SOLUȚII SOLIDE $La_{1-x}Sr_xCoO_{3-\delta}$ CU STRUCTURĂ PEROVSKIT (x = 0,4 și 0,5)

$La_{1-x}Sr_xCoO_{3-\delta}$ SOLID SOLUTIONS WITH A PEROVSKITE STRUCTURE (x = 0.4 and 0.5)

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Two types of $La_{0,6}Sr_{0,4}Co_{3-\delta}$ and $La_{0,5}Sr_{0,5}Co_{3-\delta}$ compositions were studied. The preparation of mixtures from La_2O_3, $SrCoO_3$ and Co_3O_4 was made by mechanical activation. The obtained powders have a monomodal distribution of particle sizes and low dispersion. Reactions occurring in the formation of compounds in these mixtures were studied by complex thermal analysis. The two compositions have been sintered at a temperature of 1250°C. The mineralogical composition determined on thermally treated samples showed that in case $La_{0,6}Sr_{0,4}Co_{3-\delta}$ compound a solid solution was formed with the cubic structure derived from $LaCoO_3$, and for $La_{0,5}Sr_{0,5}Co_{3-\delta}$ a solid solution with a hexagonal structure corresponding to $SrCoO_3$. The samples formed single-phase at 1250°C. The electrical conductivity measurements showed a semiconductor behavior for $La_{0,6}Sr_{0,4}Co_{3-\delta}$, and conductor behavior for $La_{0,5}Sr_{0,5}Co_{3-\delta}$.

Au fost studiate două tipuri de compoziții $La_{0.6}Sr_{0.4}Co_{3-\delta}$ și $La_{0.5}Sr_{0.5}Co_{3-\delta}$. Prepararea amestecurilor din La_2O_3, $SrCoO_3$ și Co_3O_4 a fost făcută prin activare mecanică. Pulberile obținute au o distribuție monomodală a dimensiunilor particulelor și dispersie redusă. Reacțiile care au apărut la formarea compușilor din aceste amestecuri au fost studiate prin analize termice complexe. Cele două compoziții au fost sinterizate la o temperatură de 1250°C. Compoziția mineralogică determinată pe eșantioanele tratate termic a arătat că în cazul compusului $La_{0.6}Sr_{0.4}Co_{3-\delta}$ s-a format o soluție solidă cu structura cubică derivată din $LaCoO_3$ și pentru $La_{0.5}Sr_{0.5}Co_{3-\delta}$ o soluție solidă cu o structură hexagonală corespunzătoare la $SrCoO_3$. Probele au format o singură fază la 1250°C. Măsurătorile de conductivitate electrică au arătat un comportament semiconductor pentru $La_{0.6}Sr_{0.4}Co_{3-\delta}$, și comportament tip conductor pentru $La_{0.5}Sr_{0.5}Co_{3-\delta}$.

Keywords: solid solution, electrical conductivity, SEM

1. Introduction

Perovskite-like compounds with cations of transition metals are highly appreciated for several properties such as high dielectric strength, ferroelectric polarization, and high magnetoresistance, superconductivity, mixed electrical conductivity and so on. The ideal structure of perovskite is cubic and has the general formula ABO_3. This type of structure is very important because a large part of the metal elements adopt it and there is also the possibility to synthesize multicomponent materials based on their solid solutions. In this type of structure, both component A and component B can be substituted by a wide variety of elements that determines deviations from the ideal structure and changes of the tolerance factor and of Jahn Teller effect. Condition of electrical neutrality, i.e. the sum of the electrical charges positive of the cations must be equal to the negative electric charge of the oxygen ions is mandatory [1]. However, there are non-stoichiometric and oxygen-lacking structures. The vacancies of oxygen are very common in this type of structure and quite often they are arranged in orderly way in the network [2]. The existence of solid solutions of the $La_{1-x}Sr_xCoO_{3-\delta}$ type in the ternary system La_2O_3-SrO-CoO was studied in the paper [3]. The two limits of the solid solution are the $LaCoO_3$ and $Sr_2Co_2O_5$ compounds. The first of these compounds has the rhombohedral structure [4] which shifts into cubic at 1337°C. By replacing La^{3+} with divalent cations [5 - 8] the crystalline structure gradually changes from rhombohedral to cubic depending on the substituted proportion. The compound corresponding to the second limit crystallizes into two types of structures depending on the oxygen content and temperature. Thus, at elevated temperature it has a rhombohedral structure and, at low temperature, a hexagonal structure [9]. By forming solid solutions of the type $La_{1-x}Sr_xCoO_{3-\delta}$, intermediary structures resulting from deformation of the initial structures may occur. When La^{3+} is substituted with Sr^{2+} a change of the cobalt valence is produced from 3+ to 4+, and the carriers of charge are holes of electron [5]. The solid solutions have electrical properties which vary

