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LMO CERAMICS MICROSTRUCTURE

The aim of this work was to characterize the microstructure of LMO type ceramics. The ceramics obtained by the free sintering at two temperatures 1473 K and 1573 K and two sintering times 6 and 12 h was the test material. One series was also obtained by the hot pressing method for a comparison. In all the cases the material synthesis was conducted by the solid-state reaction method at 1173 for 24 h. Photographs of the specimen fractures were taken by a scanning electron microscope to characterize the microstructure of the ceramics obtained in a more detailed way. The VISILOG 4 system, enabling to calculate a lot of parameters characterizing the material microstructure, such as e.g.: a number of grains on the unit area, an average grain size, shape indexes of the grains in question, was used as well. It allows determining a grain size distribution, and a frequency of presence of grains with the specific shape index.

By analyzing a set of the parameters obtained an influence of the technological conditions on the microstructure of the material in question, and on its properties and applicability at the same time can be determined.

Keywords: LMO, microstructure, hot pressing, free sintering

1. Introduction

The oxide materials crystallizing in the perovskite structure are a continuous object of intensive investigations due to their intrigue physical properties, resulting from strong electron-electron influences (interaction between the electrons) and a strong electron-phonon coupling. This coupling leads to a correlation between spin, charge and structural degrees of freedom. For this reason there are such variable physical phenomena in the perovskite structure such as: high temperature superconductivity, band ferromagnetism or enormous magneto-resistance. Strong interactions between magnetic moments, charge carriers or phonons result in a separation of magnetic and electron phases, manifested by existence of areas of completely different physical properties in the same crystal. Manganites can be differentiated among a lot of materials, in which the phenomena mentioned above are present.

The manganites are characterized by an enormous magneto-resistance phenomenon, discovered at the beginning of 90-ties of the last century [1-3]. Great expectations are connected with their practical applications as magnetic field sensors, heads for reading out magnetically recorded information [4, 5].

LMO - $LaMnO_3$ ceramics is also a promising electrode material for solid-oxide fuel cell because of its ability to accommodate excess of oxygen with good ionic conductivity [6, 7].

It is generally known that the LMO properties like properties of other compounds of the perovskite-like structure are influenced by a technology of their production. Each stage of the technology is important: a synthesis (time and a method used), compacting (a method, temperature, sintering time). The production technology has a significant importance on the ceramic material microstructure. Thus, the microstructure decides about the ceramics properties, which decides about possibility of its use. Therefore, the microstructure optimization is the main way to obtain a material of better properties [8]. Comprehensive investigations which aim at learning about all the factors deciding about the microstructure of this material and their influence on the properties of the LMO ceramics become a must.

2. The test material

The LMO – $LaMnO_3$ ceramics was the test material. The synthesis of the ceramic powders was conducted by the reaction method in the solid phase from the simple oxides – La_2O_3 and MnO_2. The oxides after weighing in the stoichiometric amounts were ground in a ball mill of the Fritsch firm for 15 hours with an addition of the propyl alcohol. The powder synthesis was made after pressing into discs of 2×10^{-2} m diameters and thickness of about 3×10^{-3} m at 1173 K for 24 hours. The synthesis conducted in such a way made the initial components react precisely.

After the synthesis the specimens were crushed, and then they were ground again for 3 hours and compacts were prepared in a form of the discs of 1×10^{-2} m diameter and $3\times4\times10^{-3}$ m for sintering.

To compact the ceramic specimens two methods were used: the conventional sintering method and the hot pressing

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method. While obtaining the ceramics by the conventional sintering method (the free sintering) the prepared compacts were sintered in a FCF 4/150 M chamber furnace at different temperatures and at different time: at 1473 K for 6 hours (series 1), at 1473 K for 12 hours (series 2), at 1573 K for 6 hours (series 3), at 1573 K for 12 hours (series 4). The aluminum oxide was used as sand bed at the sintering.

While obtaining the ceramic by the hot pressing method the prepared compacts were sintered at 1473 K for 5 hours under 20 MPa pressure also in the Al_2O_3 bed sand (series 5).

3. Investigation results and their discussion

Photographs of the specimen fractures were taken by a HITACH S-4700 scanning electron microscope to characterize the microstructure of the ceramics obtained (fig. 1).

From an analysis of the photographs of LMO type ceramics microstructure obtained in different technological conditions, it results that the material obtained is characterized by high porosity.

