

In case of $x = 0.16$ stoichiometry, after annealing at 600 °C, La_2O_3 presents the main phase, whereas SrCO_3 , Mn_3O_4 and a slight amount of perovskite manganite, are present as the secondary phases. With increasing the calcination temperature, initial oxide phases react yielding at 1000 °C pure LaSr-manganite. Similar situation is observed in the case of $x = 0$ stoichiometry, when La_2O_3 and Mn_3O_4 that, beside slight amount of perovskite manganite phase comprise the sample annealed at 600 °C, gradually react forming as a result monophase LaSr-manganite at 1000 °C.

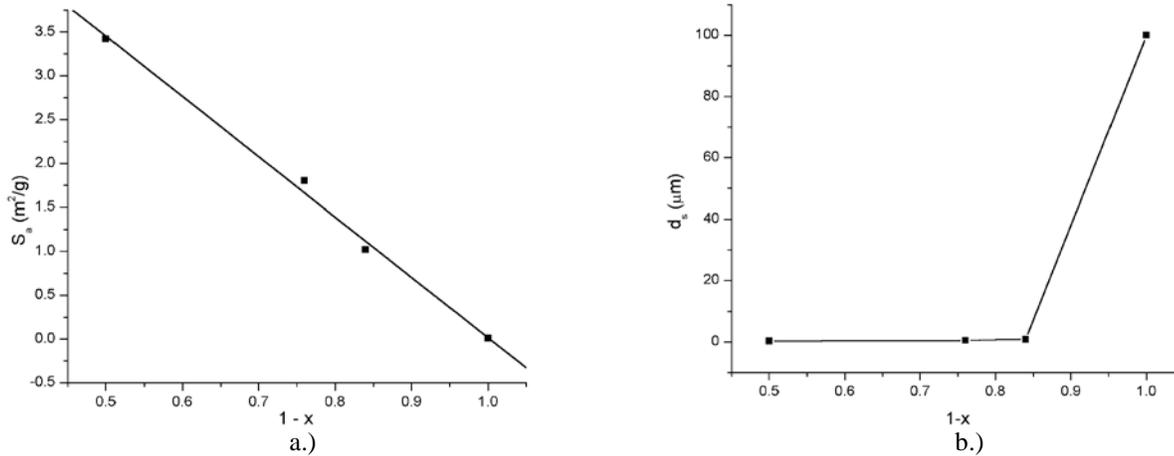


Fig.2. Specific-surface area (a) and average particle size (b) calculated therefrom, as a function of parameter x in the stoichiometric formula of the synthesized $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$ compounds, all calcined at 1200°C .

The reason for the linear dependence of specific-surface area of the samples versus stoichiometric parameter x , presented in Fig. 2a, is that for the four investigated samples, all calcined at 1200°C , calcination temperature at which manganite compound forms gradually decreases with the decrease of parameter x . Thus, $x = 0.5$ manganite forms at 1200°C , $x = 0.24$ and $x = 0.16$ manganites form at 1100°C , whereas $x = 0$ manganite forms already at 1000°C . All of the heat content introduced in the calcined system after the formation of the desired manganite compound, leads to sintering processes followed by intensive densification and grain growth, inducing the subsequent decrease in the specific-surface area of the samples. Average grain size, calculated from the measured specific-surface areas by using theoretical density derived from the respective unit cell volume and stoichiometry, together with the approximation of spherical grain shapes, thus, from the values of ~ 300 , 500 and 900 nm for $x = 0.5$, $x = 0.24$ and $x = 0.16$ samples, respectively, jumps to $\sim 100 \mu\text{m}$ for the LaMnO_3 ($x = 0$) sample (Fig. 2b).