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depending on the proportion of substituted La^{3+}.

In the present paper the synthesis of two ternary compositions $La_{0.6}Sr_{0.4}CoO_3$ and $La_{0.5}Sr_{0.5}CoO_3$ by the mechanical activation method was studied. These compositions were chosen based on the literature data that established for the compositions in the mentioned domain a sudden variation of the properties. Although the researches carried out are numerous, the obtained results are often contradictory.

2.Experimental

The synthesis of the two compositions was made using La_2O_3, $SrCO_3$ and Co_3O_4 as starting materials. Mixtures were made with the chemical composition $La_{0,6}Sr_{0,4}CoO_3$ (LSC4) and $La_{0.5}Sr_{0.5}CoO_3$ (LSC5), which were mechanically activated for 10 hours in a Pulverisette mill. The dispersing medium upon grinding was ethyl alcohol. Ethyl alcohol was removed in the oven at 60°C up to constant weight. Granule size distribution was determined for the resulting powders with the Brookhaven 90 Plus laser granulometer. This was differentially represented, and the main characteristics were calculated [10]. The behavior of samples at thermal treatment was determined by complex thermal analysis with STA 449 F3 Jupiter. The powders were uniaxial pressed in the form of tablets and were heat treated at temperatures between 1000 and 1250°C with a two-hour plateau at maximum temperature. Their phase composition was determined by X-ray diffraction (Shimadzu 6100 Diffractometer), and the morphology by the scanning electron microscopy (FEG SEM FIB Auriga Microscope). The apparent density was measured by the Archimedes' method and main sintering curves of the two samples was established. The electrical conductivity for the two samples was determined using the Solartron SI 1260 installation.

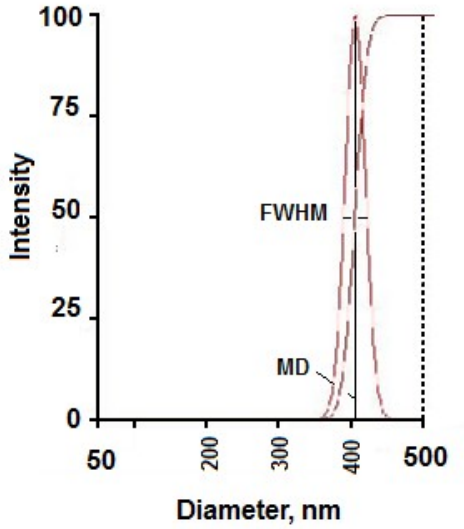
3. Characterization of powders after mechanical activation

3.1. Distribution of particle sizes

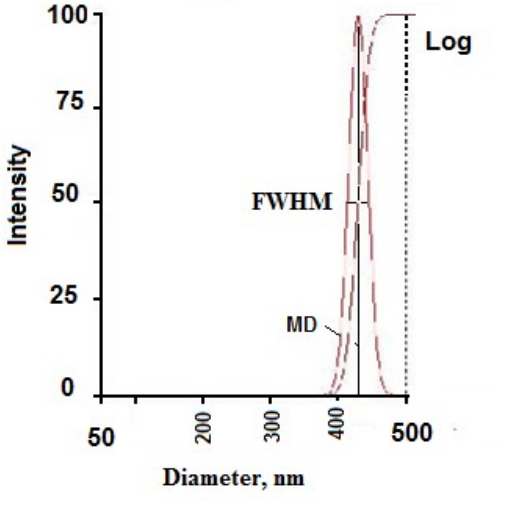
The particle size distribution was differentially represented, and the curves obtained for the two samples are given in Figure 1. In both cases the curve is monomodal with a modal diameter of 405 and 430 nm, respectively. The relative fraction width Wr is small, which shows a low dispersion degree.