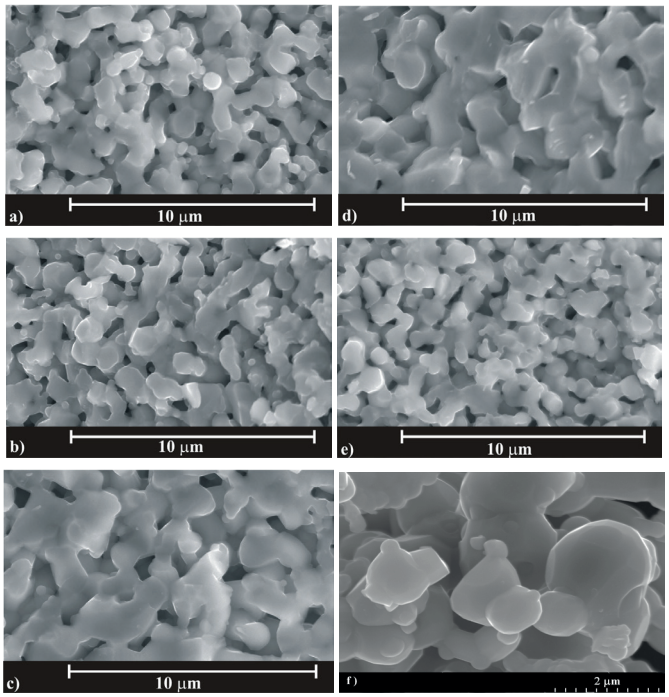

Fig. 1. The microstructure of the LMO ceramics: a) series 1, b) series 2, c) series 3, d) series 4, e) series 5, f) smaller grains of a micrometer size fused together

Looking at the photographs taken, at small magnifications in particular, it can be stated that the ceramic grains are much elongated of small width. However, an observation of the specimens at higher magnifications reveals that those elongated forms constitute a series of much smaller grains of a micrometer size fused together (Table 1).

Comprehensive determination of parameters characterizing the microstructure of the material in question is possible by use of the VISILOG 4 system [9, 10]. The main emphasis is put on the complex use of a computer image analysis in the stereological examinations – providing a full quantitative description of integral parameters, object size distributions – both statistical and geometrical ones – and indexes of a shape and homogeneity.

The VISILOG 4 system is an object oriented programming environment, fitted for a transformation, an analysis and a measurement of images. It is based on a very big library of procedures of image processing, containing more than 350 predefined transformations. The basic task of the system is, first of all, to determine stereological parameters of the microstructure in question, necessary for an evaluation of a production process of a given material and its properties. The basic aim of the transformations used by the system is such a transformation of an image, which allows detecting the objects selected for an analysis. A condition of the appropriate detection is to obtain the same degree of greyness by the objects in question and the object boundaries determined unequivocally (grain boundaries). The image prepared in such a way can undergo a conversion and be subjected to geometrical measurements of objects.

Therefore, a conversion of the microstructure photographs obtained from the scanning electron microscope into binary images should have been made. Those images were used as input files for an analysis of the grain size and the grain size distribution in particular specimens of the LMO type ceramics.

Calculations of the stereological parameters of the grain were made by the following relationships [9]:

- number of particles N_A on the unit surface of the polished section:

$$N_A = \frac{N}{A}, \tag{1}$$

where: N - number of grains on researched surface, A - size of researched surface;

- relative volume of the examined V_V phase:

$$V_V = \frac{\sum A_i}{A} \times 100\,\%, \tag{2}$$

where: A_i - the cross-section area of the grain;

- a shape coefficient of flat structures:

$$\xi_m = \frac{4\pi A_i}{L_i^2}, \tag{3}$$

where: L_i - the boundary length of the grain; (the maximum value $\xi_{max} = 1$ for the grain surface in a shape of a circle and it reaches lower values for other shapes);

- frequency of occurrence of a grain with a specific shape coefficient ξ:

$$\frac{N(\xi)}{N}, \tag{4}$$

- an equiaxial index:

$$\alpha_m = \frac{D_{max}}{d_2}, \tag{5}$$

where: D_m - the maximum grain diameter, d_2 the apparent diameter of its cross-section;

- the grain elongation index:

$$\delta_m = \frac{X_i}{Y_i}, \tag{6}$$

where: X_i, Y_i - length of grain projection on axis x and y;