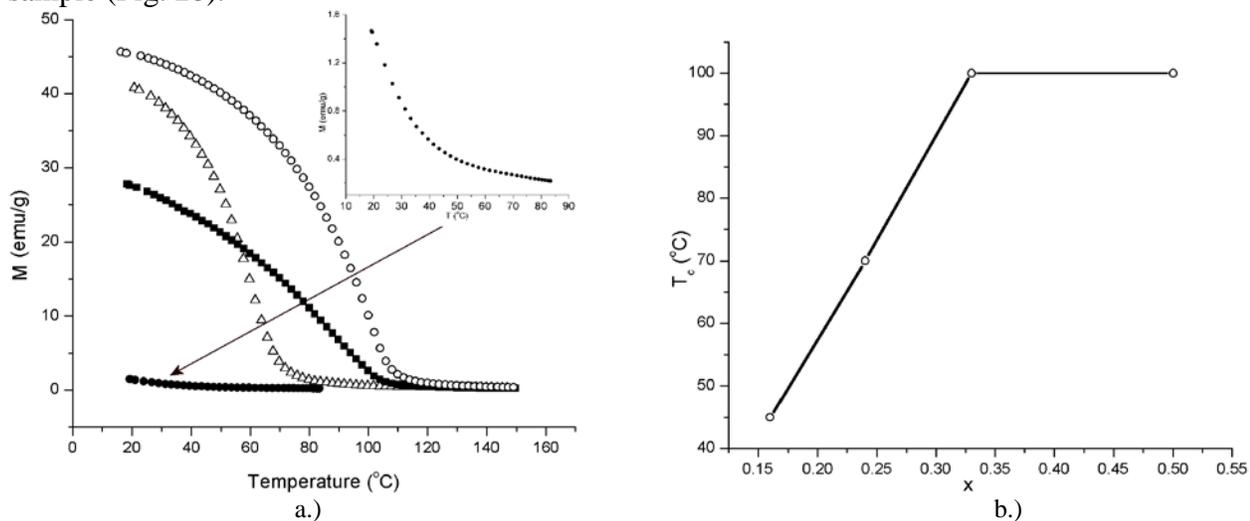


Fig. 3. a) Specific magnetization at $H = 0.1$ T vs. measuring temperature dependencies for $x = 0.16$ (\bullet), 0.24 (Δ), 0.33 (\circ) and 0.5 (\blacksquare) samples, all calcined at 1200°C ; b) Curie temperature of the samples vs. stoichiometric content of strontium (x).

Curie temperature of rare-earth manganite compounds is known to vary with a number of synthesis parameters, such as calcination temperature and the corresponding average grain size [7], sintering temperature [8], oxygen nonstoichiometry (parameter δ) [9], La/Mn ratio [10], overall

stoichiometry [11], porosity [12], pressure [13], additional silica content [14], etc. The dependency of Curie point on the stoichiometric composition is obvious from Fig. 3. Curie point as obtained by extrapolation technique, is found at ~ 100 °C for the samples with $x = 0.5$ and $x = 0.33$ stoichiometries, whereas with a further decrease in Sr content, it decreases to ~ 70 °C for $x = 0.24$ and ~ 45 °C for $x = 0.16$ samples, with $x = 0$ sample having Curie point below room temperature (Fig. 3b). Curie transitions are in all cases not sharp, but gradual ones. In general, small inclination of $M = f(T)$ curve might be a sign of either the wide particle size distribution or weak inter-domain interactions, whereas in our case, the smaller the grains (as calculated from the specific-surface area measurement) of the sample, the smaller the slope of the $M = f(T)$ curve in the range of Curie phase transition (Fig. 3a).

4. Conclusions

Different mechanisms of the LaSr-manganite formation were observed depending on the stoichiometry of the synthesized compound. The major difference in the mechanism of the formation of lanthanum-strontium manganite phase by the induced high-temperature treatment, between the cases of $\text{LaMnO}_{3+\delta}$ and $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_{3+\delta}$ on one side, and the cases of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_{3+\delta}$ and $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_{3+\delta}$ on the other hand, is that in the latter two cases hexagonal SrMnO_3 forms as the transient phase that gradually incorporates La_2O_3 phase giving pure hexagonal manganite as the result, whereby in the former two cases La_2O_3 and Mn_3O_4 directly react gradually building hexagonal manganite phase. The formation process of $\text{La}_{0.74}\text{Sr}_{0.24}\text{MnO}_{3+\delta}$ was specific in a sense that only in that case $\text{La}_2\text{O}_2\text{CO}_3$ was observed as a transient phase. The peculiar, stoichiometry-dependent formation pathways of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$ might be significant in contributing to the understanding of complex chemistry that defines potential spectrum of inherent properties of perovskite manganites, and the field of application thereof. It was also found out that specific-surface area linearly decreases with strontium content (due to the decrease in the manganite formation temperature with strontium content), as well as that Curie temperature follows a trend of linear increase between $x = 0.16$ ($T_c = 45$ °C) and $x = 0.33$ ($T_c = 100$ °C) stoichiometries, after which it remains constant at 100 °C with the further increase in strontium content, showing also the trend of increasing the phase transition sharpness with the increase in average particle size of the manganite compound, being the consequence of weaker inter-domain interactions within the systems comprising smaller grains.

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