3.2. Behavior of powders at thermal treatment

The behavior of the powders at thermal treatment was studied by complex thermal analysis and the curves obtained for the LSC4 and LSC5 samples are shown in Figures 2 and 3. Thermal curves for the first sample have two endothermic effects at 362 and 380°C, both with mass loss. The first effect can be attributed to dehydration of $La(OH)_3$, formed by the hydration of La_2O_3 during milling process, and corresponds to the passage of $La(OH)_3$ into LaOOH. Lanthanum hydroxide, is also partially carbonated and for this reason a second effect occurs at a temperature of 380°C. This compound has a low structural ordering and therefore it could not be identified by XRD. By increasing the temperature this compound transforms into $La_2O_2CO_3$. The effect from 540°C it can be attributed of water removal from LaOOH and its transforming into La_2O_3. A small amount of carbon dioxide is also released from the above-mentioned $La_2O_2CO_3$ compound [11]. At temperatures above 700°C there are three endothermic effects. These are the dissociation effects of Co_3O_4, and $SrCO_3$, the latter compound dissociating in two steps. It is noted that all of these temperatures are shifted to lower values compared to pure substances, due to the structural changes that occur by grinding. Figure 3 represents the thermal curves for the LSC5 sample, where temperatures below 600°C are the



a) MD-405 nm;FWHM-30 nm; Wr-3,70%



b)MD-430 nm; FWHM-32 nm; Wr-3,72%

Fig.1 - Grains size distribution a) LSC4; b) LSC5/ *Distributia dimensiunilor granulelor a) LSC4; b) LSC5.*

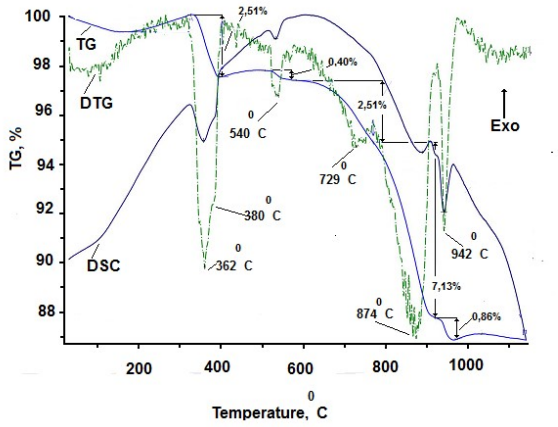


Fig. 2 - Thermal analysis curves for LSC4 sample / *Curbele de analiză termică pentru proba LSC4.*

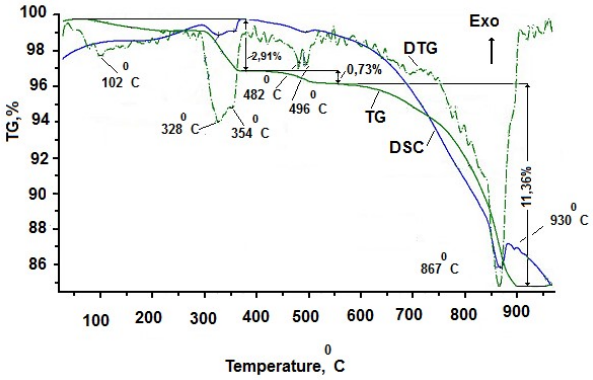


Fig.3 - Thermal analysis curves for the LSC 5 sample / *Curbele de analiză termică pentru proba LSC 5.*