- the shape change coefficient:

$$v(\xi) = \frac{\sigma(\xi)}{\xi_m}, \tag{7}$$

were $\sigma(\xi)$ - the deviation of shape

- the elongation change coefficient:

$$v(\delta) = \frac{\sigma(\delta)}{\delta_m} \tag{8}$$

were $\sigma(\delta)$ – the change of elongation

- the grain diameter variability coefficient:

$$v(d) = \frac{\sigma(d)}{d_m}, \tag{9}$$

were $\sigma(d)$ – the deviation of diameters , d_m – the mean diameter

The average grain size determined by a multiple measurement of the grain diameters in a lot of directions is presented in Table 1. The grain size distribution for the ceramics in question obtained by the free sintering method and the hot pressing is presented in Fig. 2. Both the statistical and geometrical distributions, presenting the volume fraction of the grains in different classes of sizes, were determined. The latter ones are considered to be the most comprehensive characteristic of the grain size. They are preferred, first of all, when the grain size is the oldest and natural structural criterion of a quality evaluation of the polycrystalline materials.

TABLE 1
A list of the average grain sizes for the ceramics in question

Type of the specimen		Sintering condition	Average grain size [μm]
free sintering	series 1	1473 K / 6 h	0.83
	series 2	1473 K / 12 h	1.02
	series 3	1573 K / 6 h	1.19
	series 4	1573 K / 12 h	1.33
hot pressing	series 5	1473 K / 5 h	0.73
		p = 20 MPa	

The grain size distribution for all the series in question was single modal one (Fig. 2). By analyzing the microstructure (Fig. 1) of the LMO type ceramics, on basis of the average grain size analysis and the grain distribution, it has been found that the ceramics obtained by the hot pressing method is characterized by higher homogeneity of the grain size and the average grain size lower than in the specimens obtained by the free sintering method. The grains with the size near the average value (about 61%) have the greatest fraction in the microstructure of the ceramic obtained by the hot pressing method.

The grains of the ceramics obtained by the hot pressing method are better formed. This ceramics is also characterized by a higher density, a lower porosity comparing to the ceramic obtained by the free sintering method ($\rho_{series\,1} = 4438$ kg/m^3, $\rho_{series5} = 4545$ kg/m^3). For this reason there are a higher number of the grains in the ceramics obtained by the hot pressing method in the measurement field (of the same size) in the analysis of the microstructure parameters of the ceramic

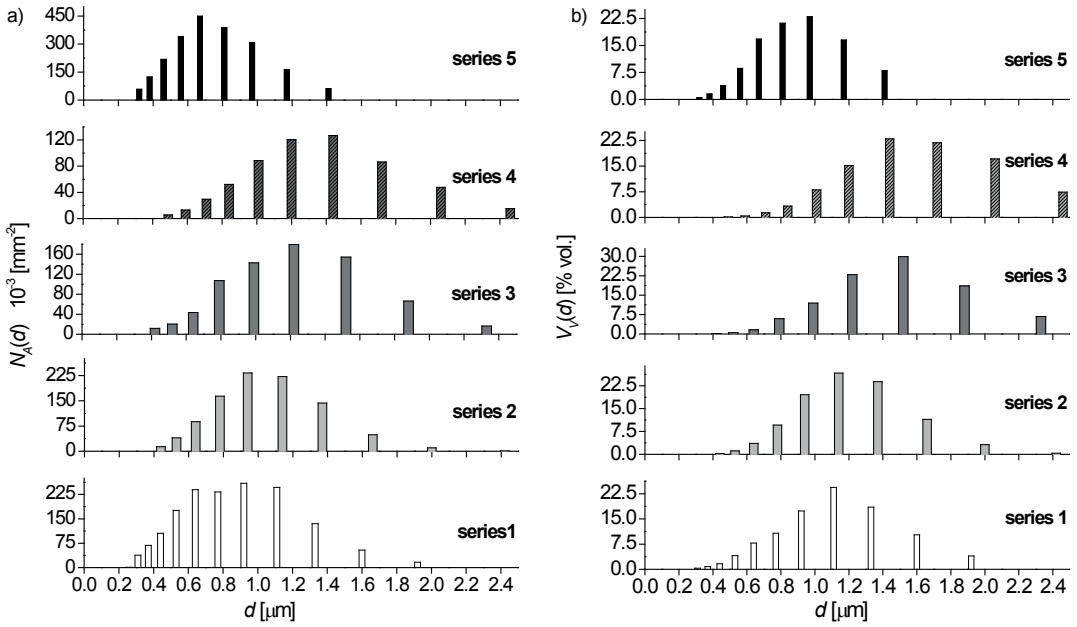

Fig. 2. The grain size distribution a) the dependence of the N_A grain number of a given size on the unit area on the d grain size (the statistical distribution), b) the dependence of the V_V grain volume of a given size on the d grain size (the geometrical distribution)