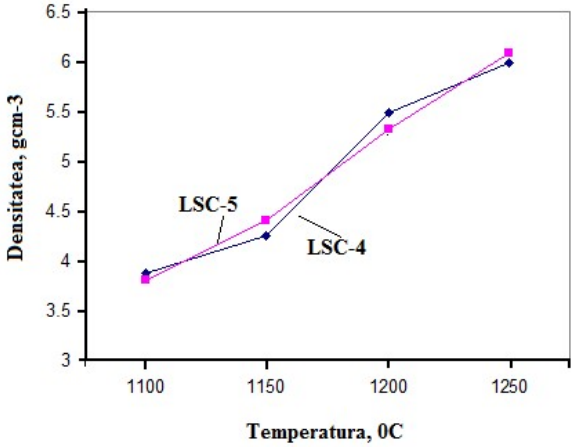


Fig. 4 - Apparent density variation according to the sintering temperature / *Variaţia densităţii aparente în funcţie de temperatura de ardere.*

effects of dehydration and decarbonation of prepared powder. At higher temperatures, one can observe a large and complex effect comprising the dissociation effects of Co_3O_4 and $SrCO_3$. At 930°C, an exothermic effect was found which shows that the first compound formed in this mixture was $SrCoO_3$.

4. Characterization of samples after heat treatment

4.1. Main sintering curves

For both synthesized samples, the main sintering curves were determined experimentally [12-14]. The discs from pressed powders were heat treated at temperatures between 1100 and 1250°C with a two-hour range at maximum temperature and then apparent density was measured. The obtained values are graphically represented in the Figure 4. There is a continuous increase of the density according to the thermal treatment temperature. The behavior of the two samples at sintering is almost identical.

4.2. Phase composition

The two samples were heat treated in the electric furnace at temperatures between 1000 and 1250°C and the phase compositions was determined by X-ray diffraction. The results obtained are given in Figures 5 and 6.

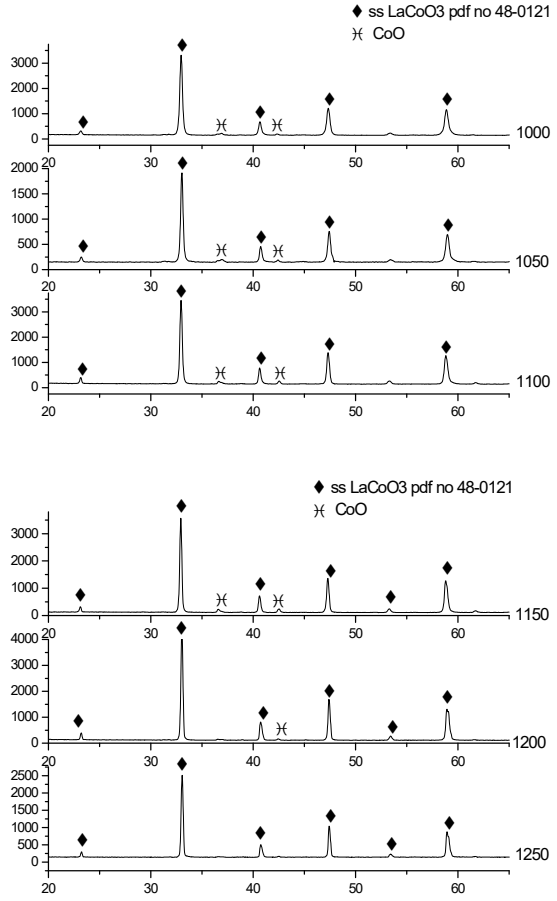


Fig. 5 - Variation of the mineralogical composition of the LSC4 sample depending on the treatment temperature / *Variația compoziției mineralogice a probei LSC4 în funcție de temperatura de tratament termic.*

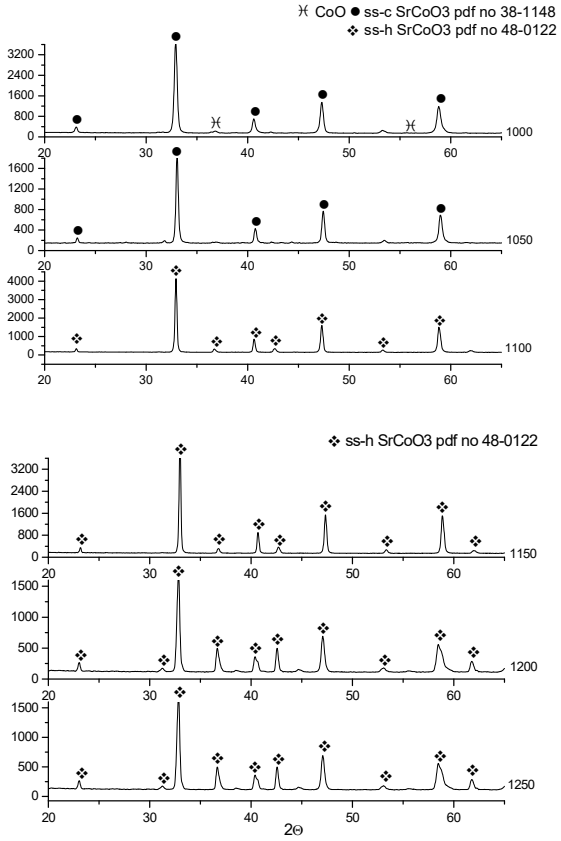
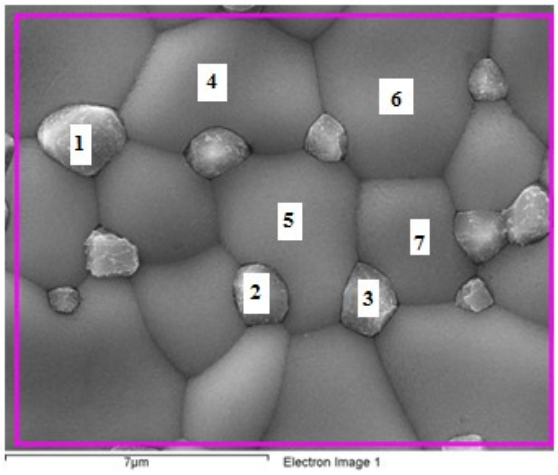


Fig. 6 - Variation of the mineralogical composition of the *LSC5* sample depending on the treatment temperature / *Variația compoziției mineralogice a probei LSC5 în funcție de temperatura de tratament termic*.

Thus, for the LSC4 sample it was found that the first phase formed at thermal treatment is $LaCoO_3$ and along with it a very low amount of Co_3O_4 is found up to the temperature of 1050°C.CoO is a phase which is observed up to 1200°C. At 1250°C it was found a single phase, namely a solid solution with cubic structure and a network parameter equal to 3.84 Å. This fact confirms the results from the paper [15] where it was shown that through the solubilization of SrO into $LaCoO_3$ structural changes occur that lead to the modification of the rhombohedral $LaCoO_3$ network in terms of increasing the degree of symmetry. The characteristic diffraction lines for the LSC5 sample are shown in Figure 6. It is observed that at 1000°C a solid solution is formed based on c-$SrCoO_3$ and the cobalt oxide. At 1050°C the cobalt oxide is no longer found, and at 1 150°C the cubic network of $SrCoO_3$ begins to deform, resulting in the appearance of some diffraction lines at 36.7 and 42.6 degrees, respectively. The intensity of these lines increases at temperatures of 1200°C and 1250°C, respectively. At this last temperature it is observed that almost all lines tend to double and a hexagonal structure with a = 5,42 and c = 13,24 Å parameters is formed. The obtained results show that the cubic network of $SrCoO_3$ can be stabilized through forming a solid solution with $LaCoO_3$ but only at temperatures below 1150°C. At higher temperatures its network changes and it forms a hexagonal structure.