in question ($N_{A\_series1} = 1520$, $N_{A\_series5} = 1674$). However, in the microstructure of the ceramics obtained by the free sintering method there are both grains of a size smaller than the average grain size and much bigger size.

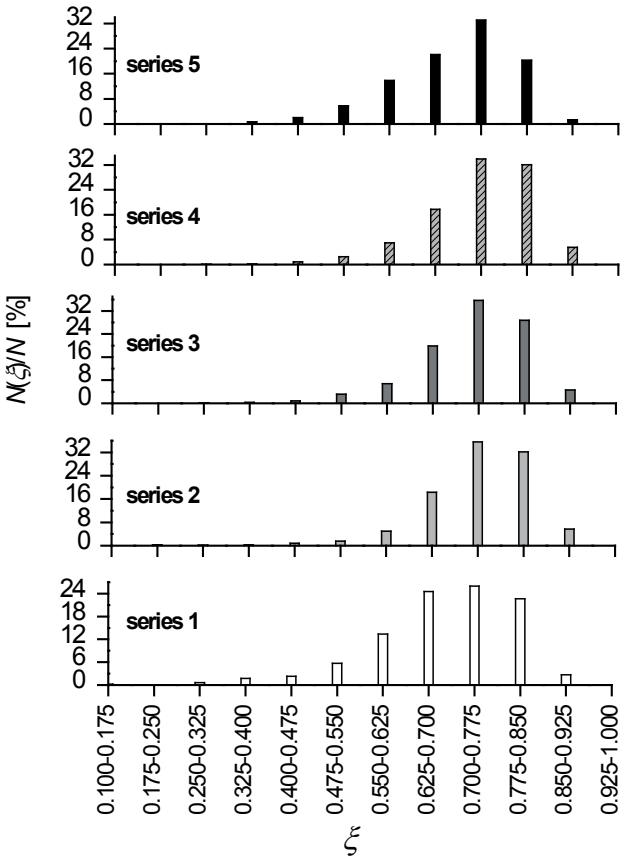

Fig. 3. A frequency of presence of the grains with the ξ shape index

The grains of the ceramics in question are not equiaxial. It is confirmed by the indexes characterizing the grain shape-equiaxiality determined for all the series of the ceramic specimens (Table 2) that the grains are not spherical. The calculated values of the shape coefficient deviate from the unity (Fig.3, Fig.4). An increase in the temperature of the ceramics production results in an increase in the ξ_m value.

It can be seen that the sintering temperature increase during the free sintering leads to the average grain size increase (Table 1). The similar phenomenon took place while lengthening of the sintering time. The sintering temperature increase or lengthening of the sintering time also resulted in an increase in the density of the ceramics obtained ($\rho_{series1} = 4438$ kg/m^3, $\rho_{series2} = 4507$ kg/m^3, $\rho_{series3} = 4542$ kg/m^3, $\rho_{series4} = 4544$ kg/m^3, $\rho_{series5} = 4545$ kg/m^3. It was found that lengthening of the sintering time from 6 to 12 hours at the sintering temperature of 1573 K did not lead to a significant increase in the density of the material obtained. However, lengthening of the sintering time at this temperature results in the average grain size increase, what can have a disadvantageous influence on the ceramic properties.