4.3. Morphology of the samples

Morphology of sintered samples was studied by electronic microscopy and the images obtained for LSC4 and LSC5 thermally treated at 1250°C are given in Figures 7 and 8. Polygonal granules of different sizes can be observed. Figure 7a shows that the LSC4 sample consists of two types of granules, some of which are large, while others are much smaller and are located at a triple point. EDX analysis (Figure 7b) showed that the large predominant grains have a constant composition consisting of the three elements and they represent the solid solution determined by X-ray. The small granules have very large cobalt



a

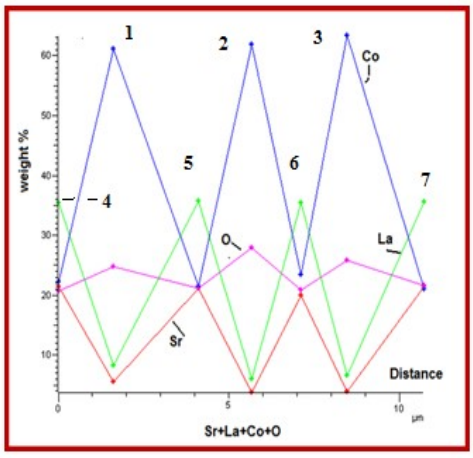


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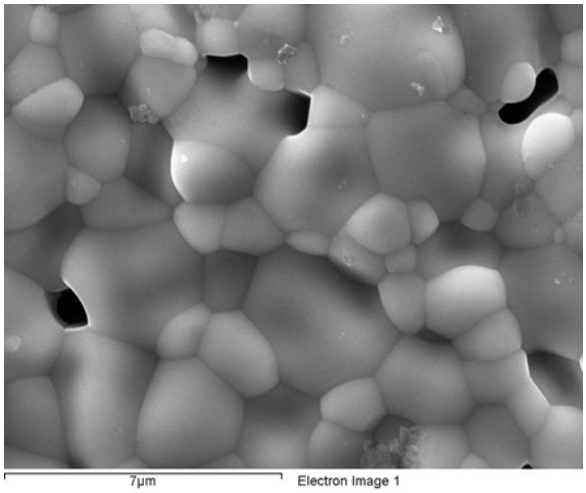
Fig.7 - The SEM (a) and EDX image (b) for the LSC 4 thermally treated at 1250°C / *Imaginea SEM (a) și EDX pentru proba LSC 4 tratată termic la 1250°C.*



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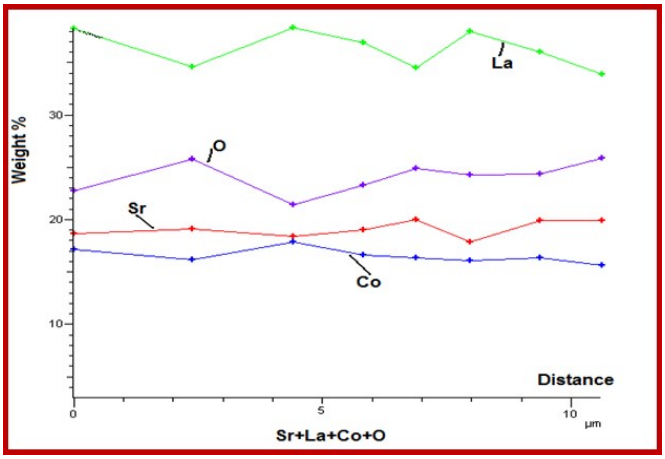

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Fig.8 - The SEM (a) and EDX image (b) for the LSC 5 thermally treated at 1250°C / *Imaginea SEM (a) si EDX (b) pentru proba LSC 5 tratată termic la 1250^{0}C .*

content and represented cobalt oxide in which small amounts of lanthanum and strontium have been diffused. The fact that this oxide has not been identified by XRD shows that it is present in very low proportion. As it results from the paper [3], the solubility of $SrCoO_3$ in $LaCoO_3$ is partial. Upon exceeding the solubility limit, the strontium cobaltite dissociates, because is an incongruent compound [16] and the elimination of the cobalt oxide is mainly observed. Figure 8a shows the electron microscopic image of LSC5 which also has polygonal granules of different sizes, but EDX analysis has shown that all have the same chemical composition (Figure 8b). This confirms the results obtained by X-ray diffraction, which shows a single solid solution at this temperature.

4.4. Electrical properties

The variation in electrical conductivity for the two samples, thermally treated at 1250°C, depending on the temperature, is given in Figure 9. In case of LSC4, there is a continuous increase of the conductivity with temperature. The LSC5 sample has a more complex behavior in that it has an approximately constant conductivity up to 1000 K, after which a transition from metal to semiconductor is observed.

For the variation of the electrical properties of solid LSC solutions, depending on the composition, it is considered that the main cause is the valence difference between La^{3+} and Sr^{2+}. To maintain the neutrality of the electrical charge on the network, there are two possibilities: one is the change the cobalt valence in the base network and the other is the formation of oxygen vacancies in the network. At low proportions of the substituent it was found that the Co^{4+} ions and a reduced number of oxygen vacancies appear in the network. For average proportions it is possible an equilibrium according to follow relation:

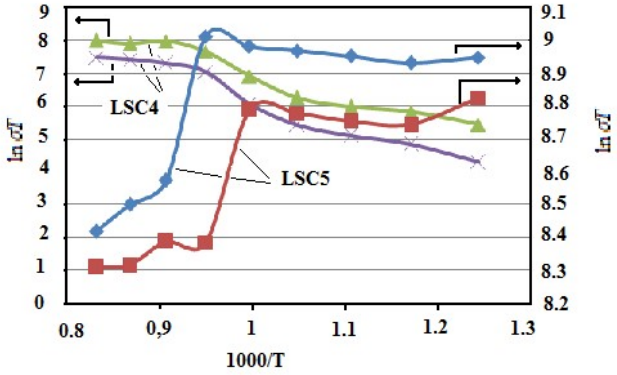

Fig. 9 - Variation of electrical conductivity of samples according to the temperature / *Variația conductivității electrice a probelor în funcție de temperatură.*

$$2Co^{3+} \rightarrow Co^{2+} + Co^{4+}$$

so that both divalent as well tetravalent cobalt ions contribute to conductivity [16]. Wang et al. [17,18] studied the structure of LSC5 and showed that the valence of cobalt ion is 2+, but the oxygen vacancies are arranged in an orderly manner in the network and this contributes to increased conductivity.

5.Conclusions

The performed studies have shown that homogenous powders of $La_{0,6}Sr_{0,4}Co_{3-\delta}$ and $La_{0,5}Sr_{0,5}Co_{3-\delta}$ with a low dispersion degree and a modal diameter of about 400 nm can be obtained by intensive mechanical activation. Thermal treatment of these powders leads, through reactions in the solid phase, to formation of two types of solid solutions of which the first ($La_{0,6}Sr_{0,4}Co_{3-\delta}$) has cubic structure and the other ($La_{0,5}Sr_{0,5}Co_{3-\delta}$) a hexagonal structure. Both types of compounds have a very good sintering

tendency. By scanning electron microscopy (SEM) it was shown that the two samples are made up of polygonal granules of different sizes. However, for the $La_{0,6}Sr_{0,4}Co_{3-\delta}$ sample, the presence of CoO under the detection limit of the X-ray apparatus was observed. Electrical measurements showed that $La_{0,6}Sr_{0,4}Co_{3-\delta}$ is semiconductor and $La_{0,5}Sr_{0,5}Co_{3-\delta}$ is a conductor with a semiconductor transition at 1000°K.

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REFERENCES

1.A. Kumar, A.S. Verma and S.R. Bhardwaj, Prediction of Formability in Perovskite-Type Oxides, The Open Applied Physics Journal, 2008, ***1***, 11-19.

2.M. A. Pena and J. L. G. Fierro, Chemical Structures and Performance of Perovskite Oxides, Chem. Rev. 2001**, 101**, 1981.