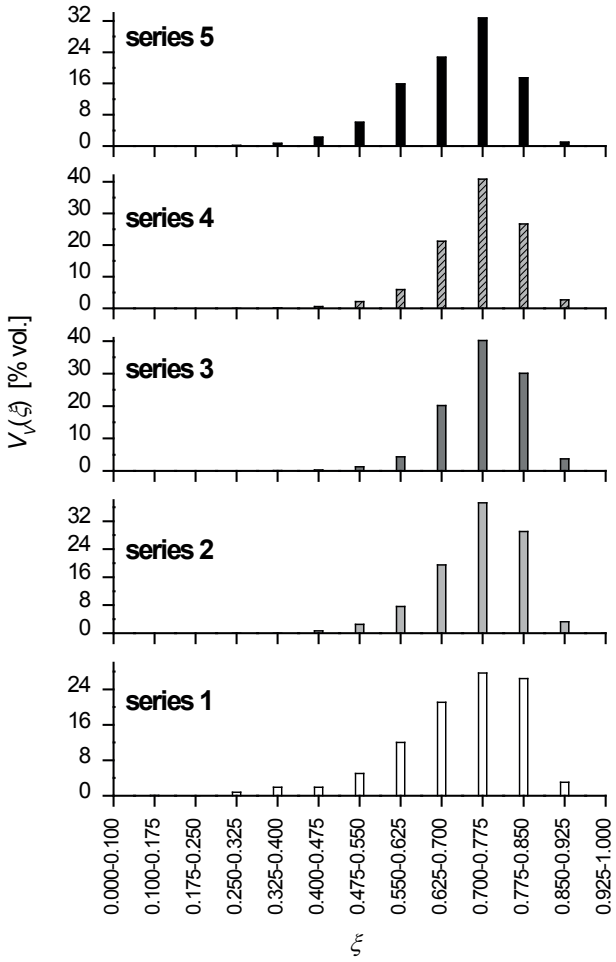

Fig. 4. A volume fraction of the grains with the ξ shape index

An application of the hot pressing method enabled to obtain the ceramics with the grain size much smaller than in the case of the ceramics obtained by the free sintering method and of a higher density. The hot pressing use provides shortening of the sintering time needed to obtain a material of a high density owing to a pressure applied during the sintering.

TABLE 2
A list of shape indexes, measures of shape non-homogeneity and grain size non-homogeneity

Type of the specimen	shape coefficient ξ_m	equiaxiality α_m	shape variability coefficient $\nu(\xi)$
series 1	0.68	1.64	0.17
series 2	0.73	1.55	0.13
series 3	0.74	1.55	0.12
series 4	0.74	1.56	0.12
series 5	0.70	1.64	0.13
Type of the specimen	grain elongation coefficient δ_m	grain elongation variability coefficient $\nu(\delta)$	grain diameter variability coefficient $\nu(d)$
series 1	1.02	0.49	0.40
series 2	1.10	0.43	0.35
series 3	1.15	0.38	0.33
series 4	1.15	0.38	0.32
series 5	0.99	0.39	0.25

The ceramics obtained by the free sintering method at 1573 K is characterized by a more homogenous microstructure. It is confirmed by lower values of the shape variability coefficients and grain elongation variability coefficients. By comparing the coefficients presented in Table 2 for the ceramics compacted by different methods (at the same temperature) it can be stated that the ceramics obtained by the hot pressing method is characterized by a lower value of the shape variability coefficient, the elongation variability coefficient, and also a lower value of the grain diameter variability coefficient. The relationships obtained show that the material obtained by the hot pressing method is characterized by greater homogeneity of both the size of grains and their shape. It is well known that the material of a greater homogeneity has better properties, too. Therefore, use of the hot pressing method enabled to obtain a material of a high quality and homogeneity. An application of this method allows obtaining a material of a higher density than by the free sintering method while shortening the sintering time simultaneously. The higher density of the ceramic and an increase in the microstructure homogeneity can be also obtained by the sintering temperature increase. However, it results in the significant increase in the average grain size, what can have a disadvantageous influence on the ceramics properties.

4. Conclusions

A technological process of a ceramics production has an influence on its properties. It is influenced by each stage of the process. Both use of different methods of ceramic compacting and use of different sintering temperatures and holding times at the maximum temperature determine the properties of ceramics.

The ceramics compacted by the hot pressing method is characterized by a more homogenous microstructure than the ceramics compacted by the free sintering method. Such homogeneity is present in both the size of grains and their shape.

Both the sintering temperature increase and the holding time at this temperature lead to the grain size increase. However, the excessive grain growth can have a disadvantageous influence on the material properties. Therefore, while selecting technological conditions of the ceramic material production, the relationships between the ceramics production temperature, holding time at this temperature, a grain size, a density and specific properties necessary for given applications should be considered.

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