3.V.A. Cerepanov, L.Ya. Gavrilova, L.Iu. Barkhatova, V.I. Voronin, M.V.Trifonova and O.A. Barkhner, Phase Equilibria in the La-Me-Co-O (Me=Ca,Sr,Ba) Systems, Ionics, 1998, **4**, 309.

4.P. Ravindran, P. A. Korzhavyi, H. Fjellvag, A. Kjekshus, Electronic structure, phase stability, and magnetic properties of $La_{2-x}Sr_xCoO_3$ from first-principles full-potential calculations, Physical Review B, 2015, **60** (24), 16 423 -16 434.

5.T.Bak, J.Nowotny, M.Rekas, S.Ringer and C.C.Sorell, Defect Chemistry and Electrical Properties of $La_{1-x}Sr_xCoO_{3-\delta}$. I.Defect Equilibria, Ionics, 2001, **7**, 360.

6.D.A. Kumar, S.Selvasekarapandian, H. Nithya, J. Leiro, Y. Masuda, S.D. Kim, S. K. Woo, Effect of calciumndoping on $LaCoO_3$ prepared by Pechini method, Powder Technology 2013, **235**, 140-147.

7.Y. Tao, J. Shao, J. Wang Wei, G. Wang, Synthesis and properties of $La_{0,6}Sr_{0,4}CoO_{3-\delta}$ nanopowder, Journal of Power Sources, 2008, **185**, 600-614.

8. J. E. Sunstrom, K. V. Ramanujachary, M. Greenblatt and M. Croft, The Synthesis and Properties of the Chemically Oxidized Perovskite, $La_{1-x}Sr_xCoO_{3-\delta}$ ($0.5 \leq x \leq 0.9$), Journal of Solid State Chemistry, 1998, **139**, 388-397 .

9.C. de la Calle, J. A. Alonso, and M. T. Fernandez-Dıaz, Polymorphism of $Ba_{1-x}Sr_xCoO_{3-\delta}$ ($0 \leq x \leq 1$) Perovskites: A Thermal and Structural Study by Neutron Diffraction, Z. Naturforsch. 2008, **63**, 647- 654;

10.B. B. Weiner, What is a Continuous Particle Size Distribution?, Brookhaven Instruments Corporation White Paper, 2011.

11, G. Velciu, A. Melinescu, V. Marinescu, M. Preda $LaCoO_3$ synthesis by intensive mechanical activation, Ceramic International 2015, **41**, 6876-6881.

12. V. Pouchly, K. Maca, Master Sintering Curve – A Practical Approach to its Construction, Science of Sintering, 2010, **42**, 25-32.

13.H. Naceur, A. Megriche, M. El Maoui, Effect of sintering temperature on microstructure and electrical properties of $Sr_{1-x}(Na_{0.5}Bi_{0.5})xBi_2Nb_2O_9$ solid solutions, Journal of Advanced Ceramics 2014, **3** (1),17-30.

14.W. Shao, S. Chen, D. LI, H. Cao, S. Zhang, Construction of the master sintering curve for submicron size α-Al_2O_3 based on non-isothermal sintering containing lower heating rates only, Materials Science, 2009, **27**, (1), 2000.

15.G.Velciu, A. Ianculescu, A. Melinescu, V. Marinescu, M. Preda, Study of the reactions at formation of $La_{1-x}Sr_xCoO_{3-\delta}$ prepared by mechanical activation, Revista de Chimie, 2017, **68**, (9), 2043-2047.

16. O. Jankovsky, D. Sedmidubsky, J. Vitek, P. Simek and Z. Sofer, Phase diagram of the system Sr-Co-O, Journal of the European Ceramic Society, 2015, **35**, 935-940.

17.T.Bak, J.Nowotny, M.Rekas, S.Ringer and C. Sorrell, Defekt chemistry and electrical properties of $La_{1-x}Sr_xCoO_{3-\delta}$, Ionics 2001, **7**, 380-384.

18. Z. Wang and J. S.Yin, Cobalt valence and crystal structure of $La_{0.5}Sr_{0.5}CoO_{2.25}$, Philosophical Magazine B, 1998, **77**, (1), 49-65.

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